A Study on the Transport Behaviour of Single and Mixed Electrolytes

ABSTRACT

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To

THE NORTH-EASTERN HILL UNIVERSITY
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(283K to 323K) the MAE on electrical conductance is found to be almost independent of temperature.

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$$\Lambda = \Lambda_{FLK} \exp (B_1' c + C_1' c^2) \quad (A.1)$$

where Λ_{FLK} is the Falkenhagen-Leist-Kelbg(FLK) equation for Λ, c is the molar concentration and the parameters B_1' and C_1' are the empirical constants. The best-fit parameters of this equation, viz., a_o (ion-size parameter), B_1' and C_1', are tabulated. C_1' is found to have always negative values. The value of B_1' is found to be positive for electrolytes exhibiting negative viscosity (relative viscosity < 1) and is negative otherwise.

In the experimental temperature range from 283K to 323K Λ shows a slight non-Arrhenius type of dependence on temperature. The Λ versus T data are therefore fitted to the Vogel-Tammann-Fulcher (VTF) equation. From the best-fit values of the VTF parameters activation energies (E_Λ) for conductance flow are calculated. The plot of E_Λ versus concentration exhibits minimum in the case of both single and mixed electrolytic solutions.

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The dependence of Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system on T in the range from 283K to 313K is also found to be slightly non-Arrhenius type.

In Chapter V an attempt has been made to provide a theoretical basis to the above empirically introduced isothermal equation(A.1). This has been achieved by expressing the drift velocity v_d of an ion in solution as

$$v_d = v_d^* \, p(m) \tag{A.2}$$

where p(m) is the probability that the ion possesses the minimum requirement necessary for the ionic transport to take place and is dependent on the concentration (m) of the solution. v_d^* is equal to v_d only when p(m) is approximated to 1. v_d^* is evaluated using the Debye-Hückel ionic atmosphere concept. The Falkenhagen-Leist-Kelbg approach has been employed to obtain an expression for Λ which is of the form, $\Lambda = \Lambda_{FLK}p(m)$. p(m) has been evaluated separately from the transition state theory, the free volume model and the configuration entropy model. In all the cases equation (A.1) for Λ has been deduced after using the solution of infinite dilution as the reference frame of $p(o) \equiv 1$. An expression for p(m) has also been obtained directly in the light of a newly proposed simple two-state model. The applicability of equation(A.1) has been further tested by fitting the reported Λ versus concentration data of several 1:1 electrolytic solutions.

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I certify that the thesis entitled ***"A Study on the Transport Behaviour of Single and Mixed Electrolytes"*** *submitted by Mr.* ***Ratan Lal Gupta*** *for the Degree of Doctor of Philosophy of the North-Eastern Hill University, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any Degree of any other University.*

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No.	Course No.	Title	Grade
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2.	Chem 640	Chemical Kinetics	A
3.	SPS 632	Magnetic Resonance	A
4.	SPS 601	French Language	A

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TO

MY UNCLE

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CHAPTER - I

GENERAL INTRODUCTION

One of the aims of physical chemistry since its earliest days has been to study the thermodynamic (equilibrium) and transport (non-equilibrium) properties of electrolytic systems. Out of these two types of properties of electrolytes, the transport properties are relatively more difficult to deal with and have provided a most challenging field for experimental as well as theoretical research. Most commonly studied transport properties are electrical conductance, viscosity and diffusion. An inter-relation exists between these three properties as evident from Stokes-Einstein and Nernst-Einstein relations. A large amount of the systems whose transport properties have been investigated may be classified as solutions of single inorganic salts in various solvents. Aqueous medium is obviously the most extensively used solvent medium. Organic and molten solvents are normally used as the non-aqueous medium. In addition, pure molten salts (systems with no solvent medium or solutions of infinite concentration) form another interesting type of system for investigating transport properties and mechanism of transport.

The transport properties of a system like its thermodynamic properties have dependence on temperature, pressure and concentration (if the system is a solution). In the last few decades interpretation of the behaviour pattern of transport properties with respect to temperature, pressure and concentration has been a subject of active research. A brief review of this is made below. The discussion is mostly confined to electrical conductance since our study in this work deals with only electrical conductance of electrolytic systems.

1.1 Temperature Dependence

Normally Arrhenius-type (temperature independent activation energy for the transport) of temperature dependence of electrical conductance is observed at high temperatures which changes over to non-Arrhenius-type at lower temperatures. The temperature range at which switch-over from Arrhenius to non-Arrhenius-type of behaviour takes place depends upon the system under consideration. The non-Arrhenius behaviour is more pronounced if the transport property is measured over a wide range of temperature. Therefore, sometimes when the transport property measurement is made over a narrow temperature range the non-Arrhenius behaviour is not observed. A return to the Arrhenius-type behaviour at very low temperature is also known. The deviation from the familiar Arrhenius-type of temperature dependence of transport property therefore necessitated a rethinking about the transport mechanism in liquid or electrolytic systems leading to the development of several empirical[1-6] as well as statistical-mechanical[7-13] models for describing the transport mechanism in liquids/electrolytes. Some of these models are discussed in the following section.

1.1.1 Models

The most widely used expression for describing the non-Arrhenius-type of transport property versus temperature behaviour is the Vogel-Tammann-Fulcher(VTF)[1-3] equation of the form

$$Y = A_y \exp[-B_y/(T-T_o)] \qquad (1.1)$$

where Y is the electrical conductance. Y can be fluidity or diffusion coefficient also. A_y, B_y and T_o are empirical constants and T is the absolute temperature. Although the VTF equation was originally reported as an empirical equation, it may now be derived from theoretical models. The first model which provided a theoretical basis to the VTF equation or to the Doolittle's empirical equation[4] is the free volume model of Cohen and Turnbull.[7] This model is based on the following assumptions: (i) A hard-sphere potential function is considered for the liquid. (ii) It is possible to associate a local volume v of molecular scale with each molecule. (iii) When v reaches some critical value

v_c, the excess $v-v_c$ is regarded as free volume. (iv) Molecular transport occurs only when voids having a volume greater than some critical value v* approximately equal to the molecular volume v_m are formed by the redistribution of the free volume or by the density fluctuation. (v) No local free energy is required for free volume redistribution. According to this model any transport property Y is proportional to p(v), the probability that the moving species has free volume v. Cohen and Turnbull[7] derived that

$$p(v) = \exp(-\gamma V^*/V_f) \qquad (1.2)$$

where V* and V_f are the critical volume and the average free volume, respectively, per mole. γ is a factor which corrects for the overlapping of free volumes. Since $V_f \propto (T-T_o)$, equation (1.1) is deducible from this free volume model. Naghizadeh[9] showed that in the neighbourhood of the average free volume per molecule, v_f, even if the void energy varies linearly with the void volume, the expression of Cohen and Turnbull for transport property holds good. Recently Cohen and Crest[13] formulated more precisely the free volume model by the introduction of the percolation theory. Angell and coworkers[14-21] initiated the extensive use of the Cohen-Turnbull model to describe the transport properties of glass-forming molten salt systems and concentrated electrolytic systems.

Macedo and Litovitz[10] used the concept of both energy and free volume requirement for the molecular transport to take place and obtained a hybrid-type equation for transport property of liquids. A similar equation was later derived theoretically by Chung[22] also. Brummer,[23] however, made a comment on the inadequacy of this hybrid equation to account for the density dependence of the activation energy at constant volume.

Other two models which also account for the non-Arrhenius-type of temperature dependence of transport property are the significant liquid structure model[24] and the environmental relaxation model.[11] These models are, however, relatively less used. The significant liquid structure model is although based on a sound concept and one of the best models to describe the thermodynamic properties of liquids, its effective application to describe the transport properties still requires an improved alternative treatment.

Another statistical-mechanical model which is very frequently employed to describe the non-Arrhenius-type of temperature dependence of transport property is the Adam-Gibbs configurational entropy model.[8] This model is many a times considered to have an edge over the free volume model.[7] For instance, it can qualitatively, if not quantitatively, account for the volume dependence of constant volume activation energy for transport processes, whereas the free volume model fails to explain this.[20,25] Since this model has been employed here to describe the temperature dependence of transport property of mixed alkali systems, it would be useful to give the description of this model. In this model the system is assumed to be an isobaric-isothermal ensemble of N independent, equivalent and distinguishable subsystems composed of z particles each. Any transport property is then considered to be proportional to the probability of rearrangement of the subsystems from one configuration into another independent of the environment. This probability is known as the transition probability. The cooperative rearrangement is controlled by the energy requirement and can occur due to a sufficient fluctuation in energy. Therefore, out of the N subsystems only n may be in states which allow a cooperative rearrnagement. Moreover, for the transition to occur the size of the subsystem must be larger than a critical size, z*. Based on such a model Adam and Gibbs derived an expression for the transition probability, w(T) of the form

$$w(T) = A\ \exp(-B/TS_c) \qquad (1.3)$$

where A and B are constants and S_c is the configurational entropy of the system. T is the absolute temperature and B is directly related to the activation free energy per particle. Any transport property, Y like electrical conductance, diffusion coefficient or fluidity may be directly correlated to this transition probability and therefore

$$Y = A'_y \exp(-B'_y/TS_c) \tag{1.4}$$

A'_y and B'_y are again empirical constants corresponding to the transport property, Y. S_c is estimated from the relation

$$S_c = \int_{T_o}^{T} \Delta C_p d\ln T \tag{1.5}$$

where ΔC_p is the difference in the heat capacities of the melt and the glass. T_o is the same term which appears in the VTF equation (1.1). Generally, ΔC_p is assumed to be temperature independent and equation (1.5) becomes

$$S_c = \Delta C_p \ln(T/T_o) \tag{1.6}$$

Equation (1.4) is reduced to the VTF equation by approximating at temperature not too far above T_o that $T\ln(T/T_o) \approx (T-T_o)$.

1.1.2 Glass Transition Phenomenon

In the VTF equation T_o is a very significant parameter known as the ideal glass transition temperature. In order to realize its significance better, a brief account of the glass transition phenomenon is given below.

In the conventional sense the temperature range of the liquid state is usually considered to be from the normal boiling point (upper limit) to the equilibrium freezing point (lower limit). It is, however, possible to extend this normal temperature range of the liquid state by bypassing both the upper and lower limits. The upper limit may be extended by performing measurements either in closed vessels or, in general, at pressures higher than the atmospheric pressure. In such cases the upper boundary for the liquid state is more appropriately taken as the critical temperature, T_c. The lower limit may like-wise be bypassed by supercooling a liquid as liquids have a tendency to remain in a state of internal equilibrium even below their normal freezing points. In nature some of the liquids, e.g., hydrate melts or highly concentrated aqueous electrolytes, have inherent tendency to supercool whereas in the rest of the liquids supercooling may be induced. The inherent tendency of some of the liquids to supercool may be understood in terms of the model developed by Turnbull and Cohen[26] based on the kinetic considerations of crystallization. In the absence of a foreign nucleating agent crystallization is governed by the two parameters, ΔG_1 and ΔG_2. ΔG_1 is the kinetic free energy barrier to the nucleation and ΔG_2 is the kinetic free energy barrier to the growth of the finite crystal. In any system, if one of these energy terms has a high value then crystallization of such a system will be hindered. In liquids which do not have an inherent tendency to supercool, crystallization may be averted by the sudden quenching of the system such that there may not be sufficient time for the crystal nuclei to form.

The tendency of a liquid to supercool as well as the duration of its existence in the supercooled state vary considerably from system to system. If the properties of a supercooled liquid are measured at increasingly low temperatures without the onset of crystallization, a point is eventually reached at which equilibrium properties can no longer be determined for the liquid due to the intervention of a non-equilibrium process, the glass transition. Therefore, glass is a supercooled liquid which has undergone the glass transition. The transition of a supercooled liquid into glass is characterized by a more or less sudden decrease in the intensive thermodynamic properties like heat capacity, expansion coefficient and compressibility from liquid-like values to values which are very close to, but generally greater than, those of the crystalline phase of the substance. In the temperature region where transition occurs, the viscosity increases rapidly, but not discontinuously, to values in the vicinity of 10^{13}P. It must be emphasized that changes in the thermodynamic properties do not occur merely because the viscosity becomes high, rather the changes must occur in order to save from the occurrence of a thermodynamic catastrophe as pointed out by Kauzmann[27] viz., the production of an amorphous phase of lower entropy than the crystalline phase of the same substance at the same temperature. The value of experimental glass transition temperature depends upon the cooling and heating rates of the system. However, the glass transition, although it is a non-equilibrium phenomenon, possesses many of the characteristics of a second order thermodynamic transition. It may be pointed out that the experimental glass transition temperature, T_g is generally ca. 10-20K higher than the ideal (reversible) glass transition temperature T_o obtainable from curve-fitting of the transport properties to the VTF equation.

1.2 Pressure Dependence

Generally one expects an increase in electrical conductance of a melt/electrolytic solution with increasing temperature. The experiments carried out by Grantham and Yosim[28-31] on pure melts at high temperatures, however, showed for the first time that a decrease in the electrical conductance of molten salts takes place with increase in temperature in the very high temperature region. This revealed the dependence of conductance on density also besides having temperature dependence. Since the density of a system varies by changing the temperature, the temperature dependence of conductance also includes an inherent volume dependence part of conductance. A precise interpretation of the temperature dependence of electrical conductance therefore requires separation of the temperature and volume dependence parts of the conductance. This prompted, in fact, the measurement of electrical conductance as a function of pressure as well as the PVT measurements of electrolytes. For completely ionized melts with increasing pressure the molar conductance decreases whereas for partially ionized molten salts it exhibits an initial increase with increase in pressure before showing a decreasing trend.[32] In general, electrical conductance decreases with decreasing density of a fully ionized system. In fact, in the supercritical region where the density can be varied continuously by applying pressure without the interference of any phase change a change-over from an ionic conductor to insulator has been observed.[33]

In aqueous electrolytic solutions the dependence of pressure on electrical conductance is slightly different because of the effect of pressure on solvent structure.[34] At infinite dilution and ambient temperatures the molar conductance increases with pressure to a maximum in the vicinity of 1 to 1.5 kbar and thereafter it decreases continuously.[35,36] Such a behaviour is attributed to the breakdown of water structure with increasing pressure as reflected by the viscosity of water which passes through a minimum at 1 kbar.[36] Above 40°C the molar conductance of electrolytic solutions at infinite dilution decreases monotonically with increase in pressure without exhibiting any maximum.[35,36] This behaviour of conductance is attributed to the fact that the minimum observed in the viscosity of water around 1 kbar disappears above 30°C.[37] The decrease in molar conductance with increasing pressure (beyond ~1.5 kbar at ambient temperatures) is due to the decrease in the mobility of ions at higher pressures. Similar behaviour of molar conductance with respect to pressure is observed for completely dissociated electrolytes like alkali halide solutions even at finite concentrations.[36,38,39] Molar conductance of associated electrolytes at finite concentrations also exhibits a similar behaviour with respect to pressure.[40-43] However, in this case the ascending portion of the molar conductance versus pressure or density curve is predominantly due to the increased ionization of the electrolyte. At the conductance maximum the electrolyte is completely ionized. With increasing concentration of the associated electrolytes the conductance maximum is shifted to higher pressures. At high temperatures, the dependence of molar conductance of fully ionized electrolytic solutions on pressure becomes similar to that of associated electrolytes.[45-52] This is because at high temperatures due to lowering in the dielectric constant of water even fully ionized electrolytes, e.g., alkali halide solutions, are appreciably associated. As the pressure increases the dielectric constant of the solvent also increases causing increase in the degree of dissociation which in turn increases the conductance of the solution. Beyond a particular pressure again dependence of ionic mobility on pressure dominates resulting in the decrease of molar conductance with pressure. Therefore, the dependence of molar conductance on pressure is the same in the case of both partially ionized molten salts and electrolytic solutions. In general, increase in pressure or density enhances the degree of dissociation of an electrolyte.

1.3 Concentration Dependence

Concentration dependence of transport properties of electrolytic systems has been bothering the physical chemists from the time of Ostwald (1888) onwards. Several empirical, semi-empirical and theoretical equations have been reported for expressing the concentration dependence of transport properties which are compiled comprehensively in the recent review work of Horvath.[53] It may, however, be pointed out that despite intensive work over several decades in both the theoretical and experimental areas, there still does not exist a satisfactory equation which explains the concentration dependence of the electrical conductivity of simple electrolytes in the high concentration range. Yet it is precisely this range of concentration that is used in practical electrochemical devices.

Two approaches are generally being used to tackle this problem. One of these approaches[18,21,54-57] uses the available theory for the transport processes in liquid or molten salt systems, for e.g., configurational entropy model[8] which is already outlined above. In this approach an isothermal equation to describe the concentration dependence of transport property is obtained by substituting in equation (1.1) the concentration dependence of A_y, B_y and T_o. Since the concentration dependence of T_o dominates, variations in A_y and B_y with concentration are sometimes ignored. In the other approach extensions of the existing electrostatic hydrodynamic theories are made by introducing empirical or semi-empirical parameters. All the electrostatic hydrodynamic theories use the primitive model (solvent as a dielectric continuum) and are essentially based on the ionic-cloud concept of Debye-Hückel. One of the electrostatic hydrodynamic equations widely used for interpreting the concentration dependence of equivalent or molar conductance of electrolytic solutions was derived by Falkenhagen, Leist and Kelbg.[58] It is of the form

$$\Lambda = \left[\Lambda_o - \frac{B_1 c^{\frac{1}{2}}}{1+B_o a_o c^{\frac{1}{2}}}\right]\left[1 - \frac{B_2 c^{\frac{1}{2}} F_o}{1+B_o a_o c^{\frac{1}{2}}}\right] \tag{1.7}$$

where Λ_o=equivalent or molar conductance at infinite dilution, $B_o=50.29\times10^8/(\varepsilon_o T)^{\frac{1}{2}}$, $B_1=82.5/(\eta_o(\varepsilon_o T)^{\frac{1}{2}})$, $B_2=8.204\times10^5/(\varepsilon_o T)^{\frac{3}{2}}$ and $F_o=[\exp(0.2929 B_o a_o c^{\frac{1}{2}})-1]/(0.2929 B_o a_o c^{\frac{1}{2}})$. c is the concentration in $mol.dm^{-3}$, a_o is the ion-size parameter, ε_o is the dielectric constant of water, η_o is the viscosity of water. All the expressions hitherto reported for describing the concentration dependence of Λ of concentrated electrolytic solutions are obtained by doing modification to the above equation (1.7) of Falkenhagen, Leist and Kelbg (FLK).

The first modification to the FLK equation (1.7) was made by Wishaw and Stokes[59] by multiplying the right hand side of equation (1.7) by (η_o/η), the reciprocal of the relative viscosity of the electrolytic solution. η is the viscosity of the solution. The Wishaw-Stokes (WS) equation is therefore of the form

$$\Lambda = (\eta_o/\eta)\left[\Lambda_o - \frac{B_1 c^{\frac{1}{2}}}{1+B_o a_o c^{\frac{1}{2}}}\right]\left[1 - \frac{B_2 c^{\frac{1}{2}} F_o}{1+B_o a_o c^{\frac{1}{2}}}\right] \tag{1.8}$$

This modification was suggested by Wishaw and Stokes in the light of the Walden rule which postulates an inversely proportional relation between ion mobility and medium viscosity. Equation (1.8) has been found to fit with moderate success the conductance data of electrolytic solutions upto fairly high concentrations. However, equation (1.8) fails to reproduce the conductance data when the viscosity ratio, η / η_o, becomes very high (at high concentrations). Postler[60,61] proposed a modification by using instead of η_o/η term an adjustable term equal to exp(-B'c) where B' is an empirical parameter. In the work of Postler the modification was, however, introduced in the Pitts equation.[62] One obtains the same result if the FLK equation (1.7) is used instead of the Pitts equation. Recently Monica et al.[63-65] made another modification to equation (1.7) by taking into account the dependence of electrophoretic term B_1 on the solution viscosity. From the expression for B_1 it is obvious that B_1 is inversely dependent on the viscosity of the solvent, η_o. Monica et al. modified the expression for B_1 by substituting the viscosity of the solution, η in the place of η_o. This modification was, however, incorporated by Monica et al. in equation (1.8) rather than in the FLK equation (1.7) and the new equation can be written as

$$\Lambda = (\eta_o/\eta)\left[\Lambda_o - \frac{B_{1\eta}c^{\frac{1}{2}}}{1+B_oa_oc^{\frac{1}{2}}}\right]\left[1 - \frac{B_2c^{\frac{1}{2}}F_o}{1+B_oa_oc^{\frac{1}{2}}}\right] \tag{1.9}$$

where $B_{1\eta}=B_1\eta_o/\eta$. Equation (1.9) was found to describe the concentration dependence of Λ of several 1:1 electrolytes upto high concentrations.

A comment can, however, be made on the success of equation (1.9). After writing equation (1.8) in the form

$$\Lambda = \left[\frac{\Lambda_o\eta_o}{\eta} - \frac{B_{1\eta}c^{\frac{1}{2}}}{1+B_oa_oc^{\frac{1}{2}}}\right]\left[1 - \frac{B_2c^{\frac{1}{2}}F_o}{1+B_oa_oc^{\frac{1}{2}}}\right] \tag{1.10}$$

it may be realized that in the WS equation (1.8) itself the effect of solution viscosity on the B_1 parameter has been taken into account. In fact, this may partly be the reason why the modification of Wishaw and Stokes to equation (1.7) extends the applicability of the latter to higher concentration. The combined effect of the viscosity corrections to ionic mobility (WS equation) and to the electrophoretic term (Monica's correction), therefore, makes equation (1.9) applicable at still higher concentrations.[65]

Goldsack et al.[66] made another modification to equation (1.7) by taking into account the effect of ionic hydration on a_o. This modification actually introduces into equation (1.7) the concentration dependence of a_o. The variation of a_o with concentration was also studied by Monica et al.[67] and observed that the nature of the concentration dependence of a_o is different for different electrolytic solutions. In another recent modification[68] to equation (1.7) viscosity and dielectric constant of the solution were substituted for those of the solvent in equation (1.7). Although the form of this modified equation remains the same as that of equation (1.7), in the new equation B_o, B_1 and B_2 become concentration dependent unlike the case in equation (1.7). Dielectric constant of electrolytic solutions decrease with increasing concentration. This new equation with only one adjustable parameter a_o has been found to explain satisfactorily the concentration dependence of Λ of NaCl, LiCl and KF solutions upto 5 $mol.dm^{-3}$

1.3.1 Mixed Alkali Effect

Almost all the studies on the above type of concentration dependence of electrical conductance are made using electrolytic solutions containing single salts in aqueous or non-aqueous media. A mixture of aqueous and non-aqueous solvents is also used sometimes. Much interest has been shown recently on a different type of concentration dependence of transport properties observed originally in glassy medium. This phenomenon is known as the mixed alkali effect

(MAE) and has long been known to occur in a glassy or molten medium.[69-74] It is a phenomenon observable only in mixed electrolytic systems and refers to deviations from additivity in isotherms of various physical properties as a function of composition which is being varied by progressively replacing one alkali ion by another in a glass or melt. In a more general term this effect is known as a mixed monovalent cation effect. Systems in which MAE may be observed can be classified as a ternary system containing in a chosen medium, glass or melt, a mixture of two alkali salts with constant alkali ion content. The deviations from additivity in isotherms of various properties are found to be negative with only one exception reported very recently.[75] Normally MAE is more pronounced for properties related to ionic transport. For example, in systems like $(XNa_2O + (1-X)K_2O)+3SiO_2$ where all of the electrical current is carried by the Na^+ and/or K^+ ions, the conductivity of mixed glasses can be reduced by a factor of 10^4 to 10^5 compared with that of single-alkali glasses measured at the same temperature.[76] Such large deviations from additivity indicate a major breakdown of the principle of independent migration of ions, which works well for dilute aqueous electrolytes. Other properties like viscosity and alkali ion diffusion also show similarly large deviations from additivity. In contrast to transport properties, equilibrium properties such as molar volume are additive or sometimes nearly additive functions of composition even when transport properties show a large MAE.

Continuing interests are being shown on the MAE mainly because of the following reasons. Firstly, it has a direct relevance to glass industry. A knowledge about the MAE helps a glass technologist in deciding about the glass compositions for achieving glasses with specific properties. Secondly, the problem of providing a completely satisfactory explanation for the existence of MAE is not yet settled. Thirdly, curiosity has recently arisen among workers to look for the MAE in media other than glass or melt of rigid network structure. Investigations made using the hydrate melt medium also revealed the presence of MAE, but to a lesser extent.[68,75,77-81]

It may be worthwhile to introduce here some of the explanations given for the existence of MAE. Many theories have been developed, but no one theory has received universal acceptance. Some of them have now been shown experimentally to be incorrect, e.g., the theory that the MAE is due to phase separation. Most theories have been developed specifically to explain the effect on electrical conductivity and it is difficult to see what result they would predict for properties such as viscosity which do not depend simply on the cationic mobilities. Moynihan[77] classified the existing theories into two general categories: cationic interaction theories and structural/mechanistic theories. The cationic interaction theories, in general, suggest that partial replacement of one monovalent cation by a second leads to some sort of attractive interaction among the cations. This in turn causes a relative reduction in the average ionic mobilities resulting in a negative deviation of conductance from additivity. An example of a structural/mechanistic theory of the MAE is that of Stevels.[82] In Stevels theory it is assumed that a variety of monovalent ion sites exist in a glass or liquid. When the glass or liquid contains a mixture of monovalent ions, each kind of ion preferentially occupies sites which are energetically most favourable to it. These most favoured sites are considered to be different for different types of ions. Mixing of the alkali or monovalent ions might lead to a net reduction in the number of ions loosely bonded to the solvent network of glass or liquid. This could cause a relative reduction in conductivity if ions loosely bonded to the solvent network are responsible for the electrical conductance.

In the present work our interest on the MAE is because of the third reason listed above, i.e., to investigate the MAE in media other than glass or melt of rigid network structure. One such most convenient medium for examining the MAE is the aqueous medium itself. Therefore, in this work we have studied the behaviour of electrical conductance of mixed inorganic salts in aqueous medium. The outline of the work done is given below.

1.4 Scheme of the Present Work

Density and electrical conductance measurements of $[xNaSCN+(1-x)KSCN]+RH_2O$ (Chapter III) and $[xNaNo_3+(1-x)KNO_3]+RH_2O$ (Chapter IV) systems are made as functions of x, R and temperature. Presence of MAE in these systems has been examined. An attempt has been made to deduce a new isothermal equation (Chapter V) to describe the concentration dependence (dependence on R) of molar conductance of several electrolytic solutions containing single (x=0.0 or 1.0) and mixed ($x \neq 0.0$ or 1.0) salts.

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CHAPTER II

EXPERIMENTAL TECHNIQUES AND TREATMENT OF DATA

2.1 Sample Preparation

The experimental systems were prepared using the recrystalized solutes. Brand names of the solutes used are mentioned in the respective chapters. All the solutions were prepared by weight (molal solutions). Conductivity water (conductance ~1-2μS) was used for solution preparation.

In this work concentrations of solutions are represented by R which is equal to the water/salt ratio. This concentration unit was first introduced by Angell and Gruen[1] and it is particularly more useful than the conventional units like molarity or molality when one discusses composition region where there are insufficient water molecules to fill more than one or two hydration shells per cation or anion. For example, 11.111m ($m=mol.kg^{-1}$) concentration is equivalent to R=55.555/ 11.111=5.

2.2 Temperature Control

A thermostated water bath was used to control the temperature during the measurement of density and electrical conductance. The water bath of about 10 litre capacity consisted of an immersion heater (1.5 kW), stirrer (Remi make), mercury contact thermometer and a calibrated check thermometer. A mercury vertical relay (Jumo-type GKT 15-0, 220V, 15A) was used to control the variations in temperatures. The temperature control of the thermostat was improved

(<±0.02°C) by connecting the immersion heater through an additional voltage divider whose output voltage was adjusted by the trial-and-error method depending upon the temperature to be maintained.

2.3 Density Measurement

Density measurements were made by using a pycnometer of approximately 7cm^3 capacity having a stem of about 9cm length graduated to about 0.01cm^3 divisions. Each mark on the stem of the pycnometer was calibrated using n-octane (Fluka A.G.) as a reference liquid. The density of n-octane at different temperatures required for calibration is given by

$$\rho = 0.71848 - 0.8239\times10^{-3}t + 0.4459\times10^{-6}t^2 - 5.293\times10^{-9}t^3$$

where t is the temperature in °C. Calibration of the pycnometer was repeated to get reproducible values. Solutions were introduced into the pycnometer by using a hypodermic syringe (10cm^3 capacity) with ca 10cm long needle. Densities were determined by recording the volume changes as a function of temperature. Measurements were made in the ascending order of temperature. Reproducibility of density data was checked by duplicate measurements. Data within ±0.1% reproducibility limit were accepted.

2.4 Electrical Conductance Measurement

For measuring conductance solutions were taken in a closed corning glass container. A dip type CDC 304 conductivity cell was then introduced into the solution and the container was closed. The closed container containing the solution and the conductivity cell was clamped in the thermostated water bath. CDC 304 conductivity cell has three electrodes in the form of pure platinum bands on a glass tube. The top and bottom bands are connected and grounded to chassis through the shield of the coaxial cable, while the centre band is connected to the centre conductor of the cable. This arrangement provided optimal electrical shielding of the current flowing between the electrodes. All the three bands of the cell are covered with the test solution. Conductivity of the solutions were measured at 1kHz using the CDM 83 conductivity meter (Radiometer, Copenhagen). The instrument was calibrated by adjusting the cell constant knob of the instrument till the specific conductance value of the reference solution (0.1mol.dm^{-3} KCl) was displayed. Data reproducible within ±0.75% accuracy were accepted.

