A Study on the Transport Behaviour of Single and Mixed Electrolytes

ABSTRACT

RATAN LAL GUPTA

Department of Chemistry
School of Physical Sciences

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ABSTRACT

The thesis entitled, 'A Study on the Transport Behaviour of Single and Mixed Electrolytes', consists of 5 chapters.

A general introduction to the study made in the thesis is given in Chapter I. In Chapter II we have described the experimental techniques used and also the computation methods used for the treatment of experimental data.

In Chapter III densities and electrical conductances of $[xNaSCN+(1-x)KSCN]+RH_2O$ system were measured as functions of x, R and temperature. The mixed alkali effect (MAE) on electrical conductance has been found to be negligible when $R > 10$ and it increased sharply with increase in concentration in the range $R \leq 10$. It has been pointed out that the value of R at which the MAE on electrical conductance starts becoming significant falls in the concentration range (lower one) where specific conductance maximum of one of the two constituent electrolytes of the mixed electrolytic solution occurs. The occurrence of the MAE on electrical conductance has been explained in terms of the anion polarization model. In the experimental temperature range

(283K to 323K) the MAE on electrical conductance is found to be almost independent of temperature.

The concentration dependence of molar conductance (Λ) of both single (x=0.0 and 1.0) and mixed (x≠0.0 or 1.0) electrolytic solutions has been described satisfactorily by an empirical equation of the form

$$\Lambda = \Lambda_{FLK} \exp (B'_1 c + C'_1 c^2) \qquad (A.1)$$

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.

In Chapter IV density and electrical conductance measurements of $[xNaNO_3+(1-x)KNO_3]+RH_2O$ system were made as functions of x,R and T. The MAE on electrical conductance has been found to be negligible upto R=25 and becomes significant beyond $R\leq 20$. In this system the value of R at which the MAE on electrical conductance starts becoming significant has no correlation with the concentration range where specific conductance maximum of one of the two constituent electrolytes of the mixed electrolytic system occurs unlike the case with the $[xNaSCN+(1-x)KSCN]+RH_2O$ system. On the other hand, it has been found that in mixed electrolytic system the concentration range at which the MAE on electrical conductance starts becoming significant coincides with the concentration range at which the plot of $\Delta\Lambda$ versus R deviates from linearity where $\Delta\Lambda$ is the difference in Λ of the two pure electrolytic solutions (x=0.0 and 1.0). From the plots of $\Delta\Lambda$ versus R drawn for different pairs of electrolytes, it has been observed that the dependence of $\Delta\Lambda$ on R follows a general trend.

The concentration dependence of molar conductance Λ has been described satisfactorily by equation(A.1). The low value of the ion-size parameter a_o obtained for pure KNO_3 solution has been discussed. The B_1' parameter has been correlated to the activation energy required per mole of water to change the equilibrium position near to the ion to one near to the bulk water.

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.

Equation (A.1) was reduced to the form of a modified Wishaw-Stokes equation given by

$$\Lambda = \Lambda_{FLK} (\eta_o / \eta)^n \tag{A.3}$$

where n is a numerical constant. η_o and η are the viscosities of water and solution, respectively. Equation (A.3) was also applied to describe the concentration dependence of Λ of several electrolytic solutions.