2.5 Treatment of Experimental Data

The experimental data on density and molar (or equivalent) conductance as functions of concentration and temperature were analysed by fitting the data to different equations explained in succeeding chapters. For this purpose, basically two types of computer programs were used. In the simple least-squares method, values of the empirical parameters of the equations used were computed by directly minimizing the square of the deviation in a single cycle. In the other method, an iterative least-squares method was used. In this program, developed essentially on the basis of Newton-Raphson method,[2,3] approximate values of the unknown parameters of the equations used were initially fed into the computer. The computer then improves the values of the parameters in every cycle by minimizing the square of the deviation. Refined values of the parameters become their initial values for the next cycle. Like this, cycles were continued till minimum square of the deviation (best-fit) was obtained. The deviation of the calculated values from the observed values has been expressed in terms of standard deviation defined as $[(\text{cal. value-obs.value})^2/\text{number of data points}]^{1/2}$ The computer programs were written in BASIC language and a HCL Busybee PC was used for the data analysis.

2.6 Symbols and Units

Throughout this work we have used CGS units to represent the different physical quantities. However, the corresponding SI units are also listed below for the sake of ready reference.

Physical quantity with symbol	Definition / Symbol of unit CGS	SI
Temperature, T	K	K
Density, ρ	$g.cm^{-3}$	$10^{3}kg.m^{-3}$
Specific conductance, κ	$S.cm^{-1}$	$10^{2}S.m^{-1}$
	(S is Siemens = ohm^{-1})	
Molar conductance, Λ	$S.cm.^{2}mol^{-1}$	$10^{-4}S.m^{2}.mol^{-1}$
Equivalent conductance Λ	$S.cm^{2}.equ^{-1}$	$10^{-4}S.m^{2}.equ^{-1}$
Concentration: molarity, c	$mol.lit^{-1}$	$10^{3}mol.m^{-3}$ ($mol.dm^{-3}$)
molality, m	$mol.10^{-3}g^{-1}$	$mol.kg^{-1}$

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CHAPTER - III

ELECTRICAL CONDUCTANCE OF A MIXTURE OF SODIUM AND POTASSIUM THIOCYANATES IN AQUEOUS MEDIUM

Publication based on this work:

Ratan Lal Gupta and K. Ismail, Bull. Chem. Soc. Japan, **61**, 2605(1988).

3.1 Introduction

As mentioned in Chapter I properties of ternary systems containing two alkali metal ions in a fixed glassy medium are interesting due to the existence of a phenomenon known as the mixed alkali effect(MAE) which has got both practical and theoretical importances.[1,2] This phenomenon refers to non-additivity of various physical properties caused when the relative amounts of the alkali metal ions are varied keeping the concentration of the glassy medium constant. Normally MAE is most pronounced for properties related to ionic transport.

Attempts are being made to look for the MAE in media other than glass. In the hydrate melt medium also MAE is found to exist, but to a lesser extent.[3-8] Another suitable medium for investigating the MAE is the aqueous medium. Investigation of the MAE on transport properties in aqueous medium involves a two-fold interest. (i) Data on the properties of mixed aqueous electrolytes are necessary because many systems of practical, biological or geological as well as chemical, interest involve mixed aqueous electrolytes. studies on the transport properties of mixed aqueous electrolytes have, however, been relatively less compared to those on their thermodynamic properties. There are some very old reports on the conductivities of mixed aqueous electrolytes containing alkali halides and nitrates.[9] In recent years only one report is made on the study of MAE in aqueous medium.[10] (ii) One of the characteristics of the MAE is that it shows a complicated dependence on the total alkali metal ion concentration. To examine this aspect, aqueous medium is a more convenient one. With a view to understanding better the dependence of the MAE on the total alkali metal ion concentration we made the electrical conductance measurements of a mixture of NaSCN and KSCN in aqueous medium with varying amounts of water at different temperatures.

3.2 Experimental Section

NaSCN (SD, Reagent Grade) and KSCN (SD, Reagent Grade) were recrystallized from their aqueous solutions prepared in doubly distilled water. Recrystallized salts were dried for several days over $CaCl_2$ in vacuum desiccator. Using these salts molal solutions were prepared. Electrical conductivity and density of these solutions were measured as described in Chapter II.

3.3 Results and Discussion

The experimental values of molar conductance (Λ) of $[xNaSCN+(I-x)KSCN]+RH_2O$ system as functions of x,R and temperature are presented in Table 3.1. The density data are presented as a function of temperature in Table 3.2. The present values of Λ of NaSCN (at 293K and 298K) and KSCN (at 293K) solutions are found to be in good agreement with the reported data[11,12] as also apparent from Fig.3.1. The measured values of conductance were found to be reproducible within ±0.75% accuracy.

Variation of Λ with x. The variation of Λ with x at different R values and at one particular temperature is shown in Fig.3.2. Similar variation of Λ with x is observed at other experimental temperatures. Λ is additive above a particular R value and deviates from additivity below this R value thereby indicating the presence of MAE on electrical conductance in the present system under investigation. In Figs.3.3 and 3.4 the dependence of Λ on x is illustrated at various temperatures for R=10 and 4, respectively. Although the deviation of Λ from additivity is expected to be temperature dependent, this dependence is negligible in the present experimental range of temperature as apparent from Figs.3.3and 3.4. Moynihan[3] suggested that r-factor defined as $r=\Lambda_{add}/\Lambda$ is a better term to estimate the deviation of Λ from additivity because r being a ratio can have more precise values. In the expression for r, $\Lambda_{add}=[x\Lambda_1+(1-x)\Lambda_2]$, where Λ_1 and Λ_2 are the molar conductances of the NaSCN and KSCN solutions, respectively. Therefore, the non-additivity in Λ is also represented here in terms of r and its dependence on concentration is shown in Fig.3.5at different temperatures for x=0.5. r varies negligibly upto a particular concentration and thereafter increases sharply with increasing concentration. Similar trend in the variation of r-factor with R is found at other x values also. Such a dependence of r on R therefore clearly indicates that MAE is dependent on the total alkali metal ion concentration. For the system under study the value of r appears to increase sharply above ca. 10R (ca.5.6m) concentration. It is interesting to note that this concentration falls in the range where the specific conductance of NaSCN solution becomes maximum. Moreover, in this concentration range the viscosity of NaSCN solution starts increasing exponentially with concentration.[11-13] Every electrolytic solution exhibits a particular concentration range of this type and it is identified as the region where a transition from primitive structure to quasi-crystalline structure takes place.[14,15] For KSCN solution such a concentration range of structural transition falls around ca.6R (ca.9.2m). In a mixed electrolyte containing NaSCN and KSCN a quasi-crystalline type structure may therefore be considered to start appearing from ca.10R and the extent of quasi-crystallinity keeps on increasing beyond this concentration. Therefore, in aqueous medium the MAE seems to become significant when the solution attains a quasi- crystalline type structure. This inference is in accordance with the empirical fact that the MAE is much prominent in the glassy media having very rigid-like structure. In the present system of interest the MAE observed for the highest concentration (4R) studied is about 8.6%, i.e., the percentage of deviation of Λ from additivity.

The dependence of r-factor or MAE on concentration may be explained in terms of the anion polarization model.[16,17] According to this model, the thiocyanate ion is considered to experience an average symmetrical field when the aqueous medium contains either NaSCN or KSCN. When Na^+ ions are partially replaced by K^+ions, some of the thiocyanate ions find themselves between fields of differing intensities. Due to this a competitive polarization of the anion occurs and the thiocyanate ion will be more polarized towards the smaller cation. Consequently, in the aqueous medium addition of KSCN to NaSCN results in a decrease in the internal mobility (with respect to the thiocyanate ion) of the Na^+ion whereas addition of NaSCN to KSCN increases the internal mobility of the K^+ion. However, the observed negative deviation of Λ from additivity implies that in the aqueous medium when both NaSCN and KSCN are present the decrease caused in the internal mobility of Na^+ion is always greater than the increase caused in the internal mobility of the K^+ion. Thus, according to anion polarization model the asymmetry created in the electric field around the thiocyanate ion owing to its competitive polarization by the unlike cations causes the MAE on electrical conductance. Such a competitive polarization can, however, cause significant MAE only when the ionic concentration is large enough (Fig.3.5). Moreover, the effect of competitive polarization is expected to be maximum when the two cations are in equal concentration. This is, in fact, observed as evident from the plot (Fig.3.6) of r vs.x at 298K which passes through a maximum in the range where x ≃ 0.5-0.6.

Variation of Λ with R. A successful theoretical expression is not available to describe the concentration dependence of Λ in the higher concentration range (cf. Chapter I). Recently we have reported[15] an expression of the form

$$\Lambda = A_o' \exp[B_o'm+C_o'm^2] \qquad (3.1)$$

for describing the conductance of aqueous electrolytes upto very high concentrations. In equation (3.1) A_o', B_o' and C_o' are adjustable parameters. This equation was shown to be obtainable from the Adam-Gibbs configurational entropy model.[18] However, equation (3.1) was found to be only partly successful in describing the conductance data of concentrated aqueous solutions. One of the draw-backs of equation (3.1) is that the computed value of A_o' for a particular electrolyte has been found to be considerably lower than the corresponding value of equivalent conductance at infinite dilution, Λ_o.[15] This indicates that the applicability range of equation (3.1) cannot extend upto very low concentration. Moreover, the fact that the T_o of a solution remains almost constant in the low concentration region[19] instead of varying linearly with concentration also envisages deviation from equation (3.1) in the dilute region. Therefore, in order to employ equation (3.1) to describe the concentration dependence of Λ in the range from very dilute to high concentration, its improvement is necessary. The incomplete success of equation (3.1) was attributed to the fact that this expression accounts only for the short-range (ion-solvent) interactions in the solution. An attempt has been made here to improve equation (3.1) by also accounting for the long-range (ion-ion) interactions in an empirical way. This is achieved by substituting Λ_{FLK} term for A'_o term where Λ_{FLK} refers to the Falkenhangen-Leist-Kelbg (FLK)[20] equation for Λ given by equation (1.7). The conductance data of the system under study were therefore least-squares fitted using an iteration program (Appendix A) to the equation

$$\Lambda = \Lambda_{FLK} \exp(B'_1 c + C'_1 c^2) \qquad (3.2)$$

In equation (3.2) in the exponential part we have used molar concentration(c) units instead of molal concentration (m) units. This does not affect the fitting because B'_o, C'_o, B'_1 and C'_1 are freely adjustable parameters. For least-squares fitting the conductance data to equation (3.2) we have chosen in the case of solutions with x=0 and x=1 the reported[21] value of Λ_o and for compositions with x values other than 0 or 1 the Λ_o values are estimated using the additivity principle.[22] Therefore, equation(3.2) essentially becomes an expression with three adjustable parameters, viz., a_o, B_1' and C_1'. The best-fit values of a_o, B_1' and C_1' corresponding to the lowest standard deviations were computed and are given in Table 3.3.

At all experimental temperatures excluding T=298K, the vlaue of a_o for NaSCN solution is found to be higher than the value of a_o for KSCN solution. If a_o behaves strictly as an ion-size parameter one expects, on the contrary, higher a_o for KSCN than for NaSCN. For the mixed electrolytes also no regular trend in the variation of a_o with x has been observed. It may therefore be pointed out as suggested by others[23,24] also that a_o behaves more like an adjustable parameter than a physically significant parameter. B_1' and C_1' parameters also have dependence on x as apparent from Table 3.3. C_1' has negative values at all x and its variation with x is relatively much less. On the other hand, B_1' has negative values at all x above 303K only. At temperatures $\leq$303K, B_1' has positive values for x=0.0 and negative values corresponding to x=1.0. In this temperature range, the value of x at which B_1' changes its sign is dependent on the temperature (Table 3.3). For example, B_1' changes its sign between x=0.5 and 0.6 at 283K whereas at 293K between x=0.3 and 0.4. This type of dependence of B_1' on x may be explained by correlating, in the light of the WS equation (1.8),[25] the exponential part of equation(3.2) to the reciprocal of viscosity of the system. Accordingly a positive value of B_1' and a negative value of C_1' indicate that the solution exhibits negative viscosity upto a concentration equal to B'_1/C'_1. In fact, KSCN solution (x=0.0) is known to exhibit negative viscosity.[11] For example, at 293K KSCN solution exhibits[11] negative viscosity upto ~1.7c which is in good agreement with the ratio B_1'/C_1'=1.67. In general, irrespective of the fact that B_1' is negative or positive, there is always an overall decrease in the value of B_1' with increasing x. In the light of the WS equation[25] again, such a trend in the dependence of B_1' on x may be due to the increase in the viscosity of the mixed electrolytic solution as the content of NaSCN in the solution increases, because NaSCN solution has higher viscosity than KSCN solution.[11] Furthermore, it is interesting to find that at low concentrations, if one ignores the negligible contribution made by the $C_1'c^2$ term, equation(3.2) reduces to the Postler equation.[26]

Variation of Λ with T. In order to analyze the temperature dependence of Λ, ln Λ has been plotted versus 1/T. Such plots are shown in Figs.3.7-3.9 for x=0.0, 0.5 and 1.0, respectively at 3 different R values. The plots look similar at other x and R values also. From the shape of these plots it is apparent that the variation of Λ with T in the experimental range of temperature is slightly non-Arrhenius-type. This is an expected behaviour and it becomes more pronounced as one extends the temperature range to further low values. The Λ vs. T data were therefore least-squares fitted using an iteration program (Appendix B) to the VTF equation[27-29] (cf. Chapter I) of the form

$$\ln \Lambda = \ln A_{\Lambda} - B_{\Lambda}/(T-T_{o}) \qquad (3.3)$$

The best-fit values of the empirical parameters $\ln A_{\Lambda}$, B_{Λ} and T_o are listed in Table 3.4. No regular trend in the variation of $\ln A_{\Lambda}$ or B_{Λ} or T_o with R and x is observed. However, in the higher concentration region (at low R values) the value of T_o, in general, shows an increase with decrease in R for all x values. This is in accordance with the observations made in electrolytic solutions containing single salts. Although the vlaue of T_o gives an idea about the glass transition temperature of a system, in the present case due to the smallness of the non-Arrhenius behaviour the value of T_o may not reflect correctly on the glass transition temperatures of the solutions. In such a situation T_o rather behaves like an adjustable parameter only.

Using the best-fit values of B_Λ and T_o the activation energy (E_Λ) for conductance flow was calculated from the relation

$$E_\Lambda = B_\Lambda R'[T/(T-T_o)]^2 \qquad (3.4)$$

where R' is the gas constant. The dependence of E_Λ on concentration is illustrated in Fig.3.10 for x=0.0, 0.5 and 1.0 at 283K and 303K. The shape of this type of plots is found to be similar for systems of other x values. The broad minimum in the plot of E_Λ vs. concentration is a general feature of electrolytic solutions containing single salts. The present study reveals that the appearance of broad minimum in the plot of E_Λ vs.concentration is a general trend in the case of mixed electrolytic solutions also.[30]

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Table 3.1 Molar conductance data for [xNaSCN+(1-x)KSCN]+RH_2O system

R	Λ /S cm^2mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.0				
100	80.0	89.0	98.7	108.2	118.2	128.4	139.1	149.6	160.4
40	75.1	83.2	91.4	99.7	108.2	116.9	125.6	134.2	142.7
30	72.7	80.2	87.9	95.8	103.7	111.6	119.7	127.9	135.8
20	68.7	75.4	82.3	89.3	96.4	103.5	110.7	117.9	125.2
10	59.3	64.5	69.9	75.4	81.1	86.6	92.1	97.7	103.3
8	54.3	59.0	63.9	68.8	73.7	78.6	83.3	88.2	93.2
7	51.5	55.9	60.5	65.0	69.6	74.2	78.8	83.5	88.1
6	47.5	51.7	55.9	60.2	64.5	68.8	73.0	77.4	81.6
5	41.8	45.5	49.3	53.1	56.8	60.5	64.3	68.0	71.8
4	34.4	37.7	40.9	44.1	47.3	50.5	53.7	56.9	60.1
3					36.0	38.6	41.2	43.8	46.4
					x = 0.1				
200	80.3	90.3	100.3	110.3	120.8	131.6	142.6	153.7	165.3
100	76.7	85.4	94.2	103.7	113.4	123.4	133.7	144.1	154.5

Contd..

Table 3.1 contd..

R	Λ /S cm^2mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.1				
40	71.6	79.3	87.6	95.3	103.7	112.0	120.4	128.8	137.0
20	66.0	72.0	79.5	86.3	93.3	100.3	107.2	114.5	121.7
10	56.4	61.5	66.8	72.2	77.6	83.0	88.4	93.9	99.6
8	51.5	56.2	61.0	65.8	70.5	75.4	80.3	85.4	90.2
7	48.4	52.8	57.2	61.7	66.2	70.3	74.8	79.3	83.8
6	44.4	48.4	52.5	56.6	60.8	65.0	69.1	73.3	77.5
5	39.1	42.7	46.3	50.0	53.6	57.3	61.0	64.8	68.5
4	31.8	34.8	37.9	41.1	44.2	47.3	50.5	53.7	56.8
3					32.4	35.0	37.5	40.0	42.6
					x = 0.2				
200	79.3	88.7	98.7	108.8	119.1	130.0	140.7	151.9	163.3
100	76.0	84.7	94.0	103.5	113.0	122.9	133.1	143.6	153.9
30	67.8	74.9	82.4	90.0	97.6	105.4	113.1	120.4	128.0
20	63.4	69.8	76.4	83.2	90.1	96.9	103.8	110.8	118.0

Contd..

Table 3.1 contd..

R	Λ /S cm^2mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.2				
10	53.3	58.3	63.4	68.7	74.0	79.4	84.6	90.0	95.5
8	48.5	53.0	57.8	62.4	67.2	71.9	76.7	81.5	86.4
7	45.3	49.6	53.9	58.3	62.7	67.1	71.6	76.2	80.6
6	41.2	45.1	49.1	53.1	57.2	61.3	65.4	69.5	73.7
5	35.9	39.4	43.0	46.5	50.1	53.7	57.4	61.1	64.7
4	28.9	31.8	34.8	37.8	40.9	44.0	47.0	50.1	53.2
3					29.5	32.0	34.5	37.0	39.5
					x = 0.3				
200	76.9	86.5	96.1	106.1	116.2	126.7	137.4	148.4	159.4
40	67.7	75.2	83.0	90.9	99.1	107.3	115.3	123.7	132.0
30	65.2	72.0	79.3	86.7	94.1	101.7	109.3	117.1	124.2
20	61.8	68.3	74.8	81.4	88.1	95.0	101.9	108.8	115.9
10	50.3	55.2	60.3	65.3	70.5	75.7	80.9	86.2	91.5
8	44.7	49.1	53.6	58.1	62.7	67.2	71.9	76.6	81.3

Contd...

Table 3.1 contd..

$\bar{R}$	Λ /S $cm^2 mol^{-1}$								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.3				
7	42.1	46.3	50.5	54.8	59.1	63.4	67.7	72.1	76.5
6	38.0	41.8	45.7	49.6	53.6	57.7	61.7	65.8	69.9
5	32.9	36.3	39.7	43.2	46.8	50.3	53.9	57.5	61.1
4	25.9	28.6	31.6	34.5	37.5	40.5	43.5	46.6	49.7
3					26.7	29.0	31.5	33.9	36.4
					x = 0.4				
200	74.9	84.3	93.7	103.3	113.2	123.5	133.9	145.0	156.2
100	71.7	80.1	89.0	97.6	107.1	116.8	126.4	136.4	146.7
20	59.1	65.4	71.8	78.3	84.9	91.6	98.3	105.1	112.1
10	47.6	52.5	57.4	62.5	67.5	72.6	77.7	82.9	88.1
8	41.9	46.1	50.5	54.9	59.4	63.9	68.4	73.0	77.7
7	39.3	43.3	47.5	51.6	55.8	60.1	64.3	68.5	72.9
6	35.3	39.0	42.7	46.6	50.5	54.4	58.3	62.3	66.3

Contd...

Table 3.1 contd..

R	Λ /S cm^2mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.4				
5	30.2	33.4	36.7	40.2	43.6	47.0	50.5	54.1	57.7
4	23.2	25.9	28.6	31.5	34.4	37.3	40.3	43.3	46.3
3					24.3	26.7	29.0	31.5	33.9
					x = 0.5				
200	73.3	82.3	91.9	101.5	111.3	121.2	131.7	142.2	153.1
100	69.7	78.0	86.5	95.5	104.6	114.0	123.5	133.6	143.5
30	62.5	69.3	76.5	83.8	91.3	98.8	106.3	114.0	121.4
20	57.3	63.5	69.8	76.3	82.9	89.5	96.3	103.3	110.2
10	44.8	49.4	54.2	59.1	64.0	69.1	74.1	79.1	84.4
8	39.3	43.5	47.8	52.1	56.4	60.9	65.3	69.7	74.3
7	36.7	40.5	44.5	48.5	52.6	56.7	60.8	65.0	69.2
6	32.5	36.0	39.7	43.4	47.2	51.0	54.8	58.8	62.7
5	27.6	30.7	34.0	37.2	40.6	44.0	47.4	50.9	54.4
4	21.1	23.6	26.3	29.0	31.8	34.6	37.5	40.4	43.3

Contd...

Table 3.1 contd..

R	Λ/S cm^{2}mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.5				
3					21.7	24.0	26.3	28.6	31.0
					x = 0.6				
200	72.4	81.4	90.6	100.1	109.9	120.2	130.3	140.6	151.8
100	67.7	75.8	84.3	93.0	101.9	111.0	120.4	130.2	140.1
30	60.4	67.1	74.1	81.2	88.4	95.9	103.3	110.7	118.2
20	54.8	60.6	66.8	73.1	79.7	86.0	92.5	99.1	106.0
10	41.9	46.6	51.3	56.0	60.8	65.7	70.7	75.8	80.9
8	36.7	40.7	44.8	49.0	53.3	57.7	62.0	66.5	71.0
7	33.6	37.3	41.1	45.0	49.0	53.0	57.0	61.1	65.2
6	29.9	33.3	36.9	40.5	44.2	47.9	51.7	55.5	59.4
5	25.1	28.1	31.3	34.5	37.7	41.0	44.3	47.9	51.1
4	18.6	21.0	23.6	26.2	28.9	31.6	34.4	37.2	40.1
3					19.4	21.5	23.7	26.0	28.4

Contd...

Table 3.1 cont..

R	Λ /S $cm^2 mol^{-1}$								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.7				
200	70.1	78.7	87.8	97.2	106.9	116.8	126.7	137.2	148.0
100	65.5	73.4	81.6	88.4	98.0	106.7	116.1	125.4	134.7
30	58.7	65.4	72.2	79.3	86.5	93.8	101.0	108.5	116.1
20	51.4	57.1	63.0	68.8	75.0	81.1	87.3	93.9	100.2
10	39.6	44.0	48.6	53.2	57.9	62.7	67.6	72.5	77.4
8	34.4	38.3	42.2	46.4	50.6	54.8	59.0	63.4	67.7
7	30.9	34.5	38.2	41.9	45.7	49.6	53.5	57.5	61.5
6	27.1	30.3	33.7	37.1	40.7	44.3	48.0	51.7	55.3
5	23.1	25.9	28.9	32.0	35.2	38.3	41.6	44.9	48.3
4	17.1	19.4	21.9	24.5	27.1	29.8	32.5	35.2	38.1
3					17.2	19.2	21.4	23.5	25.8
					x = 0.8				
200	68.8	77.4	86.2	95.6	105.9	115.3	125.4	135.7	146.2
30	57.0	63.5	70.3	77.2	84.4	91.7	98.9	106.3	113.8

Contd...

Table 3.1 contd..

R	Λ /S $cm^2 mol^{-1}$								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.8				
20	50.0	55.8	61.5	67.4	73.5	79.7	86.0	92.4	98.8
10	37.0	41.2	45.6	50.1	54.7	59.4	64.1	69.0	73.8
8	31.8	35.5	39.4	43.5	47.6	51.7	55.8	60.1	64.5
7	28.0	31.5	35.2	38.8	42.6	46.4	50.2	54.2	58.2
6	24.7	27.9	31.1	34.4	37.9	41.4	44.9	48.5	52.2
5	20.9	23.7	26.6	29.6	32.6	35.7	38.9	42.2	45.5
4	15.3	17.5	19.9	22.4	24.9	27.6	30.2	33.0	35.7
3					15.3	17.3	19.3	21.4	23.6
					x = 0.9				
100	61.9	69.4	77.4	85.4	93.7	102.1	110.8	120.6	130.7
30	55.2	61.5	68.1	75.0	82.1	89.0	95.9	103.3	110.8
20	47.4	53.1	58.8	64.7	70.7	76.8	83.0	89.3	95.6
10	34.8	38.9	43.2	47.6	52.1	56.7	61.4	66.2	71.0
8	29.4	33.0	36.7	40.6	44.5	48.6	52.6	56.8	61.1
7	25.7	29.1	32.5	36.1	39.7	43.4	47.2	51.1	55.0

Contd..

Table 3.1 contd..

R	Λ/S $cm^2 mol^{-1}$								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.9				
6	22.4	25.4	28.6	31.8	35.1	38.5	42.0	45.5	49.2
5	18.8	21.5	24.3	27.1	30.1	33.1	36.2	39.3	42.4
4	14.2	16.4	18.7	21.1	23.6	26.2	28.8	31.5	34.2
3					13.7	15.6	17.6	19.6	21.7
					x = 1.0				
200	65.0	73.2	82.0	90.8	99.9	109.2	119.1	129.0	139.0
40	55.1	61.4	68.4	75.3	82.5	89.9	97.4	105.1	112.8
30	51.9	57.8	64.5	71.1	77.8	84.6	92.1	99.3	106.5
20	45.9	51.3	56.9	62.7	68.6	74.7	80.8	87.1	93.3
10	32.5	36.6	40.8	45.1	49.4	54.0	58.5	63.3	67.9
8	27.2	30.6	34.3	38.0	41.9	45.8	49.8	53.9	58.0
7	23.6	26.8	30.1	33.5	37.1	40.7	44.3	48.2	52.0
6	20.1	23.0	26.0	29.0	32.2	35.5	38.9	42.3	45.8

Contd...

Table 3.1 contd..

R	Λ/S cm^{2}mol^{-1}								
	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 1.0				
5	17.2	19.8	22.5	25.3	28.1	31.0	34.0	37.1	40.2
4	12.5	14.5	16.7	19.0	21.4	23.9	26.4	29.0	31.6
3					12.0	13.8	15.6	17.6	19.6

Table 3.2 Best-fit parameters of the density equation, ρ = a-bt for [xNaSCN+(1-x)KSCN]+RH_2O system

x	a/g.cm^{-3}	b x 10^{4}/ g.cm^{-3}°C^{-1}	- (corr. coeff.)	x	a/g.cm^{-3}	b x 10^{4}/ g.cm^{-3}°C^{-1}	- (corr. coeff.)
			R = 200				
0.1	1.0079	2.9845	0.9833	0.2	1.0087	3.4977	0.9956
0.3	1.0091	3.3661	0.9919	0.4	1.0095	3.4651	0.9932
0.5	1.0094	3.0735	0.9817	0.6	1.0076	3.1113	0.9879
0.7	1.0070	3.1870	0.9898	0.8	1.0065	2.9275	0.9748
1.0	1.0076	3.2406	0.9899				
			R = 100				
0.0	1.0197	3.5334	0.9941	0.1	1.0185	3.6217	0.9960
0.2	1.0186	3.5125	0.9935	0.4	1.0181	3.4623	0.9925
0.5	1.0184	3.6390	0.9946	0.6	1.0178	3.6587	0.9954
0.7	1.0181	3.6298	0.9965	0.9	1.0175	3.7118	0.9975
			R = 40				
0.0	1.0588	4.8800	0.9992	0.1	1.0559	4.6008	0.9994
0.3	1.0576	4.8064	0.9994	1.0	1.0511	4.9143	0.9992

Contd...

Table 3.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^{\circ}C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^{\circ}C^{-1}$	- (corr. coeff.)
			R = 30				
0.0	1.0756	4.6868	0.9974	0.2	1.0737	4.7249	0.9988
0.3	1.0718	4.7348	0.9988	0.5	1.0684	4.7637	0.9982
0.6	1.0681	4.9520	0.9991	0.7	1.0673	4.8004	0.9978
0.8	1.0667	5.0041	0.9995	0.9	1.0665	4.9395	0.9988
1.0	1.0699	5.4789	0.9995				
			R = 20				
0.0	1.1090	5.3707	0.9992	0.1	1.1062	5.4275	0.9995
0.2	1.1079	5.4345	0.9996	0.3	1.1067	5.5192	0.9995
0.4	1.1037	5.3477	0.9996	0.5	1.1070	5.5286	0.9994
0.6	1.1045	5.3934	0.9995	0.7	1.1062	5.5395	0.9997
0.8	1.1054	5.6278	0.9997	0.9	1.1041	5.7130	0.9997
1.0	1.1094	5.9111	0.9999				
			R = 10				
0.0	1.1862	6.3123	1.0000	0.1	1.1871	6.3737	0.9999

Contd...

Table 3.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
			R = 10				
0.2	1.1849	6.3898	0.9999	0.3	1.1833	6.4513	1.0000
0.4	1.1819	6.4872	0.9999	0.5	1.1813	6.5069	0.9996
0.6	1.1785	6.6530	1.0000	0.7	1.1721	6.6171	0.9989
0.8	1.1795	6.9425	0.9999	0.9	1.1730	6.8053	1.0000
1.0	1.1728	6.9783	1.0000				
			R = 8				
0.0	1.2169	6.5779	1.0000	0.1	1.2192	6.5642	1.0000
0.2	1.2148	6.6598	1.0000	0.3	1.2131	6.7436	1.0000
0.4	1.2127	6.7952	1.0000	0.5	1.2104	6.7909	0.9999
0.6	1.2101	7.0742	1.0000	0.7	1.2033	6.9943	0.9999
0.8	1.2010	7.1196	1.0000	0.9	1.2093	7.3642	0.9999
1.0	1.2066	7.2897	1.0000				
			R = 7				
0.0	1.2401	6.7318	1.0000	0.1	1.2369	6.6376	1.0000

Contd...

Table 3.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
			R = 7				
0.2	1.2340	6.7586	1.0000	0.3	1.2331	6.8458	0.9999
0.4	1.2297	6.9695	1.0000	0.5	1.2287	6.8503	1.0000
0.6	1.2305	7.0575	1.0000	0.7	1.2299	7.0441	1.0000
0.8	1.2304	7.4150	1.0000	0.9	1.2272	7.3211	0.9999
1.0	1.2267	7.5112	1.0000				
			R = 6				
0.0	1.2734	6.7688	0.9999	0.1	1.2692	6.8450	0.9999
0.2	1.2665	6.9138	1.0000	0.3	1.2653	6.9731	0.9999
0.4	1.2555	7.1625	0.9999	0.5	1.2571	7.1450	0.9999
0.6	1.2529	7.2151	1.0000	0.7	1.2557	7.3465	0.9999
0.8	1.2534	7.4197	1.0000	0.9	1.2523	7.5166	1.0000
1.0	1.2544	7.6175	1.0000				
			R = 5				
0.0	1.3019	6.8479	0.9999	0.1	1.2967	6.9971	1.0000

Contd...

Table 3.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
			R = 5				
0.2	1.2959	7.1943	1.0000	0.3	1.2911	7.1535	0.9998
0.4	1.2907	7.1398	0.9999	0.5	1.2876	7.4187	0.9999
0.6	1.2828	7.3719	0.9999	0.7	1.2774	7.4696	0.9999
0.8	1.2735	7.4906	0.9999	0.9	1.2710	7.5962	0.9999
1.0	1.2646	7.7356	0.9999				
			R = 4				
0.0	1.3422	6.9996	1.0000	0.1	1.3405	7.1737	1.0000
0.2	1.3369	7.2828	0.9999	0.3	1.3350	7.2534	1.0000
0.4	1.3327	7.3685	1.0000	0.5	1.3263	7.2100	1.0000
0.6	1.3249	7.5644	0.9999	0.7	1.3179	7.6162	1.0000
0.8	1.3135	7.5513	0.9999	0.9	1.3048	7.7441	0.9999
1.0	1.3022	7.7850	0.9999				
			R = 3				
0.0	1.3917	7.3349	0.9999	0.1	1.3898	7.1605	0.9999

Contd...

Table 3.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4$/ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4$/ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
				R = 3			
0.2	1.3866	7.2466	0.9999	0.3	1.3848	7.4402	0.9999
0.4	1.3814	7.3622	0.9999	0.5	1.3793	7.4856	0.9999
0.6	1.3769	7.5452	0.9999	0.7	1.3767	7.6426	0.9999
0.8	1.3750	7.7360	0.9999	0.9	1.3719	7.7881	1.0000
1.0	1.3725	7.9718	1.0000				

Table 3.3 Best-fit parameters of the molar conductance equation (3.2) for [xNaSCN+(1-x)KSCN]+RH_2O system.

x	Λ_o/Scm^2mol^{-1}	$a_o x10^8$/cm	$-B'_1 x10^2$	$-C'_1 x10^2$	Std.dev. in Λ
			283K		
0.0	100.58	4.81	-2.6119	1.1999	0.4772
0.1	98.77	3.98	-3.8664	1.3545	0.2445
0.2	96.96	4.69	-1.4598	1.2067	0.3975
0.3	95.16	4.23	-2.1687	1.3732	0.3388
0.4	93.35	4.32	-1.3996	1.3859	0.3372
0.5	91.54	4.57	-0.7174	1.4309	0.3936
0.6	89.73	4.85	0.6788	1.3888	0.4508
0.7	87.92	4.71	1.2911	1.3910	0.6407
0.8	86.12	5.87	4.0363	1.2333	0.4947
0.9	84.31	7.56	7.1324	0.9722	0.6374
1.0	82.5	5.74	5.2329	1.2943	0.3806
			288K		
0.0	113.14	4.68	-2.2870	1.2100	0.5718
0.1	111.16	4.01	-2.7567	1.2503	0.4214

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B_1'$x10^2	$-C_1'$x10^2	Std.dev. in Λ
			288K		
0.2	109.17	4.57	-0.9676	1.1774	0.4548
0.3	107.19	4.30	-1.1396	1.2711	0.4303
0.4	105.21	4.42	-0.4003	1.2853	0.3419
0.5	103.23	4.56	0.0454	1.3423	0.4200
0.6	101.24	4.86	1.4367	1.2920	0.4788
0.7	99.26	4.68	1.9147	1.2999	0.7075
0.8	97.28	5.85	4.7553	1.1224	0.5415
0.9	95.29	7.41	7.5356	0.8957	0.6814
1.0	93.31	5.53	5.3806	1.2346	0.3239
			293K		
0.0	126.27	4.58	-2.0190	1.2100	0.7877
0.1	124.11	4.01	-2.1959	1.2170	0.3715
0.2	121.95	3.87	-1.0190	1.3100	0.7649
0.3	119.79	4.33	-0.3303	1.1917	0.4186
0.4	117.63	4.43	0.2937	1.2133	0.3584

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	-B_1'x10^2	-C_1'x10^2	Std.dev. in Λ
			293K		
0.5	115.47	4.60	0.7897	1.2577	0.4537
0.6	113.31	4.85	2.0624	1.2105	0.5120
0.7	111.15	4.68	2.5572	1.2104	0.7641
0.8	108.99	5.76	5.1399	1.0544	0.5976
0.9	106.83	7.25	8.0031	0.8109	0.7324
1.0	104.67	5.74	6.3780	1.0737	0.3917
			298K		
0.0	139.60	4.72	-0.1852	0.9943	0.5913
0.1	137.30	4.16	-1.1051	1.1230	0.3865
0.2	135.00	4.76	1.0153	0.9819	0.5309
0.3	132.70	4.62	0.9551	1.0764	0.4359
0.4	130.40	4.33	0.6264	1.1717	0.3767
0.5	128.10	4.66	1.5477	1.1753	0.4808
0.6	125.70	4.88	2.7002	1.1311	0.5465
0.7	123.40	5.33	4.0794	1.0714	0.5487

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B'_1$x10^2	$-C'_1$x10^2	Std.dev. in Λ
			298K		
0.8	121.10	4.61	2.9881	1.2369	1.1129
0.9	118.80	4.91	4.3957	1.1611	1.0512
1.0	116.50	4.58	4.0600	1.2585	0.8665
			303K		
0.0	153.99	4.38	-0.5492	1.0759	0.7467
0.1	151.48	3.72	-2.0290	1.2450	0.5730
0.2	148.97	4.29	0.1068	1.1169	0.7702
0.3	146.46	4.68	0.8586	1.1135	0.7395
0.4	143.95	4.14	0.5120	1.2002	0.5049
0.5	141.44	4.43	1.3663	1.2062	0.5911
0.6	138.93	4.60	2.3595	1.1778	0.6349
0.7	136.42	4.29	2.2877	1.2209	1.0592
0.8	133.91	5.68	5.7928	0.9756	0.7535
0.9	131.40	6.55	7.6221	0.8526	0.9926
1.0	128.89	5.20	5.8644	1.0835	0.5819

Contd...

Table 3.3 contd..

x	Λ_o/Scm^2mol^{-1}	$a_o x10^8$/cm	$-B'_1 x10^2$	$-C'_1 x10^2$	Std.dev. in Λ
			308K		
0.0	168.51	4.36	0.1415	1.0186	0.8212
0.1	165.83	4.27	0.4290	1.0300	0.8394
0.2	163.14	4.32	0.8467	1.0494	0.8403
0.3	160.46	4.05	0.5273	1.1329	0.6875
0.4	157.77	4.16	1.1931	1.1295	0.5517
0.5	155.09	4.36	1.7584	1.1568	0.6218
0.6	152.41	4.58	2.9370	1.1045	0.7055
0.7	149.72	4.23	2.7113	1.1559	1.1726
0.8	147.04	5.48	5.9660	0.9338	0.8211
0.9	144.35	6.34	7.9062	0.7954	0.9920
1.0	141.67	5.09	6.0827	1.0268	0.6037
			313K		
0.0	183.39	4.41	0.9613	0.9507	0.9232
0.1	180.54	3.54	0.4290	1.0100	0.8187
0.2	177.68	4.29	1.4162	0.9958	0.9105

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B_1'$x10^2	$-C_1'$x10^2	Std.dev. in Λ
			313K		
0.3	174.83	3.99	0.9238	1.0898	0.7051
0.4	171.97	4.12	1.6684	1.0753	0.5789
0.5	169.12	4.37	2.3475	1.0914	0.6469
0.6	166.27	4.53	3.3533	1.0496	0.7134
0.7	163.41	4.23	3.2705	1.0821	1.1602
0.8	160.56	5.44	6.4339	0.8645	0.8527
0.9	157.70	6.24	8.2920	0.7308	1.0485
1.0	154.85	5.16	6.6595	0.9433	0.6423
			318K		
0.0	198.62	4.35	1.3998	0.9166	0.9838
0.1	195.60	4.09	1.2070	0.9540	0.8666
0.2	192.57	4.27	1.9807	0.9408	1.0720
0.3	189.55	3.99	1.4761	1.0338	0.7620
0.4	186.53	4.21	2.4583	0.9973	0.5928
0.5	183.51	4.40	2.9695	1.0228	0.6802

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B_1'$x10^2	$-C_1'$x10^2	Std.dev. in Λ
			318K		
0.6	180.48	4.51	3.7934	0.9918	0.6775
0.7	177.46	4.25	3.7668	1.0200	1.1926
0.8	174.44	5.38	6.7954	0.8078	0.8658
0.9	171.41	6.27	8.7794	0.6601	1.1269
1.0	168.39	5.12	6.9602	0.8849	0.6733
			323K		
0.0	214.14	4.26	1.7331	0.8892	1.0778
0.1	210.95	3.74	0.3999	1.0371	0.8257
0.2	207.76	4.25	2.4299	0.8995	1.1629
0.3	204.58	3.89	1.6850	1.0065	0.8771
0.4	201.39	4.31	3.2370	0.9211	0.6454
0.5	198.20	4.38	3.3901	0.9741	0.6397
0.6	195.01	4.56	4.4263	0.9205	0.6876
0.7	191.82	4.27	4.3197	0.9512	1.3138
0.8	188.64	5.34	7.1546	0.7538	0.8856

Contd...

Table 3.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B'_1$x10^2	$-C'_1$x10^2	Std.dev. in Λ
			323K		
0.9	185.45	6.23	9.1645	0.5998	1.1620
1.0	182.26	5.04	7.1690	0.8376	0.6944

Table 3.4 Best-fit parameters of equation (3.3) for the molar conductance of $[xNaSCN+(1-x)KSCN]+RH_2O$ system

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.0		
100	7.5471	449.1	141.1	0.0009
40	6.9821	334.8	157.3	0.0007
30	6.9106	335.4	155.2	0.0006
20	6.8878	364.7	145.8	0.0001
10	6.5762	347.7	143.6	0.0007
8	6.3358	312.4	149.5	0.0009
7	6.3946	350.2	140.2	0.0004
6	6.2409	323.7	146.9	0.0004
5	6.0055	291.5	154.7	0.0008
4	5.7338	258.1	165.4	0.0015
3	5.7831	321.6	157.2	0.0042
		x = 0.1		
200	7.4188	390.1	154.3	0.0015
100	7.7268	518.5	129.9	0.0007

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.1		
40	6.9282	328.4	159.4	0.0011
20	6.7871	336.3	153.6	0.0025
10	6.6495	377.4	138.8	0.0006
8	6.5195	371.6	138.8	0.0011
7	6.1351	281.6	158.1	0.0015
6	6.2512	334.8	146.8	0.0003
5	6.1511	341.2	145.6	0.0003
4	5.9476	327.3	151.4	0.0006
3	5.6820	310.1	162.2	0.0005
		x = 0.2		
200	7.5335	426.7	148.0	0.0007
100	7.4719	433.6	145.0-	0.0007
30	6.7042	288.8	167.0	0.0011
20	6.8530	363.1	148.7	0.0005
10	6.5645	355.7	145.6	0.0006
8	6.4003	339.0	148.4	0.0004
7	6.3091	333.0	149.5	0.0005

Contd...

Table 3.4 contd..

R	$\ln A_{\Lambda}$	B_{Λ}/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.2		
6	6.2569	342.0	148.2	0.0003
5	6.1566	347.9	147.8	0.0004
4	5.9278	327.3	155.3	0.0006
3	5.7738	341.5	160.0	0.0009
		x = 0.3		
200	7.3983	390.9	155.0	0.0008
40	6.9475	337.6	159.5	0.0006
30	6.8362	330.1	158.9	0.0014
20	6.8854	375.7	146.9	0.0006
10	6.5351	353.5	147.9	0.0004
8	6.3720	340.5	150.5	0.0005
7	6.2887	333.7	152.0	0.0004
6	6.2790	352.5	149.4	0.0011
5	6.1306	344.1	152.4	0.0004
4	5.9744	344.8	156.2	0.0005
3	6.0002	419.1	148.7	0.0003

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.4		
200	7.5597	445.2	145.6	0.0017
100	7.5687	475.8	138.6	0.0011
20	6.8124	358.2	151.9	0.0003
10	6.4440	329.8	155.2	0.0004
8	6.3544	339.9	153.2	0.0005
7	6.2438	326.5	156.0	0.0005
6	6.2691	356.5	151.1	0.0003
5	6.1657	360.0	152.4	0.0007
4	6.0154	362.6	156.6	0.0003
3	5.9286	395.3	158.5	0.0002
		x = 0.5		
200	7.3803	394.7	155.0	0.0011
100	7.5412	470.8	140.2	0.0007
30	6.8769	341.8	158.4	0.0007
20	6.9410	396.6	145.8	0.0004
10	6.5828	377.6	147.2	0.0006
8	6.3122	333.2	156.7	0.0005

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.5		
7	6.2509	336.6	155.9	0.0004
6	6.2966	369.8	151.6	0.0005
5	6.1330	355.2	156.7	0.0005
4	5.9327	346.5	162.8	0.0004
3	5.9123	397.4	162.6	0.0009
		x = 0.6		
200	7.4931	430.2	148.9	0.0010
100	7.4598	450.4	144.1	0.0008
30	6.9066	356.0	156.1	0.0005
20	6.8293	370.9	151.8	0.0012
10	6.5082	358.5	153.5	0.0011
8	6.4086	364.8	153.0	0.0005
7	6.2530	343.2	157.6	0.0003
6	6.2581	362.7	156.1	0.0005
5	6.1181	355.1	160.2	0.0009

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.6		
4	5.8981	341.7	168.1	0.0005
3	5.9002	395.5	168.1	0.0007
		x = 0.7		
200	7.5440	450.1	146.3	0.0007
100	7.8567	601.7	119.1	0.0044
30	6.9454	369.6	154.3	0.0007
20	6.8680	397.3	147.3	0.0008
10	6.4859	357.8	155.5	0.0004
8	6.3621	357.5	156.4	0.0008
7	6.2229	341.9	160.5	0.0004
6	6.2257	362.3	159.2	0.0005
5	6.1161	361.4	161.6	0.0004
4	5.8721	337.5	171.7	0.0008
3	5.7843	367.5	177.9	0.0005

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.8		
200	7.6462	481.3	142.0	0.0013
30	6.9496	372.0	155.0	0.0005
20	6.8552	390.6	150.3	0.0006
10	6.5739	389.3	151.6	0.0002
8	6.3489	357.3	159.3	0.0009
7	6.2333	344.7	164.1	0.0007
6	6.2232	365.7	161.7	0.0004
5	6.1236	366.6	164.0	0.0002
4	5.9587	363.5	170.4	0.0007
3	5.7375	357.2	184.3	0.0001
		x = 0.9		
100	7.8623	603.2	121.5	0.0027
30	6.9518	379.6	153.9	0.0014
20	6.7345	357.0	158.7	0.0007
10	6.5353	380.7	155.5	0.0004

Contd...

Table 3.4 contd..

R	$\ln A_{\Lambda}$	B_{Λ}/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.9		
8	6.4045	379.4	157.5	0.0006
7	6.3086	371.4	161.5	0.0007
6	6.1975	362.8	165.4	0.0006
5	5.9883	336.6	172.7	0.0005
4	5.9094	353.0	174.4	0.0004
3	5.8700	394.6	181.5	0.0003
		x = 1.0		
200	7.4161	423.85	152.2	0.0010
40	7.2015	440.8	144.9	0.0010
30	7.1462	439.9	145.4	0.0016
20	6.8262	386.7	154.1	0.0002
10	6.4503	359.8	161.8	0.0009
8	6.3764	375.7	160.8	0.0006
7	6.2623	362.5	166.1	0.0003

Contd...

Table 3.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 1.0		
6	6.1635	359.1	169.4	0.0006
5	5.9354	326.7	177.2	0.0012
4	5.9390	366.2	175.5	0.0012
3	5.9030	408.3	183.4	0.0003

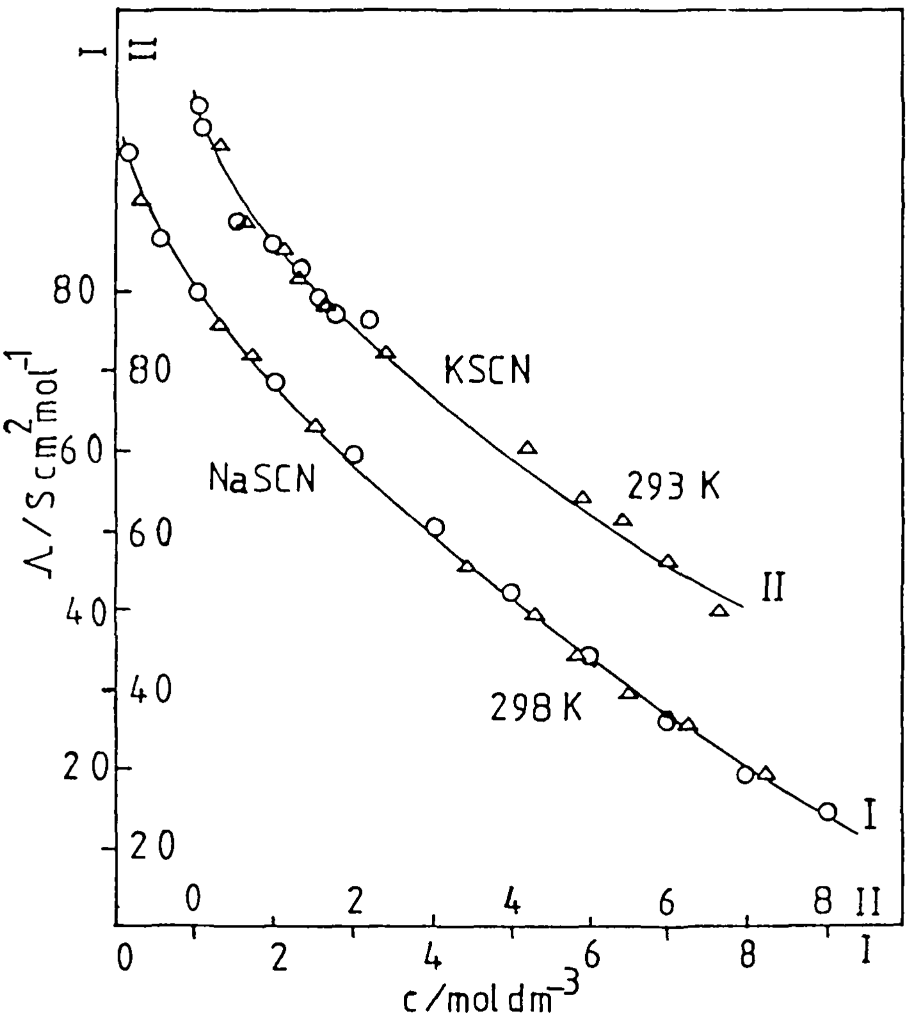

Fig.3.1 Plot of Λ vs. molar concentration for NaSCN and KSCN solutions (Δ-experimental, o-reported).

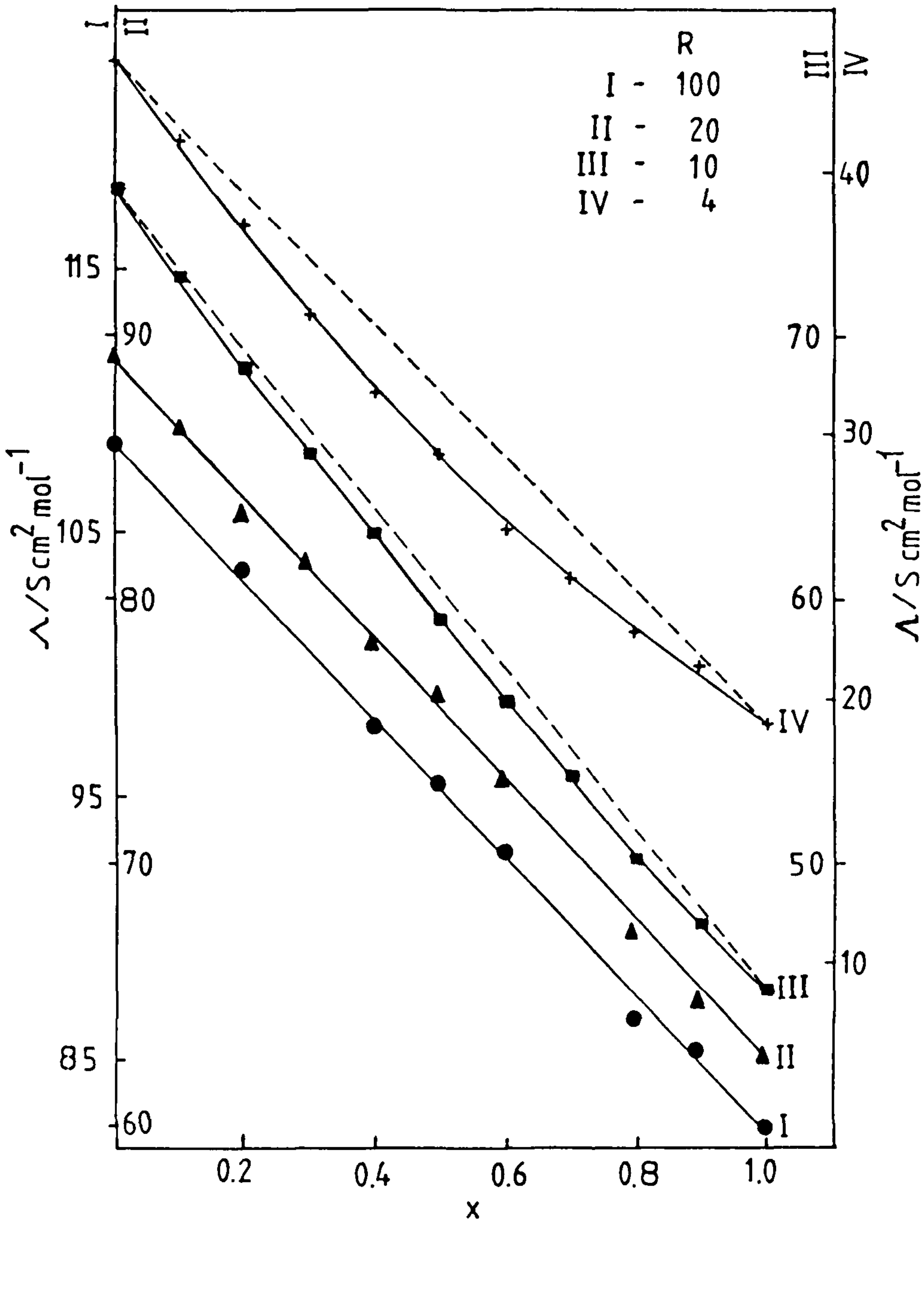

Fig.3.2 Variation of Λ of $[xNaSCN+(1-x)KSCN]+RH_2O$ system with x at different R values (T=298K).

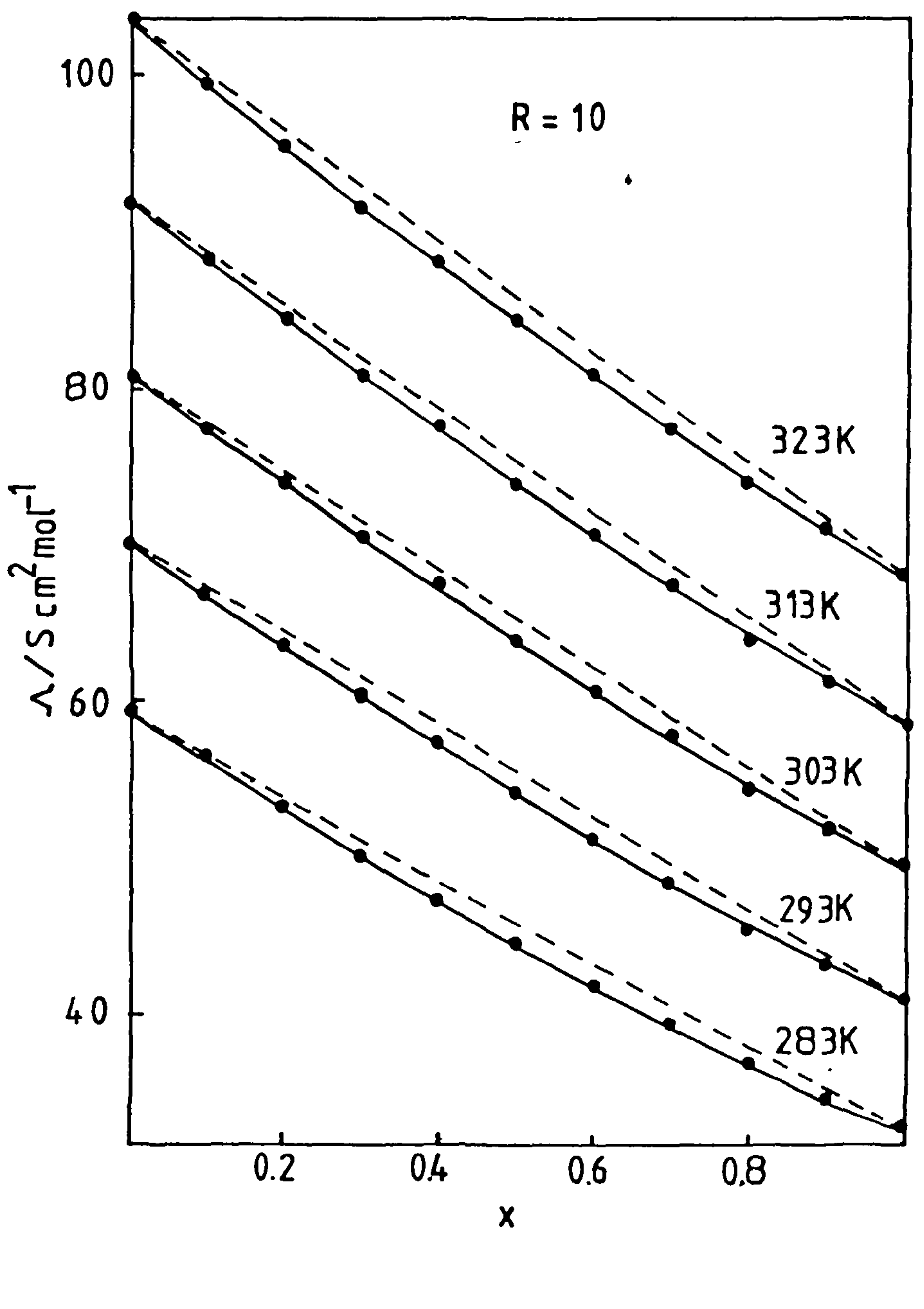

Fig.3.3 Plot of Λ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. x at different temperatures for R=10.

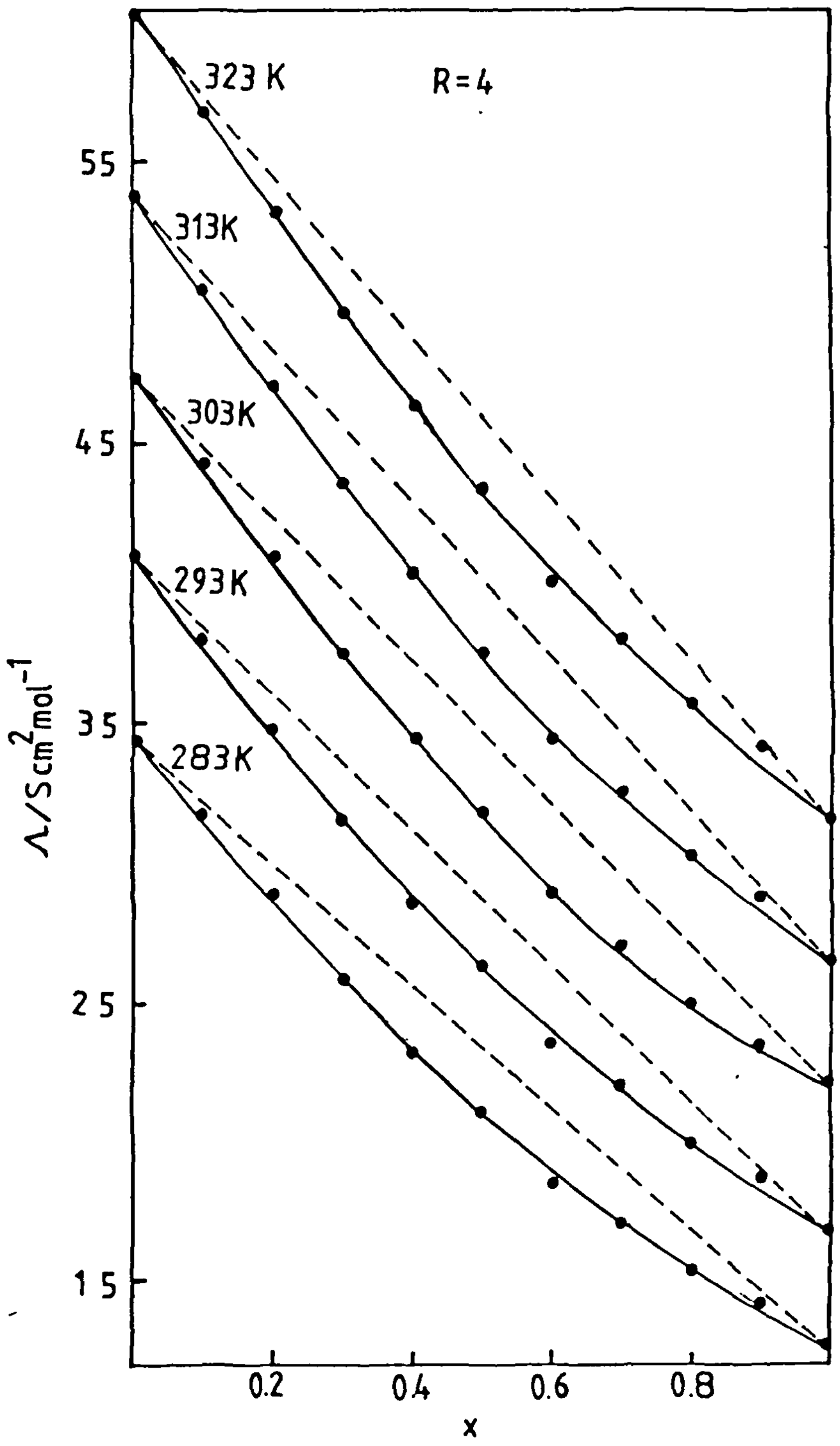

Fig.3.4 Plot of Λ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. x at different temperatures for R = 4.

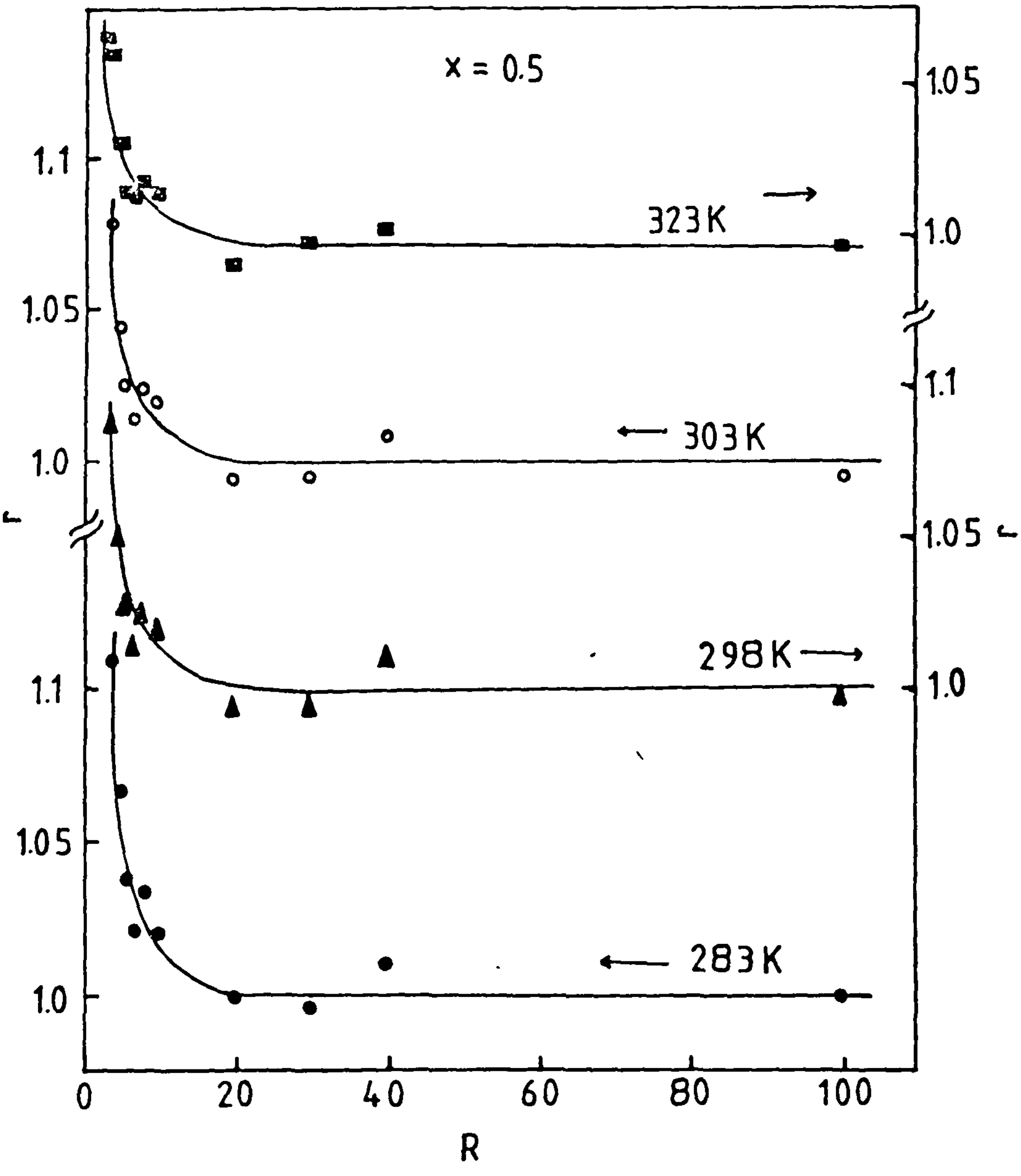

Fig.3.5 Variations of r for [xNaSCN+(1-x)KSCN]+RH_2O system with R at different temperatures.

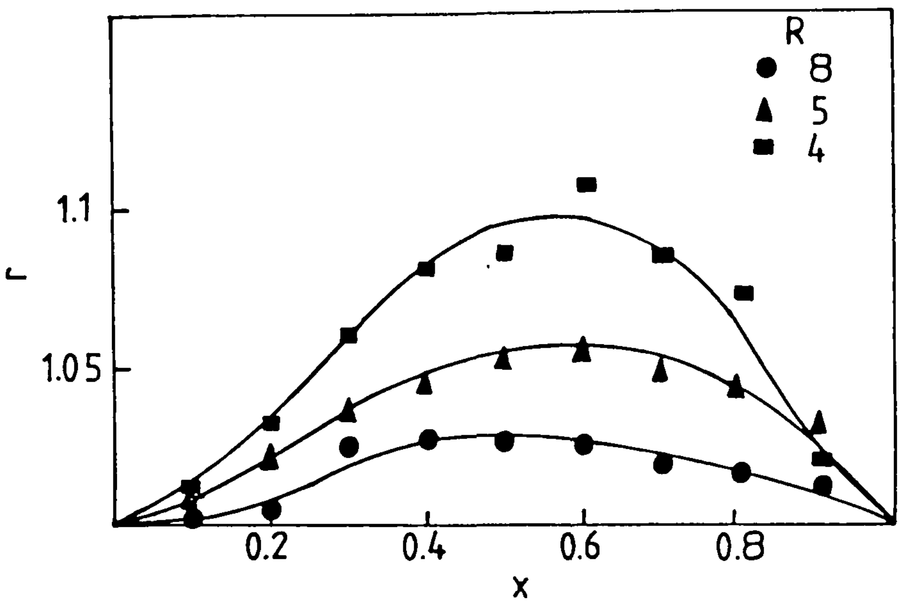

Fig.3.6 Plot of r for [xNaSCN+(1-x)KSCN]+RH_2O system vs. x at different R values.

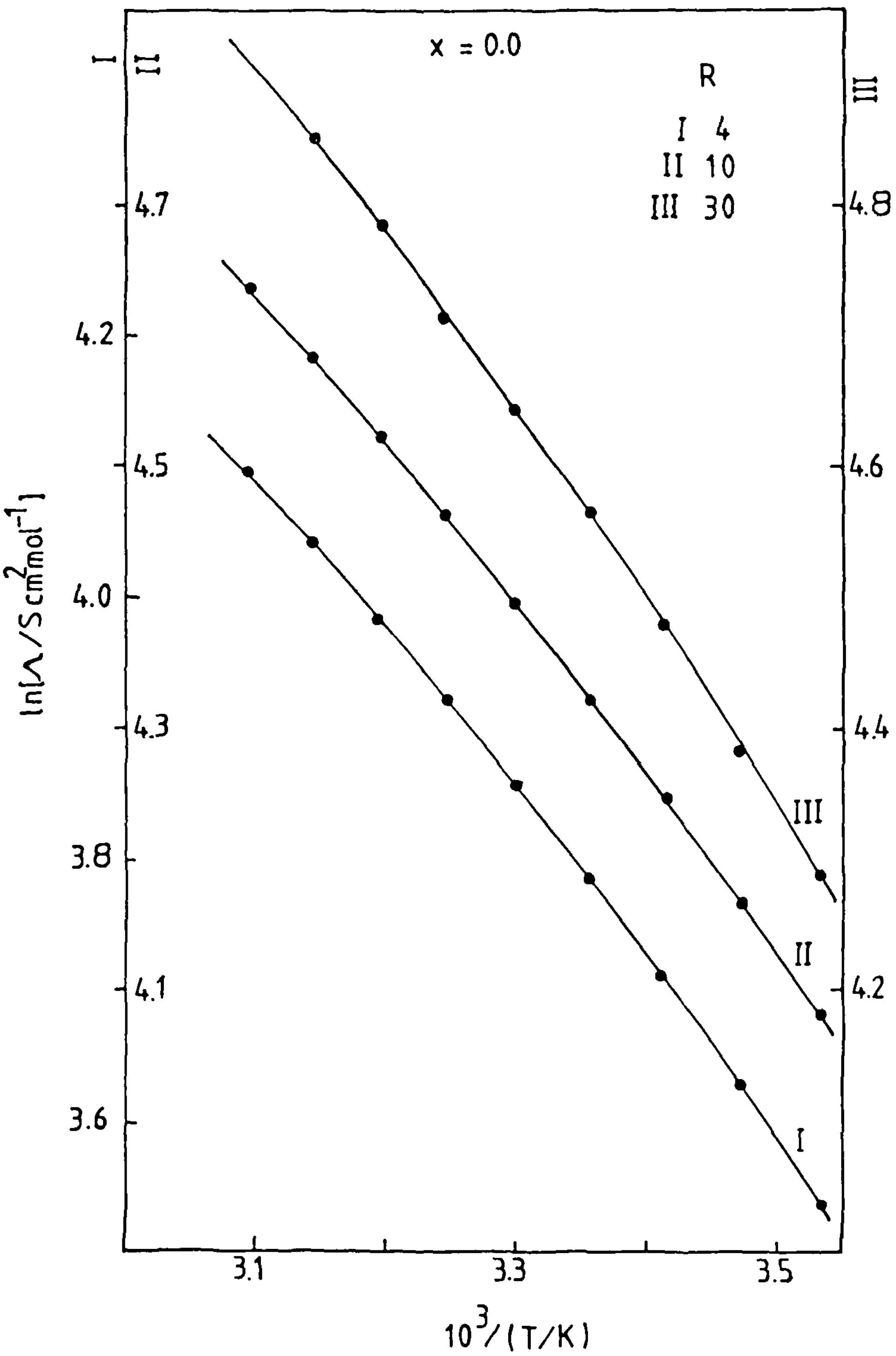

Fig.3.7 Plot of lnΛ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. 1/T at different R values for x = 0.0.

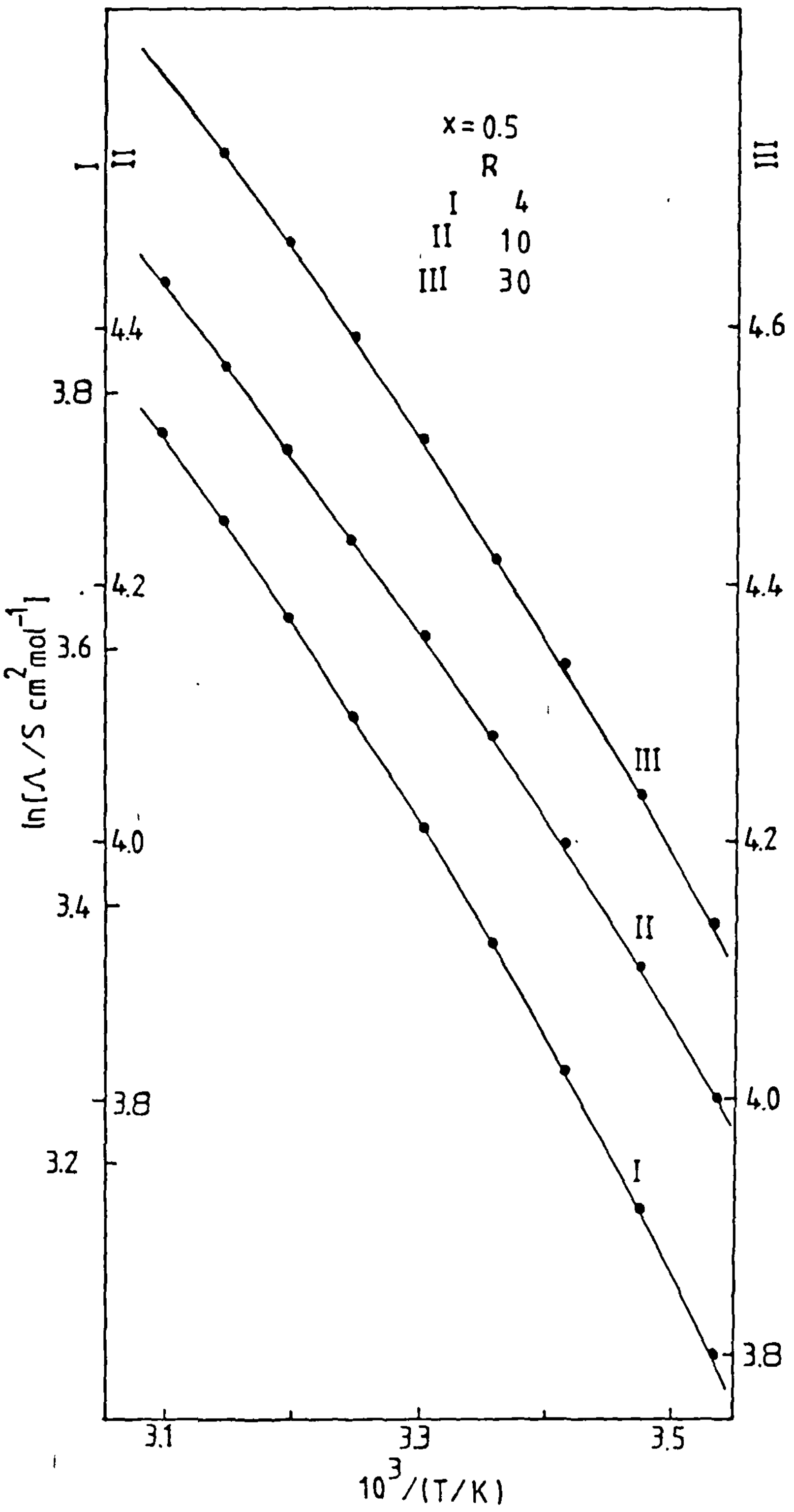

Fig.3.8 Plot of lnΛ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. 1/T at different R values for x = 0.5.

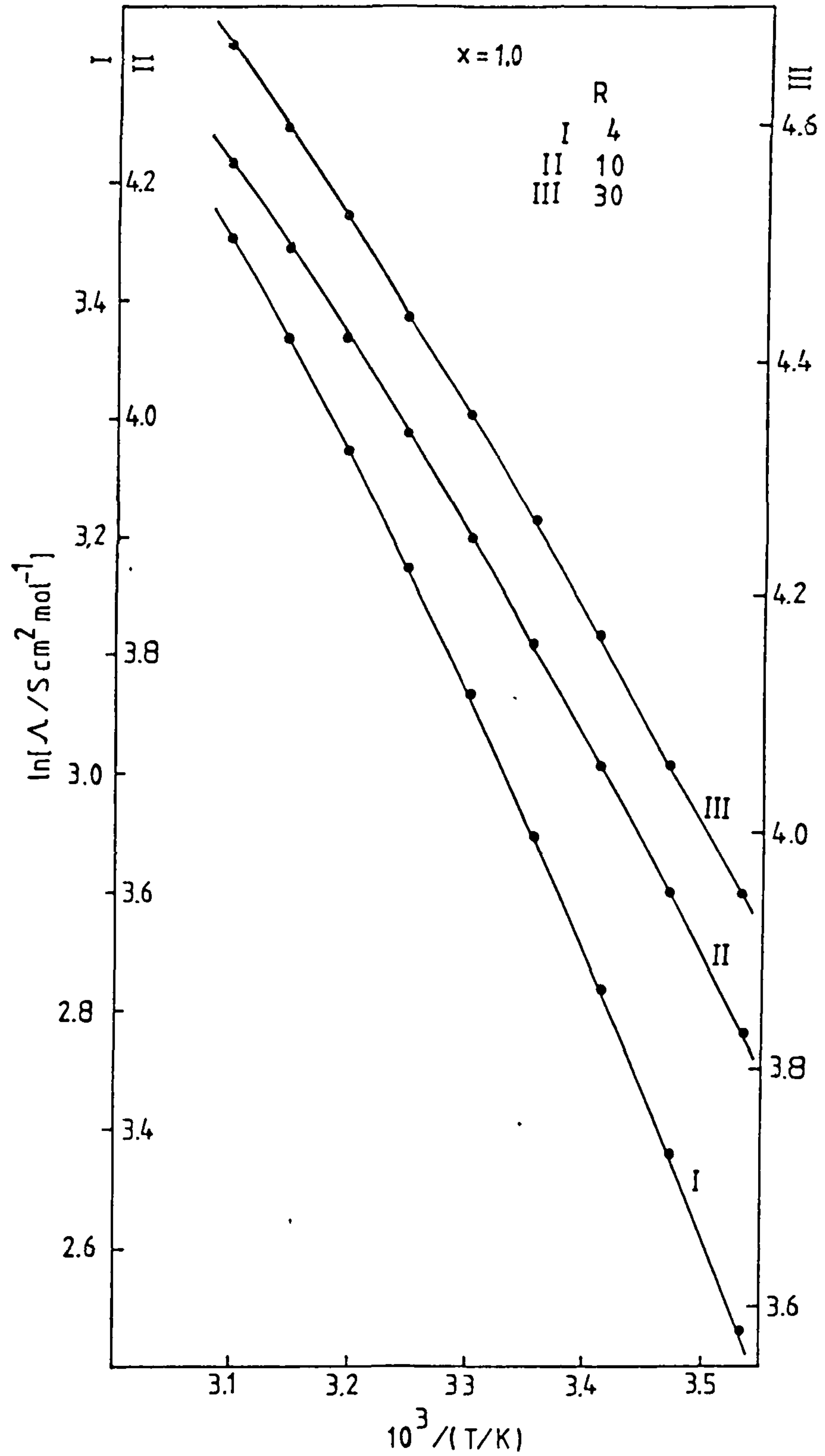

Fig.3.9 Plot of lnΛ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. 1/T at different R values for x = 1.0.

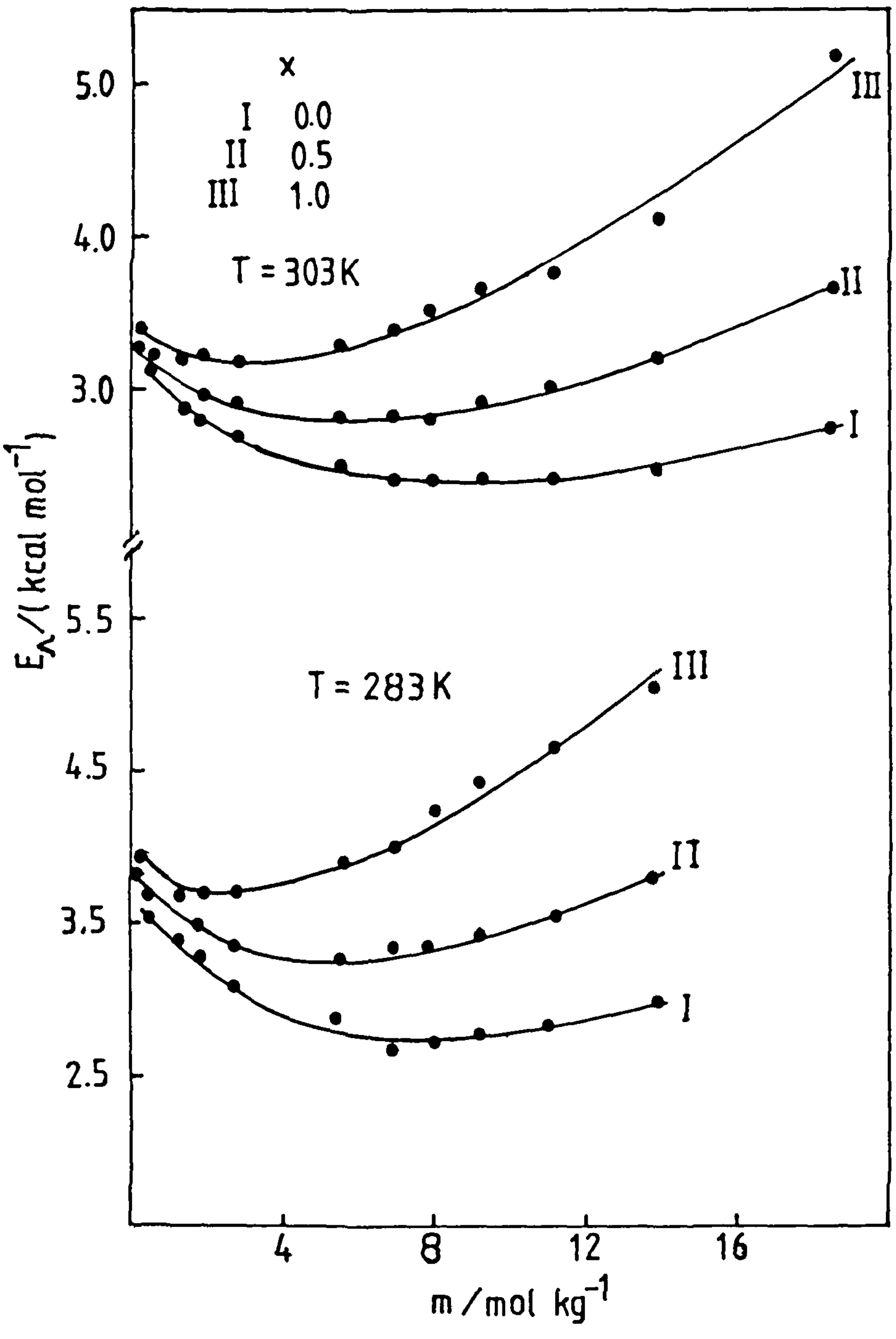

Fig.3.10 Plot of E_Λ of [xNaSCN+(1-x)KSCN]+RH_2O system vs. concentration at different *x and T*.

CHAPTER IV

ELECTRICAL CONDUCTANCE OF A MIXTURE OF SODIUM AND POTASSIUM NITRATES IN AQUEOUS MEDIUM

4.1 Introduction

With a view to understanding better the dependence of the MAE on the total alkali metal ion concentration we chose the aqueous medium and measured in Chapter III the electrical conductance of $[xNaSCN+(1-x)KSCN]+RH_2O$ system as functions of x,R and temperature. This study has shown that in the aqueous medium no MAE on electrical conductance exists in the low concentration (higher R value) region. Significant MAE occurs only above a particular concentration which is found to be in the case of $[xNaSCN+(1-x)KSCN]+RH_2O$ system the region where $R \leq 10$. It has been pointed out that the value of R at which the MAE on electrical conductance starts becoming significant is related to the lower concentration out of the two concentrations corresponding to the specific conductance maxima of the two constituent electrolytes of the mixed system. Furthermore, it has been suggested that in the region where the MAE exists the mixed electrolytic system has a quasi-crystalline-type structure. In order to examine further this type of dependence of MAE on R or on the total alkali metal ion concentration, the electrical conductances of another mixed electrolyte, viz., $[xNaNO_3+(1-x)KNO_3]+RH_2O$, are reported here as functions of x,R and temperature.

4.2 Experimental Section

$NaNO_3$(BDH, Laboratory Reagent) and KNO_3(BDH, Laboratory Reagent) were recrystallized from their solutions in doubly distilled water and were then dried for several days over $CaCl_2$ in vacuum desiccator. Using these salts solutions by weight were prepared in conductivity water. Density and electrical conductance measurements were made as described in Chapter II.

4.3 Results and Discussion

The experimental values of molar conductance of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system measured as functions of x,R and temperature are presented in Table 4.1. The density data are presented as a function of temperature in Table 4.2. The measured values of conductance were found to be reproducible within ±0.75% accuracy. A comparison of the present molar conductance data of aqueous $NaNO_3$ and KNO_3 solutions with the reported data[1] revealed an agreement of about ±1%. In the literature we could find one particular report[2] on the equivalent conductance of $[xNaNO_3+(1-x)KNO]+ 55.56H_2O$ system at 298K with x=0, 0.25, 0.5, 0.75 and 1. With this reported data our data, obtained after interpolation, are found to be in agreement within ±0.8%.

Variation of Λ with x. The variation of Λ with x at different R values is shown in Fig.4.1 Upto R=25 at all experimental temperatures less than 1% deviation of Λ from additivity has been observed. Rysselberghe and Nutting[2] also reported less than 1% deviation from additivity in Λ of $[xNaNO_3+(1-x)KNO_3]+55.56H_2O$ system at 298K. The MAE is, however, considered to be not very much significant when the non-additivity in Λ is <1%. At R=20, on the other hand, 2% deviation of Λ from additivity (Fig.4.1) has been observed for x=0.5 at 298K thereby envisaging the occurrence of the MAE on Λ. The onset of the MAE on Λ around R=20 may also be realized by evaluating the r-factor and then plotting r against R as shown in chapter III. As mentioned in the introduction (cf. Chapter III) for observing significant MAE on electrical conductance in aqueous medium the R value should be above or fall in the concentration range where conductivity maximum of atleast one of the components of the mixed electrolytic solution appears. The existence of MAE at 20R in the $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system is, however, contrary to our above suggestion since conductivity maximum has not been observed or reported for KNO_3 solution upto saturation point and for $NaNO_3$ solution it is found at ~6.9R. What is then the concentration range at which the MAE on Λ becomes significant in the aqueous medium? To seek a probable answer to this question we have plotted in Fig.4.2 the difference ($\Delta\Lambda$) in the Λ values of (i) NaSCN and KSCN solutions and (ii) $NaNO_3$ and KNO_3 solutions as a function of R at 298K. It is evident from Fig.4.2 that at high R values $\Delta\Lambda$ depends linearly on R and at some concentration range deviation from the linear dependence starts taking place. It is very interesting to observe that the concentration range at which the MAE on Λ starts becoming significant coincides with the concentration range where dependence of $\Delta\Lambda$ on R deviates from linearity. Incidentally, in the case of NaSCN and KSCN solutions the concentration range around which $\Delta\Lambda$ deviates from linearity coincides with the range at which NaSCN solution exhibits specific conductance maximum. In Fig.4.2 we also checked the dependence of $\Delta\Lambda$ on R for a few other pair of electrolytes, viz., RbCl and CsCl (at 296K), NaCl and KCl (at 298K) and LiCl and RbCl (at 296K), with the help of their reported data.[1,3,4] In all cases, the dependence of $\Delta\Lambda$ on R follows a general trend, viz., (i) linear dependence at large R values, (ii) at some concentration range, which depends on the pair of electrolytes considered, deviation from linearity is observed and (iii) the plot of $\Delta\Lambda$ vs. R passes through a maximum at some lower R value. Therefore, for mixed electrolyte systems in aqueous medium the concentration range at which the MAE on Λ begins to become significant can be predetermined by plotting the difference in Λ of the two pure electrolytic solutions versus R. Furthermore, as it was explained in Chapter III the deviation of Λ from additivity in the present system under study may also be described using the anion polarization model.[5,6]

Variation of Λ with R. Equation (3.2) which was newly introduced in Chapter III has been applied to explain the dependence of Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system on R. In the present case also while fitting the Λ data to equation (3.2) it was reduced to a 3-parameter equation, by substituting the reported[7] values of Λ_o for x=0 and x=1 and for other values of x the corresponding Λ_o values were estimated using the additivity principle.[8] The best-fit values of a_o, B_1' and C_1' obtained by using an iterative least-squares fitting program (Appendix A) are listed in Table 4.3.

For a_o one normally expects a value greater than the sum of crystallographic radii and less than the sum of solvated radii due to overlapping of the hydration spheres of the cation and anion.[9] a_o=4.36A° at 298K for $NaNO_3$ solution is in accordance with this expectation. Some of the reported values[10-12] of a_o for $NaNO_3$ solution vary from 2.7 to 5.5A°. On the contrary, a_o=1.9A° computed for KNO_3 solution is even less than the sum of the crystallographic radii of K^+ and NO_3^- ions. Kay[10] also reported a_o=1.9A° for KNO_3 solution by analyzing its conductance data at low concentrations (upto 0.01 $mol.dm^{-3}$) using the Fuoss-Onsager equation. Such a discrepancy in the computed value of a_o was reported in the case of a few other electrolytes also.[13] The variation of a_o with x seems to be almost linear as apparent from Fig.4.3. Kay[10] attributed the decrease in

a_o values of alkali salts with increasing crystallographic radii of alkali metal ions to the increasing amount of association. However, in the case of KNO_3 solution it is doubtful that its extremely low value of a_o is attributable to ion-association since, as mentioned above, a_o=1.9A° was obtained for this solution even after using its conductance data pertaining to the low concentration region only where appreciable amount of ion-association is not expected. The viscosity correction suggested by Fuoss[14] to account for the low value of a_o was proved to be inadequate.[10,13] Goldsack et al.[3] modified the FLK equation by introducing in it the concentration dependence of a_o. In order to examine whether the value of a_o increases for KNO_3 solution after accounting for its concentration dependence, we fitted the data of this solution to the equation of Goldsack et al.[3] A good fitting, but not better than the fitting using equation(3.2), was obtained only with negative value of H_o, the hydration number (Ho=-7). This indicates that the value of a_o remains less than the sum of the crystallographic radii of the ions even if one considers a_o to be concentration dependent as suggested by Goldsack et al.[3] A fit to the Monica equation,[12] which is a modified WS equation[15] with the electrophoretic term corrected for the viscosity of the solution (cf. Chapter I), also did not improve the value of a_o for KNO_3(a_o=1.83A° was obtained) solution. We also made an attempt to analyze the concentration dependence of a_o of KNO_3 solution using the recent approach of Monica et al.[16] Following this procedure of Monica et al.[16] we obtained values of a_o of KNO_3 solution at different concentrations. Such an analysis also provided extremely low values for a_o of KNO_3 solution except at one concentration, i.e., $c=0.001 mol.dm^{-3}$ ($a_o=6.3A°$) and the dependence of a_o on concentration was found to be very less. Some of the typical values obtained for a_o are 2.3A° at $c=0.002 mol.dm^{-3}$, 3.19A° at $c=0.005 mol.dm^{-3}$, 1.56A° at $c=0.01 mol.dm^{-3}$, 1.37A° at $c=0.02 mol.dm^{-3}$, 1.44A° at $c=0.005 mol.dm^{-3}$, 1.96A° at $c=0.4888 mol.dm^{-3}$ 1.84A° at $c=1.4087 mol.dm^{-3}$, 1.77A° at $c=2.6559 mol.dm^{-3}$, etc. From Fig.4.3 it is also apparent that the a_o parameter for pure $NaNO_3$ solution is almost temperature independent whereas the a_o of KNO_3 solution increases with increase in temperature. This is analogous to the observation made by Goldsack et al.[3] in the cases of NaCl and KCl solutions. The above analysis therefore emphasizes that a_o, although originally introduced in the FLK equation (1.7) to account for the ion-size, behaves more like an adjustable parameter. This observation was made during the study of [xNaSCN+(1-x)KSCN]+ RH_2O system also (cf. Chapter III).

The dependences of B_1' and C_1' parameters on x are also shown in Fig.4.3 at one particular temperature.

C_1' which is always a negative quantity, has lowest value for pure KNO_3 solution and its value increases rapidly as K^+ ions are replaced by Na^+ ions. In the range from x=0.5 to x=1.0, C_1' appears to remain almost independent of the x value. In the case of B_1', it has a highest positive value for KNO_3 solution and its value decreases with increasing x value becoming negative above a particular value of x. The value of x at which B_1' becomes zero is dependent on the temperature. For example, at 298K $B_1'=0$ at x=0.04 whereas at 288K $B_1'=0$ at x=0.16. Similar behaviour was observed in the case of $[xNaSCN+(1-x)KSCN]+RH_2O$ system also. This type of dependence of B_1' on x may be explained by correlating the exponential part of equation (3.2) to the reciprocal of viscosity of the system as it was done in Chapter III. Consequently, solutions whose B_1' is positive and C_1' is negative may be expected to show negative viscosity. In fact, aqueous KNO_3 solution is known[1] to exhibit negative viscosity nearly upto 318K. At 298K the viscosity of KNO_3 solution is therefore expected to decrease with concentration upto $c=B_1'/C_1'=1.2$ $mol.dm^{-3}$ which is in good agreement with the experimentally observed value.[1]

Furthermore, since the exponential part of equation (3.2) is identified as the term which accounts for the ion-solvent interactions (cf. Chapter III) an attempt has been made to correlate B_1' or C_1' to some ion-solvent interaction parameters. This has been done in the light of the model suggested by Samoilov[17] for hydration of ions. According to this model hydration is measured in terms of the ratio of the average time a molecule of water spends in the equilibrium position closest to the ion in solution (t_i) to that a molecule of water spends in the immediate vicinity of another water molecule in pure water(t). Samoilov gave the relation $t_i/t=\exp(\Delta E/RT)$ where ΔE is the energy of activation required per mole of water to change the equilibrium position near to the ion to one near to the bulk water. If $t_i/t>1$, the ion is strongly hydrated and for such ions ΔE is positive. Samoilov estimated at 21.5°C the ΔE values for different ions and interestingly found that Na^+ ion has positive value of ΔE whereas K^+ion has negative ΔE. Therefore, water molecule near K^+ion is more mobile than in the bulk and such ions having negative value for ΔE are said to undergo negative hydration. It is interesting to find that ΔE is similar to the B_1' parameter as both are dependent on ionic radius and change their sign when Na^+ion is replaced by K^+ion. It may therefore be inferred that $B_1' \propto -\Delta E$ and positive B_1' value of KNO_3 solution may be attributed to the negative hydration of K^+ion.

Variation of Λ with T. From Figs.4.4-4.6 it may be seen that in the present system also the variation of Λ with T in the experimental range of temperature (283K-313K) is slightly non-Arrhenius-type. The Λ vs.T data are therefore least-squares fitted to the VTF equation(3.3) and the best-fit values of the VTF parameters obtained thus are listed in Table 4.4. In $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system also we do not observe any regular trend in the variation of the VTF parameters with R. The energy of activation for conductance flow (E_Λ) calculated (equation (3.4)) using the best-fit values of the VTF parameters vary with m in the same fashion as E_Λ of $[xNaSCN+(1-x)KSCN]+RH_2O$ system.

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Table 4.1 Molar conductance data for [$xNaNO_3$+(1-x)KNO_3]+RH_2O system

R	Λ/S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.0			
200	80.3	90.0	100.0	110.2	120.7	131.4	142.2
150	77.9	87.2	96.8	106.7	116.8	127.2	137.7
100	74.0	82.8	91.9	101.2	110.6	120.3	130.1
75	71.3	79.6	88.3	97.1	106.1	115.3	124.7
50	66.7	74.4	82.4	90.5	98.8	107.2	115.7
40	64.2	71.5	79.1	86.8	94.6	103.0	111.0
30	60.3	67.1	74.0	81.4	88.6	95.9	103.2
25	57.7	64.4	70.9	77.7	84.4	91.3	98.3
20*			67.5	74.0	80.6	87.4	94.2
				x = 0.1			
200	78.8	88.3	98.2	108.3	118.6	129.2	140.0
150	76.3	85.5	95.1	104.9	114.9	125.1	135.5
100	72.5	81.2	90.1	99.3	108.7	118.2	127.8
75	69.8	78.0	86.5	95.2	104.0	113.0	122.2

*Data taken from ref.1.

Contd..

Table 4.1 contd..

R	Λ /S cm^{2}mol^{-1}						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.1			
50	65.2	72.8	80.7	88.7	96.9	105.2	113.5
40	62.7	69.9	77.3	84.9	92.5	100.7	108.7
30	58.9	65.5	72.4	79.6	86.7	94.0	101.3
25	56.3	62.6	69.4	76.0	82.7	89.6	96.4
20				71.2	77.4	83.7	90.0
				x = 0.2			
200	77.4	86.8	96.5	106.5	116.6	127.1	137.7
150	74.9	84.0	93.4	103.1	112.8	122.8	133.1
100	71.2	79.7	88.6	97.6	106.8	116.2	125.7
75	68.6	76.7	85.1	93.8	102.6	111.5	120.6
50	63.9	71.5	79.2	87.0	95.1	103.4	111.6
40	61.2	68.3	75.6	83.1	90.7	98.5	106.6
30	57.6	64.2	71.0	78.2	85.2	92.4	99.6
25	54.8	61.1	67.7	74.2	80.9	87.6	94.2
20	51.4	57.4	63.3	69.3	75.4	81.6	87.8

Contd....

Table 4.1 contd..

R	Λ /S cm^{2}mol^{-1}						
	283K	288K	293K	298K	303K	308K	313K
			x = 0.3				
200	76.1	85 3	94.9	104.7	114.8	125.1	135.5
150	73.6	82.5	91.8	101.3	111.0	121.0	131.1
100	69.8	78.2	87.0	95.9	104.9	114.4	123.8
75	67.0	74.9	83.2	91.6	100.2	109.0	118.1
50	65.5	69.9	77.5	85.3	93.2	101.3	109.5
40	60.0	67.0	74.3	81.6	89.1	96.8	104.7
30	56.1	62.6	69.3	76.3	83.2	90.2	97.3
25	53.5	59.6	66.1	72.5	79.0	85.7	92.3
20	50.0	55.8	61.7	67.5	73.7	79.6	85.7
			x = 0.4				
200	74.6	83.8	93.2	102.9	112.8	123.0	133.2
150	72.3	81.0	90.2	99.5	109.1	119.0	128.9
100	68.5	76.8	85.3	94.1	103.2	112.4	121.6
75	65.7	73.5	81.8	90.1	98.7	107.4	116.3
50	61.3	68.4	75.9	83.6	91.4	99.3	107.4

Contd...

Table 4.1 contd...

R	Λ /S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
			x = 0.4				
40	58.6	65.4	72.5	79.7	87.0	94.5	102.5
30	54.8	61.1	67.6	74.2	81.3	88.3	95.3
25	52.2	58.1	64.6	70.9	77.4	83.9	90.5
20	48.1	53.8	59.4	65.2	70.8	76.8	82.6
13				55.6	60.5	65.4	70.4
			x = 0.5				
200	73.0	81.9	91.2	100.7	110.5	120.5	130.6
150	70.7	79.3	88.3	97.5	106.9	116.6	126.4
100	67.4	75.5	84.0	92.7	101.5	110.6	119.8
75	64.3	72.1	80.1	88.3	96.7	105.3	114.1
50	60.0	67.1	74.5	82.0	89.6	97.5	105.4
40	57.3	64.0	71.0	78.1	85.3	92.7	100.4
30	53.5	59.7	66.1	72.8	79.7	86.5	93.5
25	50.8	56.6	62.7	69.1	75.4	81.8	88.1
20	47.1	52.8	58.4	64.1	69.9	75.8	81.7

Contd...

Table 4.1 contd..

R	Λ /S cm^{2}mol^{-1}						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.5			
13	40.0	44.5	49.2	53.9	58.7	63.6	68.6
11				50.2	54.6	59.2	63.8
				x = 0.6			
200	71.7	80.5	89.6	98.9	108.5	118.3	128.3
150	69.5	78.0	86.9	95.9	105.2	114.7	124.5
100	66.0	73.9	82.3	90.8	99.6	108.5	117.6
75	63.2	70.8	78.7	86.8	95.1	103.6	112.2
50	58.7	65.8	73.0	80.4	88.0	95.8	103.6
40	56.0	62.7	69.5	76.6	83.8	91.1	98.5
30	52.2	58.2	64.6	71.0	77.9	84.6	91.4
25	49.6	55.3	61.2	67.6	73.8	80.2	86.6
20	45.8	51.2	56.9	62.5	68.2	74.0	79.9
13	38.7	43.2	47.8	52.5	57.3	62.1	66.9
11	35.8	39.9	44.1	48.4	52.8	57.3	61.8

Contd....

Table 4.1 contd..

R	Λ /S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
			x = 0.6				
9				43.3	47.2	51.2	55.2
8				40.2	43.8	47.5	51.2
			x = 0.7				
200	70.5	79.2	88.2	97.5	107.0	116.8	126.7
150	68.0	76.4	85.1	94.0	103.2	112.6	122.1
100	64.8	72.6	80.9	89.2	97.8	106.6	115.7
75	61.9	69.4	77.2	85.1	93.3	101.7	110.1
50	57.7	64.6	71.7	79.1	86.6	94.3	102.1
40	54.7	61.3	68.1	75.0	82.1	89.3	96.6
30	51.0	56.9	63.2	69.5	76.3	82.9	89.6
25	48.2	53.9	59.7	65.9	72.0	78.3	84.5
20	44.7	49.8	55.4	61.0	66.6	72.3	78.1
13	37.3	41.7	46.2	50.8	55.4	60.1	64.8
11	34.4	38.4	42.5	46.7	51.0	55.4	59.9
9	30.6	34.2	37.9	41.7	45.5	49.5	53.4

Contd...

Table 4.1 contd..

R	Λ /S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.7			
8	28.4	31.7	35.1	38.7	42.2	45.9	49.6
7				35.0	38.3	41.7	45.2
				x = 0.8			
200	68.9	77.6	86.4	95.7	105.2	114.8	124.7
150	66.9	75.1	83.7	92.5	101.6	110.9	120.4
100	63.5	71.2	79.3	87.6	96.0	104.8	113.5
75	60.8	68.2	75.9	83.8	91.8	100.1	108.5
50	56.5	63.2	70.3	77.5	84.8	92.3	99.9
40	53.5	60.0	66.6	73.4	80.2	87.3	94.5
30	49.7	55.6	61.7	68.0	74.4	81.2	87.8
25	47.1	52.6	58.3	64.5	70.5	76.6	82.7
20	43.4	48.5	54.1	59.5	65.1	70.8	76.5
13	36.1	40.3	44.7	49.2	53.8	58.5	63.2
11	33.0	37.0	41.1	45.2	49.4	53.7	58.0

Contd...

Table 4.1 contd..

R	Λ /S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.8			
9	29.3	32.8	36.4	40.1	43.9	47.8	51.7
8	27.0	30.3	33.6	37.1	40.6	44.2	47.9
7	24.6	27.6	30.8	33.9	37.2	40.5	43.9
6				30.0	33.0	36.0	39.1
				x = 0.9			
200	65.5	76.0	84.7	93.8	103.0	112.6	122.2
150	65.7	73.8	82.3	91.0	99.9	109.1	118.5
100	62.4	70.0	77.9	86.1	94.5	103.1	111.8
75	59.5	66.8	74.3	82.0	90.0	98.1	106.3
50	55.3	61.9	68.9	76.0	83.2	90.6	98.2
40	52.4	58.7	65.2	71.9	78.8	85.8	93.0
30	48.5	54.4	60.4	66.6	72.8	79.6	86.2
25	45.8	51.3	57.0	62.8	68.9	75.1	81.2
20	42.3	47.3	52.8	58.1	63.6	69.3	74.9
13	34.8	39.0	43.3	47.7	52.2	56.8	61.4
11	31.7	35.5	39.5	43.5	47.7	51.9	56.1

Contd....

Table 4.1 contd..

R	Λ /S $cm^2 mol^{-1}$						
	283K	288K	293K	298K	303K	308K	313K
				x = 0.9			
9	28.0	31.4	35.0	38.6	42.4	46.2	50.1
8	25.8	29.0	32.3	35.7	39.1	42.7	46.3
7	23.4	26.4	29.4	32.4	35.7	39.0	42.4
6				28.6	31.5	34.5	37.5
				x = 1.0			
200	66.4	74.7	83.3	92.1	101.2	110.5	120.1
150	64.3	72.2	80.6	89.1	97.9	106.9	116.1
100	61.1	68.6	76.4	84.5	92.8	101.3	109.9
75	58.3	65.4	72.8	80.4	88.2	96.2	104.4
50	54.1	60.7	67.5	74.5	81.7	89.0	96.5
40	51.3	57.5	64.0	70.6	77.4	84.3	91.3
30	47.6	53.3	59.2	65.4	71.6	78.2	84.7
25	44.6	50.0	55.5	61.2	67.3	73.2	79.3
20	41.1	46.0	51.1	56.6	62.2	67.6	73.2

Contd....

Table 4.1 contd..

R	Λ /S cm^{2}mol^{-1}						
	283K	288K	293K	298K	303K	308K	313K
				x = 1.0			
13	33.6	37.6	41.8	46.1	50.5	55.1	59.7
11	30.7	34.5	38.4	42.4	46.5	50.7	54.9
9	26.8	30.1	33.6	37.2	40.8	44.6	48.4
8	24.6	27.7	31.0	34.3	37.7	41.2	44.8
7	22.4	25.1	28.0	31.1	34.3	37.5	40.8
6				27.3	30.2	33.2	36.1

Table 4.2 Best-fit parameters of the density equation, ρ =a-bt for [$xNaNO_3$+(1-x)KNO_3]+RH_2O system

x	a/g.cm^{-3}	b x 10^4/ g.cm^{-3}°C^{-1}	- (corr. coeff.)	x	a/g.cm^{-3}	b x 10^4/ g.cm^{-3}°C^{-1}	- (corr. coeff.)
			R = 200				
0.0	1.0166	2.8795	0.9303	0.1	1.0177	3.1724	0.9945
0.2	1.0160	2.6831	0.9889	0.3	1.0170	3.0279	0.9955
0.4	1.0158	2.7425	0.9920	0.5	1.0157	2.7441	0.9913
0.6	1.0153	2.6402	0.9879	0.7	1.0159	2.8671	0.9908
0.8	1.0167	3.1198	0.9940	0.9	1.0161	3.0764	0.9947
1.0	1.0153	2.7926	0.9927				
			R = 150				
0.0	1.0226	2.9924	0.9943	0.1	1.0236	3.2834	0.9947
0.2	1.0235	3.2263	0.9962	0.3	1.0234	3.3288	0.9966
0.4	1.0218	3.0040	0.9932	0.5	1.0222	3.1641	0.9932
0.6	1.0213	2.9600	0.9928	0.7	1.0218	3.1230	0.9943
0.8	1.0217	3.2008	0.9964	0.9	1.0199	2.7939	0.9937
1.0	1.0205	2.8280	0.9931				

Contd...

Table 4.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/ g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/ g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
				R = 100			
0.0	1.0341	3.3242	0.9978	0.1	1.0344	3.2621	0.9969
0.2	1.0332	3.1104	0.9949	0.3	1.0336	3.4746	0.9962
0.4	1.0339	3.4574	0.9964	0.5	1.0328	3.3356	0.9967
0.6	1.0330	3.4623	0.9969	0.7	1.0317	3.0514	0.9969
0.8	1.0313	3.1052	0.9933	0.9	1.0310	3.0492	0.9956
1.0	1.0308	2.9762	0.9951				
				R = 75			
0.0	1.0454	3.4562	0.9980	0.1	1.0440	3.0701	0.9947
0.2	1.0439	3.2557	0.9964	0.3	1.0444	3.5033	0.9971
0.4	1.0441	3.6457	0.9976	0.5	1.0430	3.4402	0.9973
0.6	1.0430	3.5001	0.9987	0.7	1.0427	3.4988	0.9968
0.8	1.0423	3.6048	0.9973	0.9	1.0418	3.5184	0.9979
1.0	1.0407	3.3905	0.9963				

Contd...

Table 4.2 contd..

x	a/g.cm^{-3}	b x 10^4/ g.cm^{-3}°C^{-1}	- (corr. coeff.)	x	a/g.cm^{-3}	b x 10^4/ g.cm^{-3}°C^{-1}	- (corr. coeff.)
			R = 50				
0.0	1.0667	3.6453	0.9989	0.1	1.0659	3.6664	0.9986
0.2	1.0649	3.5624	0.9986	0.3	1.0648	3.6205	0.9978
0.4	1.0637	3.5649	0.9975	0.5	1.0628	3.5163	0.9983
0.6	1.0629	3.5851	0.9984	0.7	1.0625	3.6717	0.9987
0.8	1.0624	3.8006	0.9989	0.9	1.0617	3.7864	0.9984
1.0	1.0593	3.8334	0.9996				
			R = 40				
0.0	1.0817	3.8685	0.9988	0.1	1.0813	3.9110	0.9990
0.2	1.0804	3.8853	0.9991	0.3	1.0799	4.0450	0.9992
0.4	1.0794	4.0607	0.9994	0.5	1.0788	4.0463	0.9992
0.6	1.0775	3.9438	0.9989	0.7	1.0770	3.9135	0.9989
0.8	1.0766	4.0023	0.9989	0.9	1.0767	4.3467	0.9995
1.0	1.0756	4.1381	0.9997				

Contd...

Table 4.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
			R = 30				
0.0	1.1069	4.2435	0.9997	0.1	1.1066	4.3000	0.9996
0.2	1.1051	4.3018	0.9994	0.3	1.1039	4.1271	0.9989
0.4	1.1035	4.3930	0.9996	0.5	1.1027	4.3549	0.9995
0.6	1.1015	4.3806	0.9992	0.7	1.1006	4.2025	0.9989
0.8	1.0995	4.3546	0.9990	0.9	1.0993	4.5286	0.9996
1.0	1.0985	4.6790	0.9992				
			R = 25				
0.0	1.1264	4.5157	0.9995	0.1	1.1241	4.5334	0.9997
0.2	1.1240	4.5171	0.9998	0.3	1.1233	4.7651	0.9995
0.4	1.1213	4.5980	0.9997	0.5	1.1210	4.5806	0.9998
0.6	1.1190	4.5480	0.9992	0.7	1.1195	4.4805	0.9996
0.8	1.1177	4.6306	0.9994	0.9	1.1167	4.5664	0.9995
1.0	1.1162	4.8031	0.9996				

Contd...

Table 4.2 contd..

x	a/g.cm^{-3}	b x 10^{4}/ g.cm^{-3}°C^{-1}	- (corr. coeff.)	x	a/g.cm^{-3}	b x 10^{4}/ g.cm^{-3}°C^{-1}	- (corr. coeff.)
				R = 20			
0.0	1.1566	5.2600	0.9996	0.1	1.1516	4.8556	0.9995
0.2	1.1506	4.9733	0.9997	0.3	1.1496	4.9585	0.9997
0.4	1.1482	4.9489	0.9997	0.5	1.1474	4.9333	0.9996
0.6	1.1465	4.9523	0.9994	0.7	1.1459	5.1179	0.9999
0.8	1.1442	5.1446	0.9999	0.9	1.1430	5.2915	0.9998
1.0	1.1412	5.2295	0.9998				
				R = 13			
0.4	1.2141	6.3432	1.0000	0.5	1.2117	5.8718	0.9998
0.6	1.2105	5.8956	0.9999	0.7	1.2080	5.9682	0.9996
0.8	1.2063	5.9833	0.9998	0.9	1.2043	6.1071	1.0000
1.0	1.2059	6.1894	0.9998				
				R = 11			
0.5	1.2417	6.2264	0.9999	0.6	1.2404	6.1930	0.9998
0.7	1.2393	6.2436	0.9999	0.8	1.2380	6.4364	1.0000

Contd...

Table 4.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}°C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}°C^{-1}$	- (corr. coeff.)
				R = 11			
0.9	1.2362	6.5052	0.9999	1.0	1.2342	6.5102	0.9999
				R = 9			
0.6	1.2808	6.9533	0.9999	0.7	1.2784	6.6720	1.0000
0.8	1.2770	6.7713	0.9999	0.9	1.2752	6.8290	1.0000
1.0	1.2744	6.8398	0.9999				
				R = 8			
0.6	1.3069	7.0644	0.9998	0.7	1.3039	6.9178	0.9999
0.8	1.3029	6.9773	1.0000	0.9	1.2999	7.0258	1.0000
1.0	1.2982	7.0842	1.0000				
				R = 7			
0.7	1.3353	7.3808	0.9998	0.8	1.3312	7.2962	0.9999
0.9	1.3307	7.2460	0.9999	1.0	1.3285	7.3588	0.9999

Contd...

Table 4.2 contd..

x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)	x	$a/g.cm^{-3}$	$b \times 10^4/$ $g.cm^{-3}{}^\circ C^{-1}$	- (corr. coeff.)
				R = 6			
0.8	1.3696	7.6177	0.9999	0.9	1.3675	7.5369	1.0000
1.0	1.3649	7.6471	0.9999				

Table 4.3 Best-fit parameters of the molar conductance equation (3.2) for $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system.

x	Λ_o/Scm^2mol^{-1}	$a_o x10^8$/cm	$-B'_1 x10^2$	$-C'_1 x10^2$	Std.dev. in Λ
			283K		
0.0	104.72	1.45	-7.2011	24.2291	0.0764
0.1	102.91	1.46	-7.4013	25.4376	0.0634
0.2	101.10	2.02	-1.1577	16.4886	0.0861
0.3	99.29	2.43	2.5100	10.9361	0.0486
0.4	97.48	2.41	1.3431	16.8003	0.0804
0.5	95.67	2.92	5.9536	6.4186	0.1561
0.6	93.86	3.28	7.9798	3.8526	0.1180
0.7	92.05	3.56	9.1540	3.1174	0.1136
0.8	90.24	3.81	9.9922	2.8838	0.1135
0.9	88.43	4.11	10.9988	2.3698	0.1227
1.0	86.62	4.34	11.5403	2.4137	0.9044
			288K		
0.0	117.68	1.88	-2.0588	15.9339	0.0965
0.1	115.69	1.78	-3.8355	21.5192	0.0594

Contd...

Table 4.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B'_1$x10^2	$-C'_1$x10^2	Std.dev. in Λ
			288K		
0.2	113.70	2.34	1.9143	11.1323	0.1046
0.3	111.72	2.57	3.7544	8.7505	0.0630
0.4	109.73	2.66	3.6618	12.2280	0.0655
0.5	107.74	2.96	6.2356	6.0891	0.1313
0.6	105.75	3.34	8.4203	3.2913	0.1285
0.7	103.76	3.61	9.5568	2.5946	0.1219
0.8	101.78	3.86	10.3808	2.3071	0.1059
0.9	99.79	4.14	11.3021	1.8124	0.1041
1.0	97.80	4.36	11.8185	1.8378	0.1073
			293K		
0.0	131.16	1.96	-1.5568	16.6658	0.0961
0.1	128.99	2.09	-0.3111	14.8661	0.0861
0.2	126.83	2.40	2.3254	10.8354	0.1074
0.3	124.66	2.63	4.1449	8.4264	0.0587
0.4	122.49	2.72	4.0547	11.8744	0.1507

Contd...

Table 4.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	-B_1'x10^2	-C_1'x10^2	Std.dev. in Λ
			293K		
0.5	120.33	3.06	6.9159	5.3720	0.1516
0.6	118.16	3.36	8.5811	3.1637	0.1177
0.7	115.99	3.64	9.7365	2.4285	0.1112
0.8	113.82	3.86	10.4914	2.1059	0.1134
0.9	111.66	4.12	11.3536	1.6544	0.1189
1.0	109.49	4.37	12.0400	1.3738	0.1206
			298K		
0.0	144.60	1.99	-2.0400	16.9000	0.3874
0.1	142.29	2.55	3.6909	7.8976	0.0595
0.2	139.98	2.65	3.9228	9.3082	0.1416
0.3	137.67	2.88	5.6173	6.8995	0.0896
0.4	135.36	3.24	8.2042	3.1257	0.2118
0.5	133.05	3.27	8.1741	3.3217	0.1689
0.6	130.74	3.46	8.9883	2.7718	0.1197
0.7	128.43	3.67	9.7621	2.5740	0.1310

Contd...

Table 4.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	$-B_1'$x10^2	$-C_1'$x10^2	Std.dev. in Λ
			298K		
0.8	126.12	3.94	10.8081	1.7621	0.0781
0.9	123.81	4.15	11.5123	1.4621	0.1060
1.0	121.50	4.36	12.0898	1.2274	0.1342
			303K		
0.0	159.46	2.04	-0.9524	1.6977	0.0685
0.1	156.94	2.36	2.4121	10.2093	0.0976
0.2	154.42	2.41	2.1557	12.5594	0.1605
0.3	151.90	2.70	4.7465	8.0454	0.0748
0.4	149.38	3.10	7.6634	4.0720	0.3011
0.5	146.86	3.13	7.6563	4.0806	0.2083
0.6	144.33	3.33	8.6100	3.2586	0.1650
0.7	141.81	3.58	9.6471	2.6174	0.1539
0.8	139.29	3.83	10.6982	1.7352	0.1008
0.9	136.77	4.04	11.3829	1.4119	0.1426
1.0	134.25	4.23	11.8674	1.2907	0.1556

Contd...

Table 4.3 contd..

x	Λ_o/Scm^2mol^{-1}	$a_o x10^8/cm$	$-B'_1 x10^2$	$-C'_1 x10^2$	Std.dev. in Λ
			308K		
0.0	174.18	2.01	-1.6186	19.6821	0.1370
0.1	171.49	2.39	2.6087	10.4910	0.1190
0.2	168.79	2.44	2.3389	12.8828	0.1727
0.3	166.10	2.73	4.8052	8.9017	0.0992
0.4	163.40	3.13	7.9517	3.8615	0.3183
0.5	160.71	3.18	8.0861	3.5129	0.2392
0.6	158.01	3.35	8.8543	3.0079	0.2045
0.7	155.32	3.61	10.0281	2.1011	0.1585
0.8	152.62	3.85	10.9770	1.3397	0.1097
0.9	149.93	4.04	11.5363	1.1362	0.1671
1.0	147.23	4.20	11.9238	1.0715	0.1952
			313K		
0.0	189.21	2.11	-0.7112	18.7935	0.1636
0.1	186.35	2.45	3.1242	10.0846	0.1613
0.2	183.48	2.48	2.6071	13.1345	0.1698

Contd...

Table 4.3 contd..

x	Λ_o/Scm^{2}mol^{-1}	a_ox10^8/cm	-B_1'x10^2	-C_1'x10^2	Std.dev. in Λ
			313K		
0.3	180.62	2.74	4.8453	9.6288	0.1081
0.4	177.75	3.13	8.0142	4.1342	0.4065
0.5	174.89	3.23	8.5843	2.9078	0.3041
0.6	172.03	3.37	9.1376	2.6739	0.2326
0.7	169.16	3.62	10.2323	1.8036	0.1876
0.8	166.30	3.84	11.1878	0.9960	0.1193
0.9	163.43	4.02	11.6524	0.8882	0.2060
1.0	160.57	4.16	11.9792	0.8481	0.2158

Table 4.4 Best-fit parameters of equation (3.3) for the molar conductance of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.0		
200	7.2910	355.8	160.5	0.0002
150	7.3488	382.3	155.3	0.0002
100	7.1716	351.5	160.4	0.0002
75	7.1467	359.0	158.3	0.0002
50	6.9715	334.9	162.1	0.0002
40	7.1193	390.0	151.1	0.0006
30	6.7742	318.5	163.9	0.0009
25	6.5932	287.4	169.7	0.0008
20	6.8241	353.5	157.7	0.0015
		x = 0.1		
200	7.3122	364.4	159.3	0.0002
150	7.2729	362.9	159.5	0.0001
100	7.1586	351.3	160.8	0.0002
75	7.1007	351.2	160.0	0.0002

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.1		
50	6.9905	343.7	160.8	0.0002
40	7.1260	397.3	150.0	0.0007
30	6.8231	334.5	161.3	0.0008
25	6.6328	299.5	167.9	0.0009
20	6.7401	351.7	135.9	0.0006
		x = 0.2		
200	7.3149	369.3	158.5	0.0002
150	7.2463	360.7	159.9	0.0003
100	7.1421	350.3	161.2	0.0003
75	7.1380	362.3	158.5	0.0001
50	7.0225	356.2	158.6	0.0003
40	7.1211	399.5	150.1	0.0005
30	6.7882	326.7	163.6	0.0009
25	6.5479	281.6	172.3	0.0008
20	6.4625	281.4	171.4	0.0009

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.3		
200	7.3141	373.1	157.9	0.0003
150	7.2669	368.8	158.7	0.0002
100	7.1963	367.8	158.3	0.0003
75	7.1969	384.9	154.3	0.0004
50	6.9795	347.2	160.9	0.0001
40	7.0228	374.9	154.9	0.0004
30	6.7417	319.7	165.2	0.0007
25	6.5977	298.0	169.2	0.0010
20	6.4666	286.8	170.6	0.0008
		x = 0.4		
200	7.2522	359.4	160.7	0.0001
150	7.3138	386.1	155.7	0.0002
100	7.1940	371.1	157.9	0.0002
75	7.1175	363.9	158.9	0.0003
50	7.0217	364.4	157.6	0.0004

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.4		
40	7.0952	401.5	150.2	0.0009
30	6.9993	395.6	151.0	0.0008
25	6.6330	310.0	167.2	0.0010
20	6.3637	269.6	174.7	0.0007
13	6.4019	327.5	160.5	0.0009
		x = 0.5		
200	7.2789	370.6	159.0	0.0002
150	7.2744	379.3	157.2	0.0002
100	7.1831	371.5	158.0	0.0004
75	7.2134	395.4	153.3	0.0001
50	6.9379	345.4	161.5	0.0003
40	7.0185	383.0	154.0	0.0005
30	6.9171	375.0	155.3	0.0007
25	6.6431	318.7	165.7	0.0013
20	6.3970	277.1	174.0	0.0006

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.5		
13	6.4252	334.8	160.6	0.0002
11	6.4381	360.9	154.9	0.0006
		x = 0.6		
200	7.3033	382.9	156.6	0.0002
150	7.3170	395.0	154.5	0.0002
100	7.2016	380.4	156.7	0.0002
75	7.1696	386.5	155.1	0.0002
50	7.0314	374.2	156.4	0.0002
40	6.9754	373.8	156.2	0.0002
30	6.9327	384.8	153.8	0.0008
25	6.8073	365.6	157.1	0.0009
20	6.4663	297.7	170.3	0.0009
13	6.3848	326.1	163.5	0.0002
11	6.3659	343.3	159.9	0.0000

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.6		
9	6.0761	290.8	172.0	0.0012
8	6.5576	451.1	140.7	0.0026
		x = 0.7		
200	7.3042	384.0	157.0	0.0003
150	7.2803	388.6	156.0	0.0004
100	7.1868	380.4	156.8	0.0004
75	7.1458	384.5	155.7	0.0001
50	7.0555	383.7	155.1	0.0002
40	6.8239	336.0	163.9	0.0004
30	6.9142	383.1	154.5	0.0009
25	6.7223	347.0	161.1	0.0010
20	6.5449	321.9	165.8	0.0010
13	6.3364	319.9	165.2	0.0001
11	6.3753	350.2	159.6	0.0002
9	6.2902	357.2	158.4	0.0001
8	6.1979	351.8	159.6	0.0003
7	5.9646	303.3	172.1	0.0000

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.8		
200	7.3098	386.9	157.2	0.0005
150	7.3411	407.9	153.0	0.0002
100	7.1558	375.7	157.9	0.0003
75	7.1412	386.1	155.7	0.0002
50	6.9805	367.9	158.1	0.0001
40	6.8277	343.1	162.4	0.0004
30	7.0214	418.9	148.5	0.0007
25	6.6777	339.0	163.1	0.0012
20	6.5052	313.7	168.3	0.0009
13	6.4367	348.9	160.6	0.0001
11	6.2298	314.8	167.8	0.0003
9	6.3101	366.4	158.0	0.0001
8	6.1887	351.8	161.3	0.0001
7	6.1051	349.3	162.6	0.0006
6	5.5823	241.2	187.3	0.0015

Contd...

Table 4.4 contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 0.9		
200	7.2545	377.0	159.0	0.0003
150	7.3049	401.4	154.3	0.0004
100	7.2454	404.3	153.1	0.0003
75	7.1177	384.2	156.2	0.0001
50	6.9943	374.9	157.2	0.0002
40	6.9304	372.9	157.5	0.0001
30	7.0767	437.5	146.0	0.0008
25	6.9160	407.5	151.1	0.0008
20	6.5375	324.7	166.8	0.0009
13	6.4153	347.9	161.5	0.0002
11	6.2972	338.2	164.0	0.0002
9	6.2872	362.2	160.4	0.0003
8	6.2100	360.7	161.1	0.0003
7	6.3708	426.5	150.4	0.0017
6	5.7924	294.0	177.4	0.0003

Contd...

Table 4.4. contd..

R	$\ln A_\Lambda$	B_Λ/K	T_o/K	Std.dev in $\ln \Lambda$
		x = 1.0		
200	7.2797	398.5	156.7	0.0003
150	7.2239	383.7	157.6	0.0002
100	7.2080	396.4	154.9	0.0002
75	7.1201	388.8	155.7	0.0002
50	6.9908	376.6	157.4	0.0001
40	6.8524	354.8	161.3	0.0003
30	7.0780	440.9	145.8	0.0007
25	6.8738	401.0	152.6	0.0009
20	6.6631	361.8	160.3	0.0013
13	6.6856	429.1	147.7	0.0006
11	6.3740	359.6	161.1	0.0002
9	6.2560	357.8	162.4	0.0001
8	6.1540	348.0	165.0	0.0002
7	6.1713	372.7	161.6	0.0002
6	5.6752	265.1	186.0	0.0005

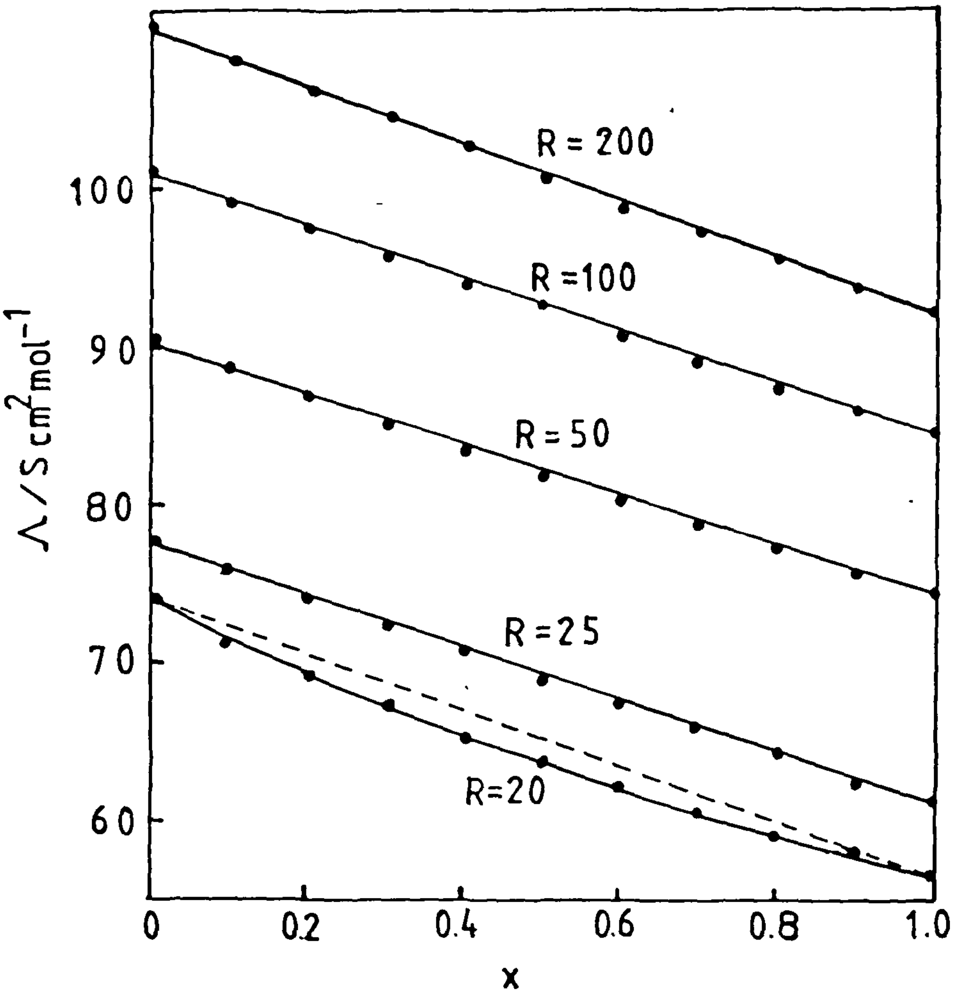

Fig.4.1 Variation of Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system with x at 298K for different R values.

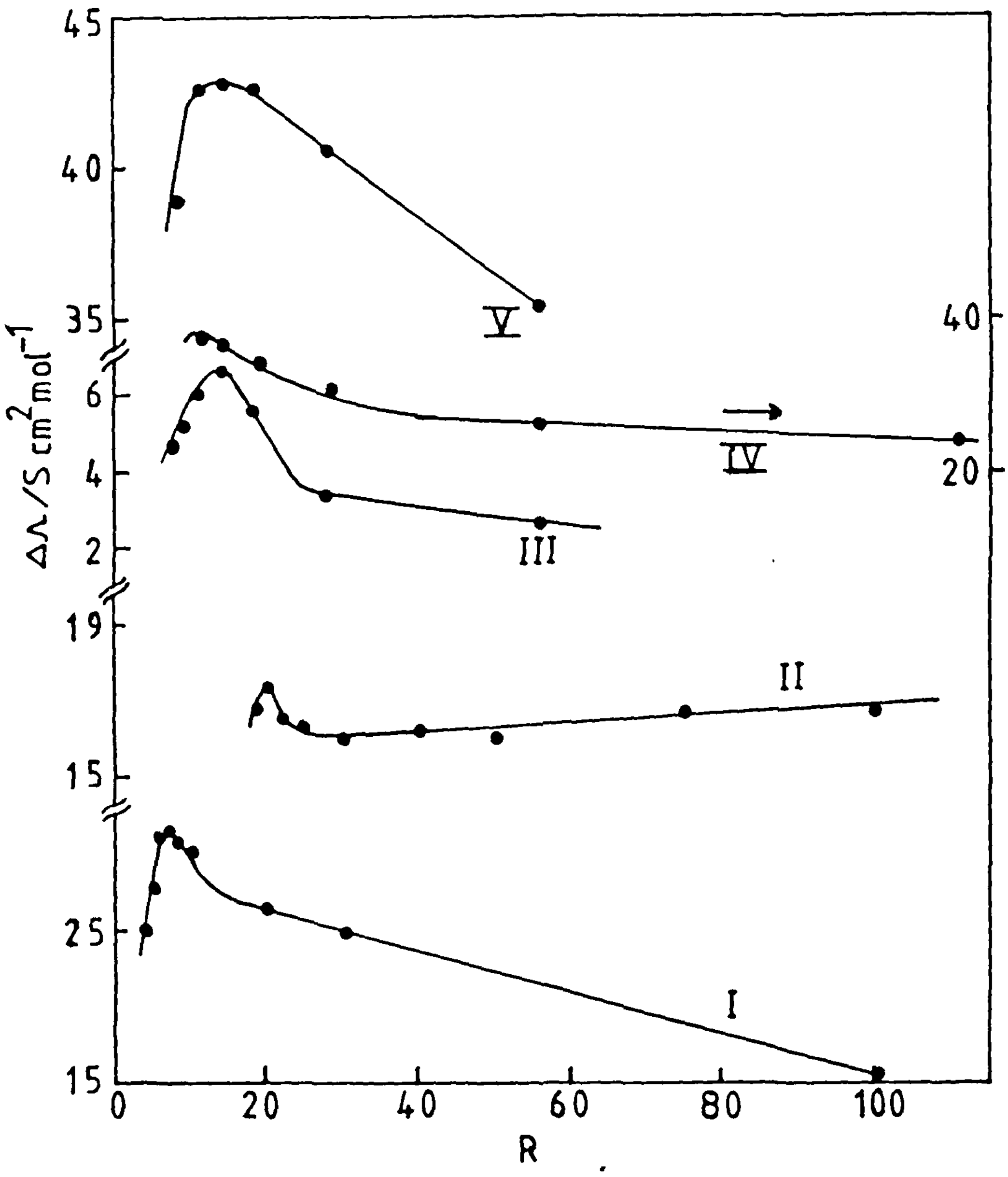

Fig.4.2 Plot of difference in Λ values of aqueous electrolytic solutions at 25°C vs. R[I.NaSCN & KSCN, II. $NaNO_3$ & KNO_3, III. RbCl & CsCl (at 23°C), IV. NaCl & KCl and V. LiCl & RbCl (at 23°C)].

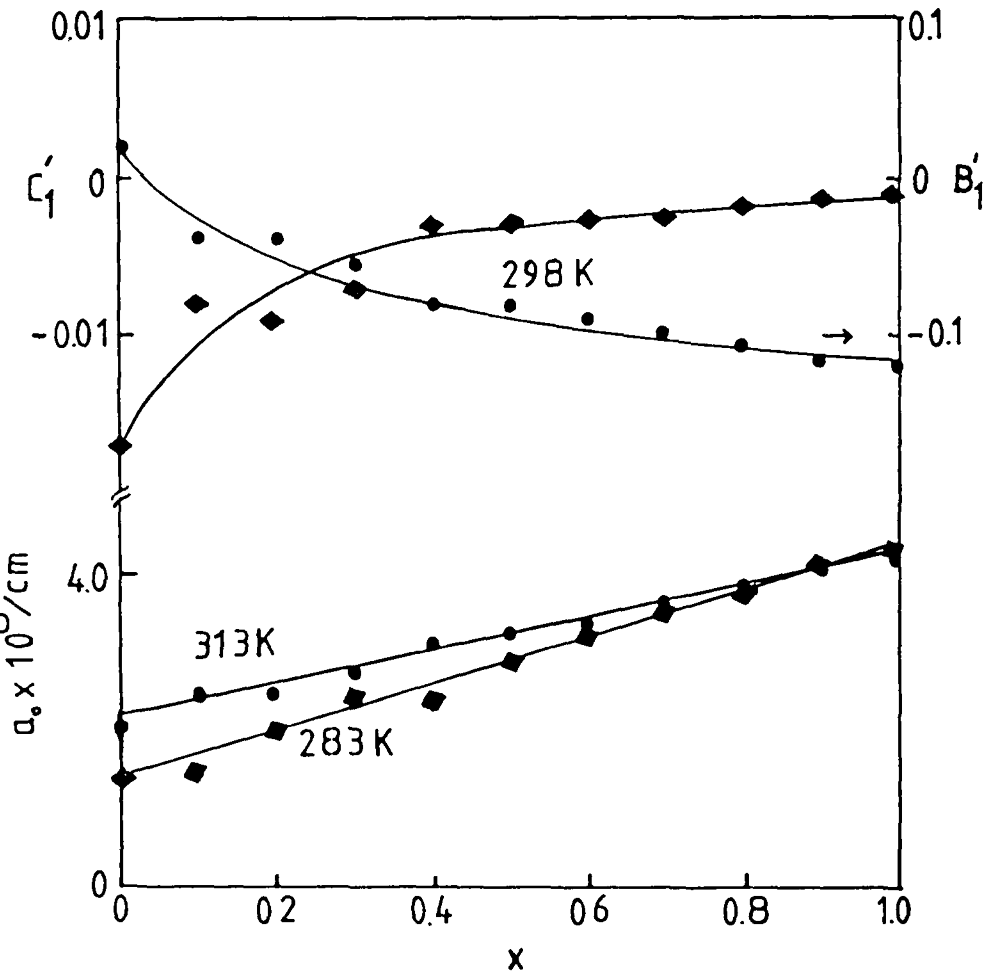

Fig.4.3 Variation of a_o, B_1' and C_1' of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system with x.

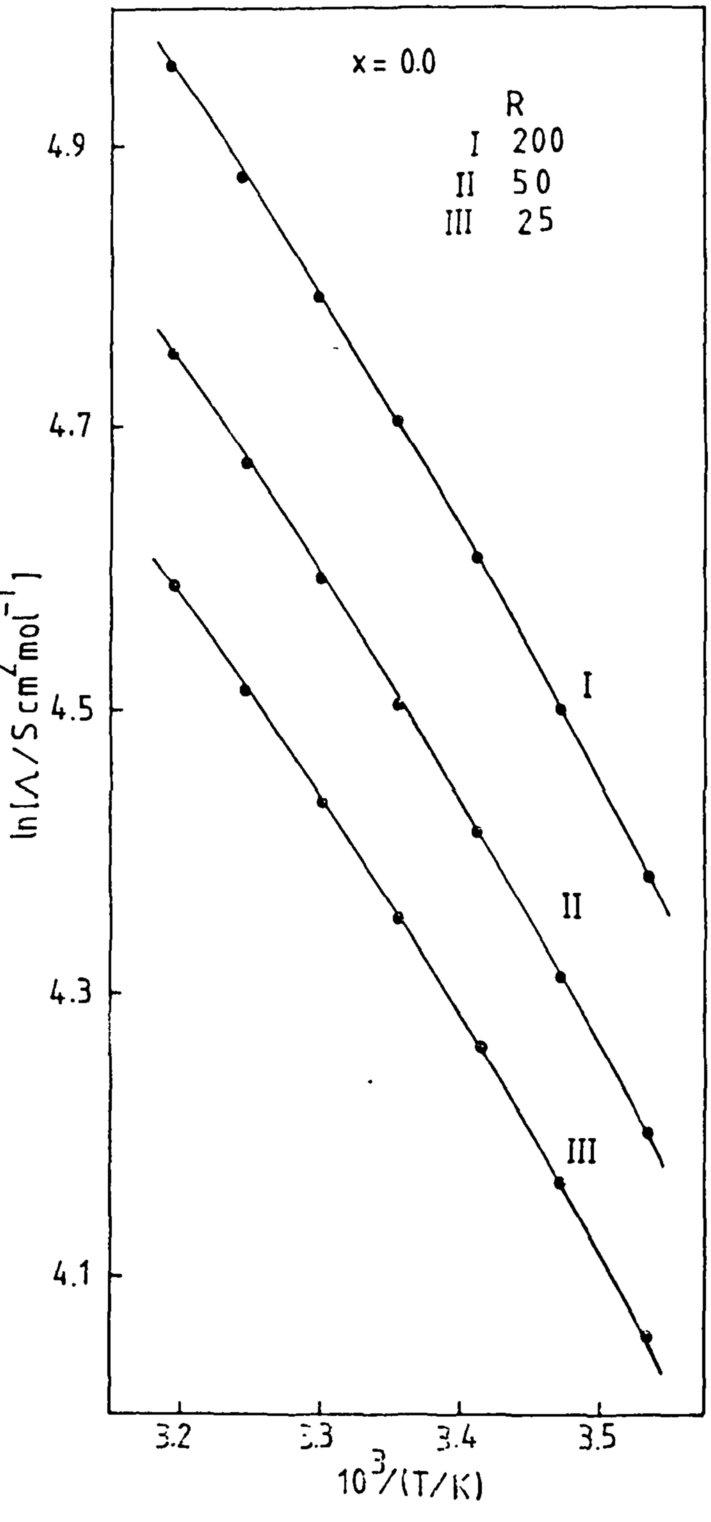

Fig.4.4 Plot of ln Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system vs. 1/T at different R values for x=0.0.

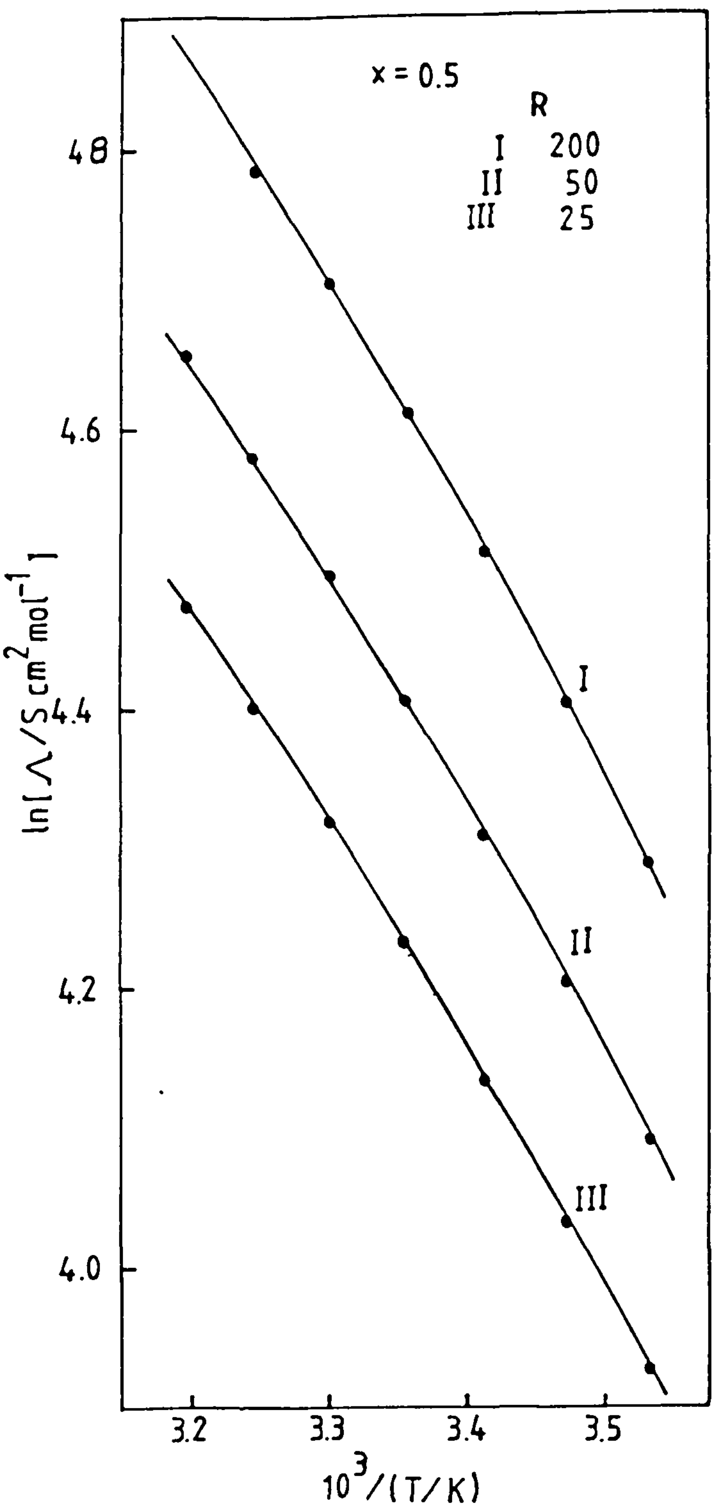

Fig.4.5 Plot of ln Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system vs. 1/T at different R values for x=0.5.

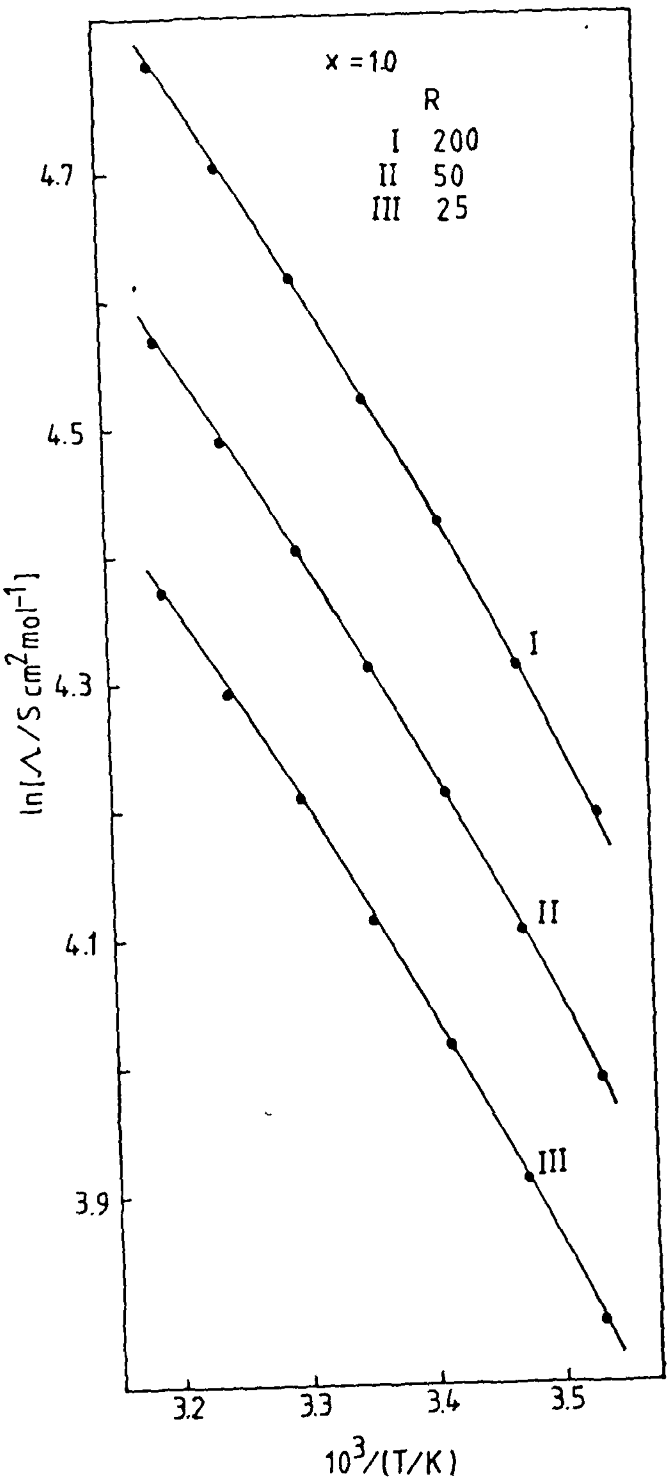

Fig.4.6 Plot of ln Λ of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system vs. 1/T at different R values for x=1.0.

CHAPTER - V

ON THE ISOTHERMAL EQUATION FOR DESCRIBING THE CONCENTRATION DEPENDENCE OF ELECTRICAL CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

5.1 Introduction

In Chapter III and IV we used a new isothermal equation of the form

$$\Lambda = \Lambda_{FLK} \exp\,(B_1'c + C_1'c^2) \qquad (5.1)$$

to explain the concentration dependence of Λ of electrolytic solutions containing both single and mixed salts. Equation (5.1) was introduced in an empirical way. In this chapter an attempt has been made to provide a probable theoretical basis to equation (5.1).

5.2 Derivation of Equation (5.1)

When random-walking ions are subjected to an electric field $\vec{E}$ they acquire a component of velocity known as drift velocity directed along the direction of the force. The drift velocity of an ion in solution may be written as

$$\vec{v}_d = \vec{v}_d^{\,*}\,p \qquad (5.2)$$

where p is the probability that the ion possesses the minimum requirement necessary for the ionic transport to take place. $\vec{v}_d$ is related to mobility u of the ion through the expression $u = \vec{v}_d/\vec{E}$ and is related to the current density $\vec{j}$ by the expression $\vec{j} = zF_o c_o \vec{v}_d$ where z is the charge on the ion, F_o is the Faraday constant and c_o is the concentration in moles per cubic centimeter. Therefore, one can eventually derive an expression for Λ from that of v_d. In electrolytic solutions the minimum requirement necessary for the ionic transport to take place will depend upon the concentration (m) and therefore p may be written as p(m).

Using the primitive model[1] one can write

$$v_d = (v_o - v_i)p(m) \tag{5.3}$$

where v_o is the velocity of the ion at infinite dilution or it is the velocity in the absence of any ion-ion interaction, v_i is the decrease in the velocity of the ion caused due to its interaction with the other ions at finite concentrations. In order to evaluate v_i the Debye-Hückel ionic atmosphere concept may be used according to which

$$v_i = v_E + v_R \tag{5.4}$$

where v_E and v_R are the decrease in velocities due to the electrophoretic and relaxation effects. Equation (5.3) may be transformed into an expression for equivalent or molar conductance by using the Falkenhagen-Leist-Kelbg[2] approach and without going into the details of the derivation it can be straight away written that

$$\Lambda = \left[\Lambda'_o - \frac{B_1 c^{\frac{1}{2}}}{1+B_o a_o c^{\frac{1}{2}}}\right]\left[1 - \frac{B_2 c^{\frac{1}{2}} F}{1+B_o a_o c^{\frac{1}{2}}}\right]p(m) \tag{5.5}$$

The different terms have their usual meaning defined in chapter I (cf. equation (1.7)). Λ'_o is related to Λ_o, the molar conductance at infinite dilution through the expression

$$\Lambda_o = \Lambda'_o p(o) \qquad (5.6)$$

If p(m) is considered to be 1, $\Lambda_o = \Lambda'_o$ and equation (5.5) becomes identical with the FLK equation (1.7). In order to evaluate p(m) one can make use of the different available models.

(i) Use of the Transition State Theory. According to this theory[3] an ion must possess a certain amount of free energy, $\Delta\varepsilon$ before it can change its position. p(m) is then equal to the probability of the ion having this free energy of activation and is given by

$$p(m) = \exp[-\Delta G(m)/RT] \qquad (5.7)$$

where $\Delta G(m)$ is the free energy of activation per mole of the ion and m inside the bracket indicates that ΔG is dependent on the concentration of the solution. The concentration dependence of ΔG may be expressed in the form of a polynomial as

$$\Delta G(m) = \Delta G_o + B'_2 m + C'_2 m^2 \qquad (5.8)$$

where ΔG_o is the activation free energy required at infinite dilution and B'_2 and C'_2 are empirical constants. Expressing the dependence of ΔG on m in the above form is justified by the empirical fact that in electrolytic solutions activation energies for both conductance and viscous flows (E_Λ and E_η) vary non-linearly with m exhibiting broad minima (cf. Chapters III and IV). At infinite dilution

$$\Lambda \equiv \Lambda_o = \Lambda_o' \exp(-\Delta G_o/RT) \qquad (5.9)$$

It is interesting to note that equation (5.9) for Λ_o is similar to the several expressions reported[4,5] for Λ_o based on the theory of transition states. By comparing therefore equation (5.9) with one of the reported[4] expression for Λ_o, Λ_o' may be recognised as

$$\Lambda_o' = \frac{eF_o}{6h} \sum_i z_i \, l_i^2 \qquad (5.10)$$

where e is the electronic charge, h is the Planck's constant, F_o is the Faraday constant, z_i is the charge on ith ion and l_i is the jump distance of ith ion. According to another expression for Λ_o derived by Bockris and coworkers[5] the activation free enrgy ΔG_o is the free energy of activation for the diffusion process.

Since at a particular temperature Λ_o is the maximum molar conductance observable for an electrolytic solution, we define at a given isothermal condition the solution of infinite dilution as the reference frame of zero activation energy for conductance flow, i.e.,

$$p(o) = \exp(-\Delta G_o/RT) \equiv 1 \qquad (5.11)$$

With respect to such a frame of reference equation (5.5), after substituting equations (5.7), (5.8) and (5.11) in it, becomes

$$\Lambda = \Lambda_{FLK} \exp\,(B_o'm + C_o'm^2) \qquad (5.12)$$

where $B_o' = -B_2'/RT$ and $C_o' = -C_2'/RT$. Equation (5.12) is similar to equation (5.1) since the unit of concentration is immaterial because during computation B_1' and C_1' or B_o' and C_o' are treated as freely adjustable parameters. Thus equation (5.1) may be derived in the light of the transition state theory.

(ii) Use of the Free Volume Model. According to this model,[6] for the ionic or molecular transport to take place a void of sufficient size must exist near the species undergoing transport. p(m) is then equal to the probability, p(v), that an ion has free volume v associated with it. Using the Cohen-Turnbull model[6] for deriving an expression for p(v) one obtains,

$$p(m) = p(v) = \exp\,(-\gamma V^*/V_f) \qquad (5.13)$$

V_f is the average molar free volume and V^* is the critical void volume per mole just required for the transport to take place and γ is a numerical factor to take care of the overlapping of the free volume. V_f is normally written as $(V-V_o)$ where V is the molar volume and V_o is the intrinsic volume. Correlating V_f to the ideal glass transition temperature, T_o equation (5.13) may be written as

$$p(m) = \exp[-B^*/(T-T_o)] \tag{5.14}$$

Both B* and T_o are functions of concentration of the electrolytic solution. Empirically it has, however, been found that the concentration dependence of T_o generally controls the concentration dependence of transport properties. By substituting in equation (5.14) the linear dependence[7-10] of T_o on m and again choosing the solution of infinite dilution as the reference state of $p(o)\equiv 1$, equation (5.14) can be approximated[9,10] to the form

$$p(m) = \exp(B_o'm + C_o'm^2) \tag{5.15}$$

Equation (5.15) again gives equation (5.12).

(iii) Use of the Configurational Entropy Model. In this model[11] the transport process is considered to be a cooperative phenomenon. Change in the position of ions or any other constituent particle of a solution is treated as a transition from one configuration to another configuration of the system and p(m) is then equal to the probability of this transition. Adam and Gibbs[11] deduced an expression for this type of transition probability and is of the form

$$p(m) = \exp(-B/TS_c) \tag{5.16}$$

where B is a term related to the activation energy for the transition and S_c is the configurational entropy of the system. It has been shown[12] that $\exp(-B/TS_c)$ can be approximated to $\exp[-B/(\Delta C_p(T-T_o))]$ where ΔC_p is the difference in the heat capacities of the liquid and glassy phases of the system. This indicates that equation (5.14) based on the free volume model can be deduced from the configurational entropy model. Earlier we have reported[9,10] that by substituting the temperature dependence of ΔC_p and the dependence of T_o on m it is possible to obtain $\exp[-B/(\Delta C_p(T-T_o))] \simeq \exp(a+B_o'm+C_o'm^2)$. Using the solution of infinite dilution as the reference state of $p(o)=\exp(a) \equiv 1$, we get $p(m)=\exp(B_o'm+C_o'm^2)$ which when substituted in equation (5.5) once again provides equation (5.12).

Alternatively, p(m) can be shown equal to $\exp(B_o'm+C_o'm^2)$ from a simple statistical mechanical consideration as described below. The configurational entropy can be evaluated from the expression

$$S_c = k\ln W \tag{5.17}$$

Where W is the number of configurations available to the electrolytic solution. In order to evaluate W, the effect of ion-solvent interactions on the structure of an electrolytic solution is taken into consideration. For this purpose we make use of the Frank and Wen model[13] according to which three different types of equilibrium positions are available to water in an aqueous electrolytic solution. (1) In the *region 1 ion-dipole interaction predominates and a water* molecule is considered to have energy ε_1 if it is around the cation and ε_1' if it is around the anion. This region is the primary hydration sheath of cation or anion. (2) In the region 2 both ion-dipole and dipole-dipole interactions are of almost equal magnitude. This region is the secondary hydration sheath of an ion and a water molecule in this region has energy, say ε_2. (3) In the region 3 water molecule has energy ε_o equal to that in pure water itself. Only dipole-dipole interaction exists in this region just as in the case of pure water. It is the bulk water region.

In the present case for the evaluation of W for 1:1 electrolytic solutions, we use a simpler two-state model by taking into consideration regions 1 and 3 only. Let N be the total number of water molecules out of which let n_1 and n_1' be present in the primary hydration sheaths of the cation and anion, respectively. Due to exchange of water molecules between regions 1 and 3 several equilibrium configurations will be produced given by

$$W = N!/n_1!n_1'!n_o! \qquad (5.18)$$

where $n_o = N-(n_1+n_1')$ is the number of bulk water molecules. The exchange of water molecules may be represented as $(n_1+n_1')(H_2O)_1 \rightleftharpoons n_o(H_2O)_3$. It may be cited here that Samoilov[14] made use of a similar model to explain the hydration phenomenon by evaluating the time of exchange of water molecules between regions 1 and 3. For a particular solution of concentration m at isothermal condition maximising W, keeping in view that $n_1+n_1'+n_o=N$ (constant) and $n_1\varepsilon_1+n_1'\varepsilon_1'+n_o\varepsilon_o = \varepsilon$(constant), gives

$$n_1 = N \exp(-\varepsilon_1/kT)/Q_c \qquad (5.19a)$$
$$n_1' = N \exp(-\varepsilon_1'/kT)/Q_c \qquad (5.19b)$$
$$n_o = N \exp(-\varepsilon_o/kT)/Q_c \qquad (5.20)$$

where k is the Boltzmann constant and $Q_c = \exp(-\varepsilon_1/kT)+\exp(-\varepsilon_1'/kT)+\exp(-\varepsilon_o/kT)$. Q_c may be called as the configurational partition function and is constant at constant temperature for a given electrolytic solution. Substituting the maximised value of W in equation (5.17) and applying the Sterling's approximation, we get

$$S_c(m) = [\varepsilon(m)/T]-k\ln Q_c \qquad (5.21)$$

This expression is true for an electrolytic solution of concentration m at temperature T. [Equation (5.21) may also be obtained by using the general statistical mechanical expression for entropy as $S_c = -k \sum_i p_i \ln p_i$ where p_i is the probability of finding the water molecule in the state i.]
Substitution for S_c in equation (5.16) gives

$$p(m) = \exp[-B/(\varepsilon(m)-kT\ln Q_c)] \qquad (5.22)$$

If n_+^o is the first hydration number of the cation and n_-^o that of the anion and presuming that the hydration number is independent of concentration, we may write that

$$\varepsilon(m) = (n_+^o m\varepsilon_1 + n_-^o m\varepsilon_1') + [55.51 - (n_+^o + n_-^o)m]\varepsilon_o \quad (5.23)$$

At isothermal condition, $\varepsilon(m)$-kTlnQ$_c$ may be written as

$$\varepsilon(m) - kT\ln Q_c = a - a_1 m \quad (5.24)$$

where $a = 55.51\varepsilon_o - kT\ln Q_c$ and $a_1 = (n_+^o + n_-^o)\ \varepsilon_o - n_+^o\varepsilon_1 - n_-^o\varepsilon_1'$. Therefore equation (5.22) now becomes

$$p(m) = \exp[-B/(a - a_1 m)] \quad (5.25)$$

It is worthwhile to comment here that from the above simple two-state model it is also possible to deduce the expression reported by Angell[7,8] for the transport property of electrolytic solutions which is shown below. Hitherto for the transport property(Y) of an electrolytic solution the expression of configurational entropy model was employed directly as

$$Y \propto p(m)$$

Substituting for p(m) from equation (5.25), we get

$$Y = A_y \exp[-B/(a - a_1 m)]$$

$$\text{or} \quad Y = A_y \exp[-B'/(a_o - m)] \quad (5.26)$$

A_y is a proportionality constant, $a_o = a/a_1$ and $B' = B/a_1$. Equation (5.26) may be recognized as the same expression obtained by Angell[7,8] by introducing the empirical concentration dependence of T_o in the expression for Y(VTF equation). In the expression of Angell concentration is expressed in mole per cent instead of in m which is immaterial because T_o exhibits similar dependence with mole percent and m. Therefore our above simple model deduces directly the isothermal expression of Angell without resorting into the empirical nature of the concentration dependence of T_o.

Equation (5.25) may be approximated as

$$p(m) \simeq \exp\ [-(B/a)(1+(a_1/a)m+(a_1^2/2a^2)m^2)]$$
$$= \exp\ [-(B/a)+B_o'm+C_o'm^2] \qquad (5.27)$$

Again using the solution of infinite dilution as the reference state of $p(o) = \exp[-(B/a)] \equiv 1$, we obtain $p(m) = \exp(B_o'm+C_o'm^2)$ which on substitution in equation (5.5) gives us equation (5.12).

5.3 Application of Equation (5.1)

Equation (5.1) has already been successfully employed to describe the concentration dependence of molar conductances of NaSCN, KSCN, $NaNO_3$ and KNO_3 aqueous solutions and also of mixed electrolytic solutions containing NaSCN+KSCN and $NaNO_3$+KNO_3 in water (cf. Chapter III and IV). In order to establish further the applicability of equation (5.1) we have least-squares fitted the reported[15-33] equivalent conductance data of several electrolytic solutions to (i) the FLK equation (1.7), (ii) the WS equation (1.8), (iii) the Monica equation (1.9) and (iv) to equation (5.1). The results of these fittings are given in Table 5.1. In all the cases equation (5.1) fitts the equivalent conductance versus concentration data much better as it is apparent from the standard deviations of the different fittings. In some of the electrolytic solutions there could be appreciable amount of association, for example, in NH_4NO_3 solution. In such solutions c has to be substituted by αc where α is the degree of dissociation. This correction has not been incorporated in the present fittings since our intention is to simply make a comparison between the fittings of the Λ data to the different equations.

Although from Table 5.1 it is obvious that equation (5.1) fitts the conductance data better, this success of equation (5.1) may be attributed to the presence of three adjustable parameters in it whereas the FLK, WS and Monica equations contain only one adjustable parameter. In order to rectify this particular weakness of equation (5.1) an attempt has been made to reduce the number of freely adjustable parameter in it. From the derivation of equation(5.1) or (5.12) given above it is obvious that the exponential part of equation(5.1) is related to the ion-solvent interactions. One of the properties of electrolytic solutions which is affected directly by the ion-solvent interactions or solvation of the ions is the viscosity of the solution. Therefore the exponential part of equation(5.1) may be expected to be correlatable to the viscosity of the electrolytic solution. This is also inferred from the studies made in chapters III and IV. It was suggested in Chapters III and IV that by looking into the signs of the values of B_1' and C_1' it is possible to predict whether a particular solution exhibits negative viscosity or not. The present analysis of the conductance data also confirms this. For example, from Table 5.1 KCl, KBr, KNO_3, NH_4Cl and NH_4NO_3 solutions would be expected to exhibit negative viscosity and experimentally they are known to do so.

According to the Frenkel equation[34] the activation energies for conductance (E_Λ) and viscous (E_η) flows of a particular system are related through the expression

$$E_\Lambda / E_\eta = n \qquad (5.28)$$

where n is a constant generally having a value less than 1. This relation has been found to hold good in molten salts[35,36] and electrolytic solutions.[10] On the basis of the transition state theory used above to derive expression (5.1) or (5.12) it may be written, in view of equation (5.8), that

$$B_1'c+C_1'c^2 = B_o'm+C_o'm^2 = -(B_2'm+C_2'm^2)/RT = -(E_\Lambda-E_{o\Lambda})/RT \quad (5.29)$$

where $E_{o\Lambda}$ is the activation energy for conductance flow of electrolytic solution at infinite dilution. $B_2'=-RTB_o'$ and $C_2'=-RTC_o'$. In the light of the relation between E_Λ and E_η given in equation (5.28), we can also write equation (5.29) as

$$(B_1'c+C_1'c^2) = -n(E_\eta-E_{o\eta})/RT \quad (5.30)$$

where $E_{o\eta}$ is the activation energy for viscous flow of electrolytic solution at infinite dilution. Equation (5.30) indicates that $\ln\eta$ of any electrolytic solution is a linear function of $B_1'c+C_1'c^2$. We have therefore plotted in Fig.5.1 the reported[15,16,19-21,26-29] viscosity values of several electrolytic solutions (cf. Table 5.1) versus their respective $B_1'c+C_1'c^2$ values and as expected these plots were found to be linear. Equation (5.1) may now be written as

$$\begin{aligned}\Lambda &= \Lambda_{FLK}(\exp[(-E_\eta+E_{o\eta})/RT])^n \\ &= \Lambda_{FLK}[\exp(-E_\eta/RT)]^n[\exp(E_{o\eta}/RT)]^n \\ &= \Lambda_{FLK}(\eta_o/\eta)^n \quad (5.31)\end{aligned}$$

Equation (5.31) is a better equation than equation (5.1) since it has only 2 adjustable parameters. Furthermore, there is a possibility to use equation (5.31) as an one-parameter equation also by substituting the value of n obtainable separately from the study of the temperature dependence of conductance and viscosity of an electrolytic solution. The conductance data of all the electrolytes listed in Table 5.1 were least-squares fitted to equation (5.31) and the results of this fitting are given in the last column of Table 5.1. The value of n for all the electrolytes except for KBr, NH_4Cl and NH_4NO_3 solutions are found to be less than 1. The fittings of conductance data to equation (5.31) are better than the fittings to the FLK, WS and Monica equations. Equation (5.31) is an improvement over the WS equation because the latter equation fails when the relative viscosity of a solution becomes high.[16]

5.4 References

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Table 5.1 Best-fit parameters and $\Lambda_{calc.}$ values of different 1:1 aqueous electrolytes at 298K

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1}				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			LiCl (Λ_o=115.0)				
						B'_1 =-7.6643 x10^{-2} C'_1 = -7.1636 x10^{-3}	n = 0.8948
0.1	1.0114	96.5	91.90	97.41	95.64	95.63	96.63
0.2	1.0299	90.3	84.40	92.15	89.80	90.28	91.14
0.5	1.0736	81.5	72.07	83.66	80.82	81.59	82.43
1.0	1.1580	73.0	61.18	74.06	71.84	73.15	73.05
1.5	1.235	66.9	54.41	67.40	65.96	66.96	66.68
2.0	1.321	61.7	49.52	61.56	61.01	61.70	61.18
2.5	1.415	56.9	45.71	56.34	56.62	56.98	56.32
3.0	1.516	52.5	42.62	51.66	52.68	52.62	51.96
3.5	1.63	48.4	40.04	47.25	48.93	48.54	47.88
4.0	1.72	44.7	37.80	44.09	46.18	44.70	44.91
5.0	2.00	37.8	34.15	36.80	39.72	37.63	38.12

Contd..

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			LiCl				
6.0	2.35	31.7	31.24	30.43	33.83	31.34	32.11
7.0	2.84	26.0	21.84	24.47	28.04	25.77	26.40
8.0	3.52	20.9	26.81	19.18	22.63	20.92	21.23
9.0	4.50	16.4	25.07	14.56	17.69	16.76	16.61
10.0	5.63	13.2	23.54	11.29	14.05	13.24	13.25
11.0	7.39	10.4	22.19	8.33	10.63	10.32	10.12
12.0	9.67	8.1	20.99	6.16	8.04	7.93	7.74
	a_o/A°	=	1.41	6.43	4.56	4.37	5.49
	Std.dev. in Λ	=	9.0466	1.4167	1.1677	0.2652	0.4494
			$LiNO_3$(Λ_o=109.8)			$B'_1 = -11.9784 \times 10^{-2}$ $C'_1 = -3.3181 \times 10^{-3}$	n=0.9413
0.00997	1.005	102.79	101.71	101.96	101.67	102.47	101.92
0.099	1.013	91.74	87.15	90.95	89.26	91.70	90.62

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				$LiNO_3$			
0.553	1.063	76.86	66.12	76.22	72.78	77.23	75.56
0.958	1.109	70.26	57.64	69.62	66.22	70.33	68.94
0.995	1.111	69.78	57.04	69.25	65.84	69.78	68.57
1.885	1.221	58.95	46.57	59.27	57.09	58.85	58.75
2.740	1.351	50.60	40.37	51.48	50.87	50.54	51.22
2.957	1.390	48.98	39.12	49.61	49.41	48.64	49.41
3.456	1.490	44.72	36.57	45.44	46.15	44.56	45.41
3.698	1.534	42.81	35.48	43.77	44.82	42.70	43.80
4.857	1.826	34.68	31.14	35.47	38.06	34.72	35.82
5.337	1.984	31.66	29.67	32.20	35.27	31.82	32.67
5.703	2.122	29.54	28.65	29.81	33.16	29.75	30.36
6.916	2.637	23.52	25.75	23.24	27.05	23.67	23.97
7.427	2.914	21.24	24.70	20.76	24.61	21.44	21.54
8.726	3.849	16.51	22.39	15.22	18.84	16.54	16.06
9.124	4.218	15.21	21.76	13.76	17.24	15.25	14.60

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_0	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				$LiNO_3$			
9.135	4.236	15.18	21.74	13.69	17.17	15.21	14.54
9.986	5.142	12.79	20.51	11.05	14.18	12.73	11.87
11.50	7.987	9.28	18.62	6.86	9.16	9.15	7.57
13.55	14.88	6.03	16.51	3.50	4.87	5.70	4.02
	a_0/A°	=	1.42	4.92	3.37	5.55	4.56
	Std.dev. in Λ	=	8.0052	1.1480	2.6168	0.1797	1.0003
				$LiClO_3$(Λ_o=104.0)			
						B'_1 = -10.1569×10^{-2} C'_1 = -5.7927×10^{-3}	n=0.8686
0.02188	1.002	93.31	92.51	94.09	93.44	93.80	93.79
0.1002	1.015	84.78	81.54	86.04	84.27	85.68	85.28
0.5121	1.067	71.85	61.95	73.14	69.87	72.30	71.72
0.8532	1.110	66.36	54.25	67.53	64.31	66.51	66.08
1.247	1.169	61.58	48.20	62.12	59.49	61.34	60.86

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_0	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				$LiClO_3$			
1.640	1.229	57.19	43.74	57.67	55.73	56.97	56.65
2.113	1.315	52.45	39.58	52.63	51.68	52.33	51.98
2.928	1.472	45.67	34.26	45.47	45.95	45.35	45.39
3.115	1.508	44.11	33.25	44.08	44.83	43.89	44.12
3.742	1.642	39.94	30.32	39.63	41.21	39.27	40.04
4.549	1.895	33.90	27.54	33.49	36.07	33.91	34.43
4.908	2.019	31.69	26.08	31.10	33.99	31.71	32.23
5.157	2.115	30.17	25.33	29.47	32.54	30.25	30.73
6.199	2.594	24.38	22.57	23.34	26.85	24.69	25.00
7.185	3.140	19.76	20.43	18.78	22.33	20.17	20.64
7.762	3.585	17.35	19.34	16.19	19.65	17.83	18.13
8.047	3.838	16.30	18.83	15.01	18.38	16.75	16.97
8.947	5.170	13.29	17.38	10.88	13.78	13.69	12.81
10.19	6.894	10.11	15.65	7.89	10.30	10.20	9.69
11.49	10.29	7.521	14.10	5.098	6.869	7.351	6.630

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			$LiClO_3$				
12.80	16.37	5.618	12.768	3.086	4.278	5.182	4.292
13.93	24.53	4.313	11.755	1.991	2.821	3.770	2.939
14.27	28.38	3.955	11.472	1.703	2.428	3.415	2.567
16.15	66.26	2.432	10.060	0.686	1.013	1.928	1.172
17.95	166.5	1.341	8.909	0.256	0.391	1.071	0.502
19.03	334.0	0.8639	8.296	0.123	0.191	0.738	0.266
	$a_o/A°$	=	1.38	5.67	3.87	4.92	4.77
	Std.dev. in Λ	=	7.9888	1.3901	1.5939	0.3933	0.7402
			NaCl (Λ_o=126.5)			B'_1=-4.3487×10^{-2} C'_1= -8.4556×10^{-3}	n=0.7216
0.002	1.00043	122.64	122.64	122.79	122.73	122.74	122.73
0.005	1.00081	120.64	120.53	120.90	120.76	120.75	120.75
0.01	1.00146	118.45	118.26	118.94	118.70	118.68	118.68

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				NaCl			
0.02	1.00259	115.67	115.23	116.46	116.05	115.98	116.00
0.05	1.00544	110.89	109.76	112.29	111.51	111.33	111.40
0.1	1.00995	106.74	104.35	108.40	107.22	106.91	107.04
0.2	1.01874	101.74	97.79	103.77	102.16	101.70	101.89
0.5	1.04603	93.62	87.51	95.98	93.99	93.42	93.60
1.0	1.09582	85.76	78.86	87.71	86.03	85.57	85.60
2.0	1.2186	74.71	69.86	74.96	74.77	74.75	74.51
3.0	1.379	65.57	64.58	63.87	65.25	65.70	65.39
4.0	1.580	57.23	60.84	54.02	56.63	57.29	57.36
5.0	1.858	49.46	57.96	44.61	48.10	49.36	49.58
	a_o/A°	=	2.35	6.44	5.16	4.48	4.84
	Std.dev. in Λ	=	4.0893	2.0774	0.5234	0.1972	0.2308

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				NaBr (Λ_o=128.3)			
						$B_1'=-3.7580\times10^{-2}$ $C_1'=-9.5085\times10^{-3}$	n=0.7843
0.0498	1.0035	113.19	111.43	114.13	113.39	113.56	113.44
0.0995	1.0058	109.37	105.95	110.39	109.25	109.43	109.32
0.4925	1.0290	97.28	88.88	98.87	96.75	97.09	96.85
0.9727	1.0605	89.95	80.17	91.86	89.76	89.95	89.81
1.8967	1.1407	80.05	71.25	81.32	80.26	80.07	80.14
2.7724	1.2475	71.81	66.14	71.92	72.26	71.86	72.03
3.6029	1.3820	64.39	62.62	63.20	64.84	64.39	64.62
5.1389	1.7549	51.21	57.89	47.59	51.04	51.18	51.26
6.5233	2.3049	40.20	54.72	34.87	38.98	40.21	39.94
	a_o/A°	=	2.27	6.24	5.07	5.1	5.07
	St.dev. in Λ	=	7.8115	2.4191	0.5099	0.1420	0.2233

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			NaI (Λ_o=127.2)			$B'_1 = -1.9958\times10^{-2}$ $C'_1 = -8.7163\times10^{-3}$	n=0.6828
0.01	1.0005	119.24	119.36	119.72	119.63	119.67	119.60
0.05	1.001	112.79	112.06	113.40	113.08	113.10	112.95
0.1	1.002	109.40	107.75	109.82	109.34	109.35	109.14
0.5	1.012	98.83	95.58	99.63	98.75	98.62	98.38
1.0	1.03	92.53	89.79	93.66	92.89	92.55	92.56
2.0	1.09	83.66	83.78	84.09	84.21	83.76	84.24
3.0	1.21	75.76	80.09	73.03	74.70	75.72	75.50
	a_o/A°	=	4.24	6.33	5.82	5.86	5.58
	St.dev.in Λ	=	2.3925	1.2153	0.5084	0.2186	0.3413
			$NaNO_3$ (Λ_o=121.5)			$B'_1 = -11.1037\times10^{-2}$ $C'_1 = -1.8775\times10^{-3}$	n=0.8125
0.0498	1.0031	104.94	104.21	105.78	104.91	106.05	105.39

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				$NaNO_3$			
0.1	1.004	101.66	98.23	101.11	99.64	101.25	100.43
0.5	1.026	85.39	78.57	86.04	82.50	85.56	84.45
1.0	1.062	75.84	67.87	77.11	73.09	75.79	75.29
1.8788	1.1588	64.46	57.49	65.53	62.79	64.15	64.21
2.0	1.169	62.95	56.45	64.45	61.85	62.81	63.17
2.7338	1.2847	55.64	51.23	56.30	55.54	55.54	55.78
3.0	1.321	53.19	49.69	54.07	53.78	53.18	53.74
3.5288	1.4274	48.60	47.01	48.92	49.89	48.84	49.16
4.0	1.518	45.17	44.96	45.17	46.98	45.31	45.79
5.0	1.756	38.47	41.36	37.75	41.05	38.67	39.14
6.0	2.078	32.89	38.48	30.97	35.26	32.99	33.02
6.2467	2.2273	31.76	37.85	28.70	33.23	31.71	30.97
7.0	2.527	28.34	36.09	24.80	29.55	28.09	27.34
	a_o/A°	=	1.54	3.59	2.55	4.26	3.05
	Std.dev.in Λ	=	5.2373	1.5546	1.7980	0.3529	0.6614

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			$NaClO_4$ (Λ_o=117.4)			B'_1 = $-7.3087x10^{-2}$ C'_1 = $-11.5048x10^{-3}$	n=0.7929
0.5	1.023	85.26	73.97	85.60	82.27	85.30	83.39
1.0	1.047	77.07	62.88	78.58	74.68	76.98	75.92
2.0	1.145	64.83	50.96	67.07	64.51	64.86	65.05
3.0	1.308	54.50	43.90	56.14	56.00	54.57	55.49
4.0	1.554	45.25	38.96	45.62	47.75	45.25	46.47
5.0	1.944	36.89	35.21	35.38	39.11	36.83	37.62
6.0	2.549	29.42	32.23	26.26	30.60	29.36	29.46
7.0	3.459	22.90	29.76	18.87	23.01	22.91	22.51
8.0	4.862	17.41	27.68	13.10	16.60	17.48	16.76
9.0	7.199	13.06	25.88	8.64	11.30	13.05	11.99
	a_o/A°	=	1.38	4.53	3.34	4.96	3.68
	Std.dev. in Λ	=	10.00	2.7728	1.8270	0.0537	0.9792

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			NaSCN (Λ_o=116.5)			B'_1 = -2.6485×10^{-2} C'_1 = -15.2570×10^{-3}	n=0.8285
0.1	0.995	97.55	93.66	100.27	98.69	98.09	99.05
0.5	1.031	86.67	74.57	88.07	85.32	86.18	86.09
1.0	1.065	79.54	64.26	81.34	78.51	79.28	79.24
2.0	1.168	68.74	53.30	70.27	68.80	69.11	68.97
3.0	1.326	59.30	46.85	59.60	60.03	59.75	59.56
4.0	1.555	50.49	42.34	49.22	51.35	50.54	50.48
5.0	1.884	42.03	38.92	39.44	42.73	41.65	41.82
6.0	2.390	33.88	36.18	30.22	34.04	33.38	33.42
7.0	3.138	26.12	33.92	22.38	26.13	25.99	26.00
8.0	4.254	19.17	31.99	16.05	19.34	19.65	19.71
9.0	6.028	14.23	30.33	11.01	13.64	14.41	14.40
	a_o/A°	=	1.6	6.23	4.77	4.86	5.11
	Std.dev. in Λ	=	11.0959	2.5364	0.7590	0.3819	0.5536

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	Λ_{obs}/ Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1}				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				KF (Λ_o=128.5)		B'_1= -3.4487×10^{-2} C'_1= -4.3866×10^{-3}	n=0.4880
0.0010	1.0001	126.04	125.72	125.83	125.78	125.75	125.76
0.0024	1.0002	124.48	124.26	124.50	124.41	124.32	124.34
0.0036	1.0004	123.72	123.35	123.69	123.56	123.44	123.46
0.0049	1.0006	122.95	122.54	122.98	122.82	122.66	122.69
0.0062	1.0007	122.30	121.85	122.39	122.20	121.99	122.03
0.0075	1.0009	121.71	121.23	121.87	121.64	121.40	121.44
0.0092	1.0010	121.05	120.50	121.28	121.00	120.71	120.77
0.3	1.0400	98.13	94.88	101.84	99.81	97.63	97.86
0.5	1.0620	91.73	88.77	97.00	94.83	92.19	92.54
1.0	1.1299	83.63	79.82	87.49	85.84	83.76	83.83
2.0	1.2800	73.45	70.49	73.54	73.52	73.42	73.10
3.0	1.4550	65.89	65.00	62.41	63.85	65.76	65.39
4.0	1.6550	59.12	61.12	52.84	55.38	59.13	58.96

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			KF				
5.0	1.9000	53.03	58.13	44.94	48.19	53.08	53.56
	a_o/A°	=	2.25	6.85	5.29	3.41	3.79
	Std.dev.in Λ	=	2.3077	3.5214	2.0532	0.2769	0.3676
			KCl (Λ_o=149.6)				
						B_1' = 4.1182×10^{-2} C_1' = -10.7250×10^{-3}	n=0.6964
0.01	1.0004	141.3	141.37	141.43	141.40	141.32	141.41
0.05	1.0003	133.4	133.78	134.15	134.05	133.66	134.04
0.1	1.0001	128.9	129.33	129.97	129.82	129.21	129.78
0.2	0.999	124.5	124.25	125.36	125.11	124.24	125.02
0.5	0.998	117.9	116.81	118.58	118.18	117.32	118.04
1.0	0.999	112.0	110.78	112.88	112.39	112.07	112.24
1.5	1.003	108.1	107.10	109.00	108.55	108.77	108.43
2.0	1.007	105.6	104.38	106.01	105.62	105.94	105.53

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				KCl			
2.5	1.014	103.6	102.19	103.21	102.96	103.17	102.92
3.0	1.033	100.7	100.32	99.55	99.71	100.26	99.81
3.5	1.054	97.2	98.68	96.04	96.61	97.12	96.86
4.0	1.073	93.4	97.19	92.96	93.90	93.72	94.25
	a_o/A°	=	4.54	5.07	4.94	4.05	4.90
	Std.dev. in Λ	=	1.4223	0.8005	0.5829	0.3677	0.5590
				KBr (Λ_o=151.4)			
						$B'_1 = 4.2225x10^{-2}$ $C'_1 = -11.2733x10^{-3}$	n=1.0896
0.00025	1.0006	150.16	149.93	149.92	149.92	149.93	149.91
0.00036	1.00007	149.87	149.64	149.63	149.63	149.64	149.63
0.00050	1.00008	149.55	149.34	149.32	149.32	149.34	149.32
0.00075	1.00009	149.12	148.90	148.87	148.88	148.89	148.87
0.001	1.00010	148.78	148.53	148.50	148.50	148.52	148.50
0.0016	1.00011	148.02	147.82	147.78	147.78	147.81	147.77

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				KBr			
0.002	1.00010	147.64	147.43	147.38	147.39	147.41	147.38
0.005	1.00009	145.47	145.36	145.27	145.29	145.33	145.27
0.01	0.99997	143.15	143.22	143.09	143.11	143.16	143.08
0.02	0.99973	140.26	140.48	140.27	140.31	140.38	140.25
0.05	0.99863	135.44	135.83	135.51	135.60	135.68	135.49
0.1	0.99678	131.19	131.55	131.16	131.29	131.40	131.14
0.2	0.99287	126.59	126.70	126.38	126.53	126.66	126.36
0.5	0.98180	120.35	119.65	119.90	119.96	120.18	119.93
1.0	0.96795	115.46	113.94	115.11	114.93	115.31	115.23
2.0	0.95744	109.37	107.79	109.42	109.01	109.45	109.58
3.0	0.96879	103.55	103.82	103.82	103.74	103.66	103.83
3.75	0.99181	98.70	101.41	98.93	99.46	98.62	98.72
	a_o/A°	=	4.95	4.31	4.44	4.40	4.26
	Std.dev.in Λ	=	0.8639	0.2346	0.3062	0.1800	0.2240

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				KNO_3 (Λ_o=144.6)			
						B'_1 = 3.2120×10^{-3}	n = 0.9674
						C'_1 = -17.0317×10^{-3}	
0.0498	0.9983	125.92	126.57	126.74	126.74	126.80	126.73
0.0993	0.9962	120.43	120.53	120.90	120.88	120.95	120.89
0.4888	0.9827	103.03	101.11	102.58	102.24	102.45	102.56
0.9583	0.9766	92.73	90.92	92.64	92.05	92.55	92.62
1.4087	0.9789	85.82	84.76	86.03	85.50	86.03	86.03
1.8419	0.9885	80.67	80.39	80.70	80.53	80.83	80.74
2.2566	1.0026	76.17	77.06	76.19	76.56	76.31	76.26
2.6559	1.0215	72.40	74.38	72.10	73.19	72.19	72.23
	a_o/A°	=	1.86	1.81	1.83	1.89	1.82
	Std.dev.in Λ	=	1.2887	0.3910	0.5980	0.4388	0.3872
				$AgNO_3$ (Λ_o=133.6)			
						B'_1 = -5.0893×10^{-2}	n=0.4443
						C'_1 = -1.0826×10^{-3}	
0.1000	1.009	109.10	108.93	110.64	109.18	109.75	109.48

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1}				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				$AgNO_3$			
0.4916	1.033	89.69	87.31	92.72	88.85	89.53	89.30
1.0515	1.078	76.74	73.75	80.60	75.99	76.63	76.44
1.6723	1.132	67.91	64.78	71.80	67.52	67.71	67.71
2.0163	1.168	63.74	61.08	67.64	63.88	63.88	63.92
2.7833	1.260	56.90	54.65	59.57	57.31	56.96	57.04
3.5913	1.382	51.15	49.59	52.04	51.60	51.17	51.14
4.3256	1.464	46.69	45.93	47.55	48.04	46.78	47.31
4.9518	1.632	43.43	43.30	41.62	43.74	43.49	43.33
4.9880	1.638	43.32	43.16	41.42	43.58	43.31	43.17
6.3476	1.942	37.34	38.57	33.36	37.14	37.26	37.18
6.5660	1.990	36.47	37.93	32.34	36.28	36.39	36.38
7.6388	2.264	32.52	35.13	27.57	32.13	32.47	32.72
8.7400	2.740	28.87	32.70	22.13	27.08	28.94	28.73
	a_o/A°	=	1.23	2.72	1.79	1.94	1.73
	Std.dev.in Λ	=	2.1511	3.5373	0.7183	0.1981	0.2650

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1} Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			$AgClO_4$ (Λ_o=129.5)			B'_1 = -5.7906×10^{-2} C'_1 = -10.5221×10^{-3}	n=0.8240
0.1074	1.002	110.10	106.40	110.18	109.17	110.11	109.47
0.2348	1.005	104.40	98.60	104.72	103.17	104.39	103.64
0.4649	1.014	98.15	90.65	99.00	96.99	98.34	97.62
0.5847	1.020	96.26	87.79	96.76	94.67	95.99	95.33
0.9001	1.040	90.70	82.22	91.79	89.74	90.90	90.38
1.4230	1.070	84.23	76.11	85.91	84.18	84.01	84.64
2.0394	1.142	76.90	71.75	77.95	77.36	76.87	77.41
2.4027	1.194	72.71	69.03	73.40	73.58	72.90	73.36
3.0731	1.302	65.83	65.70	65.64	67.14	65.85	66.49
3.5231	1.399	61.31	63.86	60.18	62.57	61.28	61.67
4.1797	1.571	54.91	61.56	52.53	55.98	54.84	54.88
5.6000	2.134	41.95	57.64	37.19	41.87	41.98	40.97
	a_o/A°	=	2.27	5.00	4.18	5.35	4.40
	Std.dev.in Λ	=	7.3899	1.7385	1.0267	0.1415	0.6186

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$				
			Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			NH_4Cl (Λ_o=150.4)				
						$B'_1 = 4.1651 \times 10^{-2}$ $C'_1 = -8.3162 \times 10^{-3}$	n=1.1237
0.1019	0.999	128.6	129.40	129.68	129.63	129.25	129.71
0.2015	0.998	123.8	124.09	124.57	124.48	124.02	124.62
0.5019	0.994	116.8	116.15	117.22	117.00	116.57	117.33
1.011	0.990	111.2	109.60	111.20	110.84	110.92	111.37
2.005	0.989	105.1	102.87	104.62	104.18	105.08	104.80
3.006	0.997	100.2	98.63	99.57	99.32	100.33	99.65
4.005	1.013	95.1	95.42	94.86	95.01	95.21	94.75
5.252	1.048	87.9	92.15	88.57	89.55	87.80	88.10
	a_o/A°	=	4.12	4.23	4.20	3.63	4.24
	Std.dev.in Λ	=	1.9140	0.6203	0.8698	0.2829	0.5875

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1} Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
			NH_4NO_3 (Λ_o=145.4)			B'_1 = 0.9852x10^{-2} C'_1 = -7.7069x10^{-3}	n=1.0016
0.01	0.999	136.47	136.76	136.95	136.93	136.96	136.95
0.02	0.998	133.32	133.58	133.95	133.91	133.96	133.96
0.03	0.998	131.26	131.27	131.69	131.63	131.82	131.69
0.04	0.997	129.33	129.42	130.00	129.92	130.11	130.01
0.048	0.996	128.13	128.14	128.89	128.78	128.94	128.89
0.05	0.998	127.86	127.85	128.34	128.25	128.67	128.34
0.06	0.996	126.66	126.47	127.25	127.12	127.43	127.25
0.07	0.997	125.50	125.24	125.93	125.80	126.32	125.93
0.08	0.996	124.54	124.12	124.97	124.82	125.33	124.97
0.09	0.996	123.70	123.10	123.98	123.81	124.42	123.98
0.10	0.995	122.83	122.16	123.19	123.00	123.59	123.19
0.15	0.993	119.39	118.27	119.66	119.38	120.19	119.66

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$ / Scm^2mol^{-1}	$\Lambda_{calc.}$ / Scm^2mol^{-1} Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				NH_4NO_3			
0.2	0.990	117.10	115.25	117.10	116.72	117.60	117.11
0.3	0.986	113.46	110.67	113.14	112.59	113.72	113.15
0.4	0.982	110.83	107.20	110.25	109.52	110.82	110.26
0.5	0.977	108.74	104.41	108.10	107.17	108.49	108.12
0.6	0.975	106.90	102.06	106.04	105.00	106.54	106.06
0.7	0.973	105.23	100.03	104.30	103.13	104.86	104.32
0.8	0.968	103.77	98.25	103.10	101.73	103.36	103.13
0.9	0.967	102.51	96.66	101.67	100.21	102.01	101.69
1.0	0.963	101.32	95.23	100.70	99.06	100.79	100.72
1.5	0.960	96.3	89.64	95.54	93.59	95.73	95.57
2.0	0.955	92.1	85.61	92.08	89.80	91.64	92.12
2.5	0.958	88.1	82.46	88.71	86.45	87.96	88.75
3.0	0.970	84.2	79.89	85.12	83.25	84.47	85.15
4.0	1.009	77.2	75.81	78.01	77.51	77.64	78.03

Contd...

Table 5.1 contd..

c (moles/lit)	η/η_o	$\Lambda_{obs.}$/ Scm^2mol^{-1}	$\Lambda_{calc.}/Scm^2mol^{-1}$ Λ_{FLK} (Eq 1.7)	Λ_{WS} (Eq 1.8)	Λ_{MONICA} (Eq 1.9)	Λ_{MFLK} (Eq 5.1)	Λ_{MWS} (Eq 5.31)
				NH_4NO_3			
5.0	1.065	70.0	72.63	71.06	72.32	70.76	71.09
6.0	1.147	63.5	70.01	63.80	67.08	63.77	63.81
7.0	1.255	56.8	67.78	56.59	61.79	56.76	56.60
8.0	1.396	50.5	65.82	49.52	56.31	49.85	49.51
	a_o/A°	=	2.38	2.62	2.55	3.19	2.62
	Std.dev.in Λ	=	4.9706	0.6250	2.0238	0.5705	0.6248

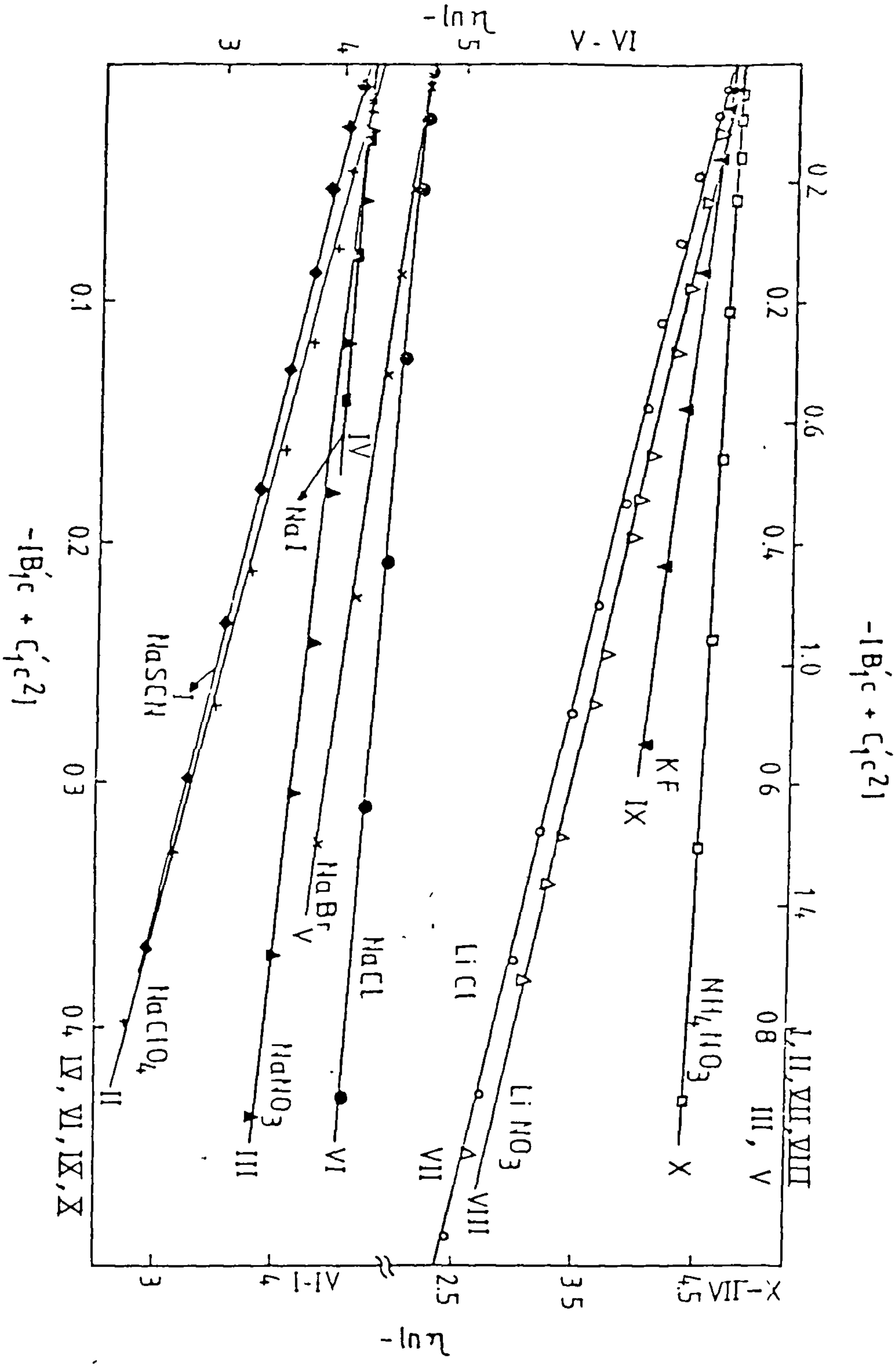

Fig.5.1 Plot of lnη vs. $[B_i'c+C_i'c^2]$ for different aqueous electrolytic solutions at 298K.

APPENDICES

APPENDIX-A

ITERATION PROGRAM OF MODIFIED FLK EQUATION(3.2 OR 5.1)

```
20      READ N,C0,A0,B,C,R0,R1,R2
30      DIM XI(50),XY(50),X1(50),X2(50),X3(50),X4(50),X5(50),X6(50)
35      DIM X7(50),X8(50),D1(50),D2(50),D3(50),D4(50),D5(50),D6(50)
40      DIM D7(50),YI(50),D8(50)
45      DT=83.95*283.0
50      FOR J=1 TO 6
60      READ S0,S1,S2,S3,S4,S5,S6,S7,S8,S9
70      A0=A0+R0
80      B=B+R1
90      C=C+R2
100     FOR I=1 TO N
105     READ XI(I),XY(I)
110     X1(I)=82.501*XY(I)^0.5/(1.3070E-02*DT^0.5)
120     X2(I)=1.0+(0.5029*A0*10`10*XY(I)^0.5)/DT^0.5
130     X3(I)=(X2(I)-1.0)/A0
140     X4(I)=(0.8204*10`6*XY(I)^0.5)/DT`1.5
150     X5(I)=0.2929*X3(I)*A0
160     X6(I)=EXP(X5(I))
170     X7(I)=(X6(I)-1.0)/X5(I)
180     X8(I)=EXP(B*XY(I)+C*XY(I)`2)
190     D1(I)=(X1(I)*X3(I)/X2(I)^2)+(X3(I)*X4(I)/X2(I) 2)*X7(I)
    *(C0-2.0*X1(I)/X2(I))
200     D2(I)=(X4(I)/X2(I))*((X1(I)/X2(I))-C0)*((1.0+X6(I)
    *(X5(I)-1.0))/X5(I)*A0)
210     D3(I)=(D1(I)+D2(I))*X8(I)
220     D4(I)=(C0-X1(I)/X2(I))*(1.0-X4(I)*X7(I)/X2(I))*X8(I)
230     D5(I)=D4(I)*XY(I)
240     D6(I)=D5(I)*XY(I)
250     D7(I)=XI(I)-D4(I)
260     S1=S1+D3(I)´2
270     S2=S2+D3(I)*D5(I)
280     S3=S3+D3(I)*D6(I)
290     S4=S4+D5(I)`2
300     S5=S5+D5(I)*D6(I)
310     S6=S6+D6(I)`2
320     S7=S7+D3(I)*D7(I)
330     S8=S8+D5(I)*D7(I)
340     S9=S9+D6(I)*D7(I)
```

```
350     S0=S0+D7(I)^2
355     D8(I)=LOG(X8(I))
360     NEXT I
370     D=S1*(S4*S6-S5^2)-S2*(S2*S6-S3*S5)+S3*(S2*S5-S3*S4)
380     R0=(S7*(S4*S6-S5^2)-S2*(S8*S6-S9*S5)+S3*(S8*S5-S9*S4))/D
390     R1=(S1*(S8*S6-S9*S5)-S7*(S2*S6-S3*S5)+S3*(S2*S9-S3*S8))/D
400     R2=(S1*(S4*S9-S5*S8)-S2*(S2*S9-S3*S8)+S7*(S2*S5-S3*S4))/D
410     SD=(S0/N)^0.5
420     PRINT
430     PRINT "DELA0="R0,"DELB="R1,"DELC="R2
440     PRINT
450     PRINT "LAMDAA0="C0,"A0="A0,"B="B,"C="C,"STD="SD
460     PRINT
470     FOR K=1 TO N
480     PRINT XI(K),XY(K),D4(K)
490     NEXT K
500     RESTORE 530
510     NEXT J
520     DATA N,C0,A0,B,C,R0,R1,R2
530     DATA S0,S1,S2,S3,S4,S5,S6,S7,S8,S9
540     DATA XI(I),XY(I)
```

APPENDIX-B

ITERATION PROGRAM FOR VTF EQUATION(3.3)

```
10      DIM XI(20),XY(20),YI(20),X1(20),X2(20),X3(20),X4(20)
15      DIM X5(20),X6(20),X7(20),X8(20),X9(20),D1(20),Y2(20)
20      READ N,Y0,Y1,Y2,A0,A1,A2
25      K=0
30      FOR K=1 TO 14
35      READ S1,S2,S3,S4,S5,S6,S7,S8,S9,DE
40      K=K+1
50      Y0=Y0+A0
60      Y1=Y1+A1
70      Y2=Y2+A2
80      FOR I=1 TO N
90      READ XI(I),XY(I)
95      XY(I)=XY(I)*10^-3
100     YI(I)=LOG(XY(I))
110     X1(I)=1/(XI(I)-Y2)
120     X3(I)=X1(I)^2
130     X2(I)=X3(I)*Y1
140     X5(I)=X1(I)^3
145     X4(I)=X5(I)*Y1
150     X6(I)=X1(I)^4*Y1
160     S1=S1+X1(I)
170     S2=S2+X2(I)
180     S3=S3+X3(I)
190     S4=S4+X4(I)
200     S5=S5+X5(I)
210     S6=S6+X6(I)
220     X7(I)=YI(I)-(Y0-Y1*X1(I))
230     X8(I)=X7(I)*X1(I)
240     X9(I)=X8(I)*X1(I)
250     S7=S7+X7(I)
260     S8=S8+X8(I)
270     S9=S9+X9(I)
280     D1(I)=X7(I)^2
290     DE=DE+D1(I)
295     Y2(I)=EXP(Y0-Y1*X1(I))
300     NEXT I
310     D=N*(S3*S6-S5*S4)+S1*(S3*S4-S1*S6)-S2*(S3 2-S1*S5)
320     A0=(S7*(S3*S6-S5*S4)+S1*(S9*S4-S8*S6)-S2*(S9*S3-S8*S5))/D
330     A1=(N*(S9*S4-S8*S6)-S7*(S3*S4-S1*S6)-S2*(S1*S9-S3*S8))/D
340     A2=(N*(S5*S8-S3*S9)+S1*(S1*S9-S3*S8)+S7*(S3^2-S1*S5))/D
```

```
350     D1=(DE/N)´0.5
360     LPRINT
370     LPRINT"DLOGA="A0,"DB="A1,"DTO="A2
380     LPRINT
390     LPRINT"LOGA="Y0."B='Y1."TO="Y2
400     LPRINT
410     FOR J=1 TO N
420     LPRINT XI(J),XY(J),Y2(J)
430     NEXT J
440     LPRINT"STD="D1
450     RESTORE 475
460     NEXT K
470     DATA N.Y0,Y1,Y2.A0,A1.A2
475     DATA S1,S2,S3.S4,S5,S6.S7,S8.S9,DE
480     DATA XI(I),XY(I)
```

APPENDIX-C

```
10                 PROGRAM FOR FLK EQUATION(1.7)
20        DIM X0(35).X1(35).X2(35).X3(35),X4(35).XI(35).XY(35).XZ(35)
30        DIM Y0(35),Y1(35).Y2(35),Y3(35).Y4(35).VI(35)
40        K=0
50        X=2.56E-08
60        FOR M=1 TO 50
70        READ N,S1.S2.S3,S4.S5.S6.LO
80        DT=78.30*298.0
90        K=K+1
100       X=X+0.01E-08
110       FOR I=1 TO N
120       READ XI(I).XY(I)
130       X1(I)=82.501*XY(I)^0.5/(8.904E-03*DT^0.5)
140       X2(I)=50.29E08*X*XY(I)^0.5/DT^0.5
150       X3(I)=8.204E05*XY(I)^0.5/DT^1.5
160       X4(I)=(EXP(0.2929*X2(I))-1.0)/(0.2929*X2(I))
170       XZ(I)=(LO-X1(I)/(1+X2(I)))*(1-X3(I)*X4(I)/(1+X2(I)))
180       Y4(I)=XZ(I)-XI(I)
190       S6=S6+Y4(I)^2
200       NEXT I
210       SD=(S6/N)^0.5
220       PRINT
230       PRINT "A0="X,"LO="LO
240       FOR L=1 TO N
250       PRINT XY(L).XI(L),XZ(L)
260       NEXT L
270       PRINT "STD="SD
280       RESTORE 300
290       NEXT M
300       DATA N,S1.S2,S3,S4.S5,S6,LO
310       DATA XI(I).XY(I)
```

APPENDIX-D

```
10          PROGRAM FOR WISHAW-STOKES EQUATION(1.8)
20     DIM XO(35),X1(35),X2(35),X3(35),X4(35),XI(35),XY(35)
30     DIM YO(35),Y1(35),Y2(35),Y3(35),Y4(35),VI(35),XZ(35)
40     K=0
50     X=2.53E-08
60     FOR M=1 TO 50
70     READ N,S1,S2,S3,S4,S5,S6,LO
80     DT=78.30*298.0
90     K=K+1
100    X=X+0.01E-08
110    FOR I=1 TO N
120    READ XI(I),XY(I),VI(I)
130    X1(I)=82.501*XY(I)^0.5/(8.904E-03*DT^0.5)
140    X2(I)=50.29E08*X*XY(I)^0.5/DT^0.5
150    X3(I)=8.204E05*XY(I)^0.5/DT^1.5
160    X4(I)=(EXP(0.2929*X2(I))-1.0)/(0.2929*X2(I)).
170    XZ(I)=(LO-X1(I)/(1+X2(I)))*(1-X3(I)*X4(I)/(1+X2(I)))^(1/VI(I))
180    Y4(I)=XZ(I)-XI(I)
190    S6=S6+Y4(I)^2
200    NEXT I
210    SD=(S6/N)^0.5
220    PRINT
230    PRINT "AO="X,"LO="LO
240    FOR L=1 TO N
250    PRINT XY(L),VI(L),XI(L),XZ(L)
260    NEXT L
270    PRINT "STD="SD
280    RESTORE 300
290    NEXT M
300    DATA N,S1,S2,S3,S4,S5,S6,LO
310    DATA XI(I),XY(I),VI(I)
```

APPENDIX-E

```
10        PROGRAM FOR MONICA'S EQUATION(1.9)
20        DIM XO(35),X1(35),X2(35),X3(35),X4(35),XI(35),XY(35)
30        DIM YO(35),Y1(35),Y2(35),Y3(35),Y4(35),VI(35),XZ(35)
40        K=0
50        X=2.53E-08
60        FOR M=1 TO 50
70        READ N,S1,S2,S3,S4,S5,S6,LO
80        DT=78.30*298.0
90        K=K+1
100       X=X+0.01E-08
110       FOR I=1 TO N
120       READ XI(I),XY(I),VI(I)
130       X1(I)=82.501*XY(I)`0.5/((8.904E-03*VI(I))*DT`0.5)
140       X2(I)=50.29E08*X*XY(I)^0.5/DT´0.5
150       X3(I)=8.204E05*XY(I)^0.5/DT^1.5
160       X4(I)=(EXP(0.2929*X2(I))-1.0)/(0.2929*X2(I))
170       XZ(I)=(LO-X1(I)/(1+X2(I)))*(1-X3(I)*X4(I)/(1+X2(I)))*(1/VI(I))
180       Y4(I)=XZ(I)-XI(I)
190       S6=S6+Y4(I)^2
200       NEXT I
210       SD=(S6/N)^0.5
220       PRINT
230       PRINT "AO="X,"LO="LO
240       FOR L=1 TO N
250       PRINT XY(L),VI(L),XI(L),XZ(L)
260       NEXT L
270       PRINT "STD="SD
280       RESTORE 300
290       NEXT M
300       DATA N,S1,S2,S3,S4,S5,S6,LO
310       DATA XI(I),XY(I),VI(I)
```

APPENDIX-F

```
10        PROGRAM FOR MODIFIED W-S EQUATION(5.31)
20    DIM X(50),Y(50),Z(50),XO(50),X1(50),X2(50),X3(50),X4(50),X5(50)
30    DIM F1(50),F2(50),F3(50),F4(50),DA(50),YC(50),DN(50),DY(50)
40    READ N,CO,AO,AN,R1,R2
50    FOR J=1 TO 20
60    READ SO,S1,S2,S3,S4,S5
65    DT=80.1*293.0
70    AO=AO+R1
80    AN=AN+R2
90    FOR I=1 TO N
100   READ Y(I),X(I),Z(I)
110   XO(I)=82.501*X(I)^0.5/(10.02E-03*DT^0.5)
120   X1(I)=1+50.29E08*AO*X(I)^0.5/DT`0.5
130   X2(I)=X1(I)-1.0
140   X3(I)=8.204E05*X(I)^0.5/DT^1.5
150   X4(I)=EXP(0.2929*X2(I))
160   X5(I)=(X4(I)-1.0)/(0.2929*X2(I))
170   F1(I)=(XO(I)+X3(I)*CO*X5(I))*(X2(I)/AO)/X1(I)^2
180   F2(I)=X3(I)*CO*(X5(I)-X4(I))/(X1(I)*AO)
190   F3(I)=2.0*X3(I)*XO(I)*X5(I)*(X2(I)/AO)/X1(I)^3
200   F4(I)=X3(I)*XO(I)*(X4(I)-X5(I))/(AO*X1(I)^2)
210   DA(I)=(F1(I)+F2(I)-F3(I)+F4(I))*(1/Z(I))´AN
220   YC(I)=(CO-(XO(I)/X1(I)))*(1.0-(X3(I)*X5(I)/X1(I)))*(1/Z(I))^AN
230   DN(I)=YC(I)*LOG(1/Z(I))
240   DY(I)=Y(I)-YC(I)
250   SO=SO+DA(I)´2
260   S1=S1+DA(I)*DN(I)
270   S2=S2+DN(I)^2
280   S3=S3+DA(I)*DY(I)
290   S4=S4+DN(I)*DY(I)
300   S5=S5+DY(I)^2
310   NEXT I
320   D=SO*S2-S1`2
330   R1=(S3*S2-S4*S1)/D
340   R2=(SO*S4-S1*S3)/D
350   SD=(S5/N)´0.5
360   PRINT "LAMDAO="CO,"AO="AO,'N="AN,"STD.DEV.="SD
370   FOR K=1 TO N
380   PRINT X(K),Z(K),Y(K),YC(K)
390   NEXT K
400   RESTORE 430
410   NEXT J
420   DATA N,CO,AO,AN,R1,R2
430   DATA SO,S1,S2,S3,S4,S5
440   DATA Y(I),X(I),Z(I)
```