

Mixed-Alkali Effect in $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ Melts

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Densities, fluidities, and conductivities of the molten $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ system were measured as functions of temperature and composition. The temperature dependence of fluidity and conductivity has been described by the Vogel-Tammann-Fulcher (VTF) equation. Deviation from additivity has been observed in the case of both fluidity and conductivity at all experimental temperatures. A three-parameter isothermal equation has been found to describe satisfactorily the composition dependence of both fluidity and conductivity. The suitability of this equation has been established by employing it to describe the composition dependence of the conductivity of other systems which exhibit a pronounced mixed-alkali effect (MAE). A mixed-alkali effect for conductivity has been observed under isofluidity conditions also. The present study has revealed that the limit of the time scale for detecting the mixed-alkali effect depends upon the system of interest unlike the universal time-scale criterion proposed by others.

Introduction

The mixed-alkali effect (MAE)¹⁻⁹ refers to deviations (mostly minima or maxima are observed) from additivity in isotherms of various physical properties as a function of composition, when one alkali-metal cation is progressively replaced by another in a glass or melt. In general, it is found that there is no MAE for equilibrium properties whereas for properties related to ionic transport a pronounced MAE is observed.

It may be pointed out that studying the MAE has two important implications. Firstly, in glasses a knowledge of the change in properties with chemical composition is important to the glass technologist because of its relevance to controlling of properties, selection and substitution of raw materials, and development of glass compositions with specific properties. Secondly, the MAE observed for the ionic conductivity is of immense theoretical importance as it envisages a major breakdown of the principle of independent migration of ions.

It has recently been suggested by Ingram et al.¹⁰ that in order to have an improved understanding of the MAE it would be worthwhile to examine the behavior of highly concentrated solutions containing mixed alkali ions. To date only a few studies of this kind have been made. Moynihan¹¹ studied the electrical conductivity of $x\text{NaNO}_3-(0.2-x)\text{KNO}_3-0.8\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ melt and failed to observe the MAE in the temperature range from -5 to 70 °C. Ingram et al.¹⁰ measured the viscosities and conductivities of $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ systems in the temperature range from -70 to ~20 °C and observed deviations from additivity in both properties. However, no minimum or maximum was found to occur in the viscosity or conductivity isotherm even at very low temperatures. On the other hand, Ingram et al.¹⁰ observed a shallow minimum in the conductivity isotherm under isofluidity conditions, that too in the low fluidity region, and they considered this as evidence for the onset of the MAE. Easteal and Emson¹² noticed the MAE for the glass transition temperature in $0.45[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}$ -

$(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ melt and they made a suggestion that the MAE becomes significant when the total alkali ion concentration is high as revealed by the study of anhydrous mixed-alkali melts¹³ also. Easteal¹⁴ also observed deviations from additivity in the case of viscosity and conductivity of $0.45[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ and $0.45[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}(\text{NO}_3)_2 \cdot 6.545\text{H}_2\text{O}$ melts.

In the present work we have measured density, viscosity, and conductivity of the molten $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ system as functions of temperature and x .

Experimental Section

Both KSCN and NaSCN (SD, reagent grade) were recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator. Calcium nitrate tetrahydrate (EM, reagent grade) was used as the solvent in the molten state without further purification. The actual $\text{H}_2\text{O}/\text{Ca}^{2+}$ mole ratio in calcium nitrate tetrahydrate was determined to be 4.06 from the EDTA titration.

Although KSCN is soluble up to ~65 mol % in calcium nitrate tetrahydrate,¹⁵ it was found that NaSCN dissolves only up to ~30 mol % at about 50 °C. Therefore, the total alkali concentration was kept as 0.3 mole fraction. Keeping the concentration of $\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ constant at 0.7 mole fraction, we prepared eight samples by varying the amounts of KSCN and NaSCN such that the total alkali concentration was always maintained at 0.3 mole fraction.

Density and viscosity measurements of these molten systems were made as described earlier.¹⁵ The viscometer constants of the Cannon-Ubbelohde viscometers used in the present work were found to be 4.98×10^{-3} and $8.42 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-2}$. Conductivity measurement (accuracy 0.1%) was made by using a conventional conductivity bridge (ELICO CM 82T type) and a dip-type cell of cell constant 1.198 cm^{-1} . All measurements were made in a thermostated water/oil bath (Ultra-Thermostat type NBE).

Results and Discussion

Densities (ρ) of $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ melts were found to be linear functions of temperature and are presented in Table I (see paragraph at end of text regarding supplementary material). The measured values of the fluidity (ϕ) and conductivity (κ) of the above systems are given in Table II (supplementary material). In Figures 1 and 2 the temperature dependence of ϕ and κ is illustrated in the form of Arrhenius plots. From these plots it is apparent that both ϕ

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TABLE IV: Least-Squares-Fitted Values of the Parameters of Eq 1 for the Conductivity ($\text{mho}\cdot\text{cm}^{-1}$) and Fluidity (cP^{-1}) of $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ Melts Selected Such That B_x and B_ϕ Values Are Almost Constant and $T_{0\kappa} \approx T_{0\phi}$ ^a

x	A_y	B_y	T_{0y}	$10^4\sigma^b$
0.0	1.4616 (5.4412)	500.35 (728.15)	211.00 (212.00)	6.62 (1.72)
0.1	1.7657 (4.1216)	535.04 (650.52)	209.75 (211.00)	1.21 (0.66)
0.15	1.8135 (3.7496)	540.44 (638.61)	209.25 (210.50)	1.82 (1.44)
0.2	1.6944 (5.0477)	533.04 (651.98)	208.60 (210.00)	1.06 (1.62)
0.4	1.7988 (5.4442)	547.54 (664.55)	207.23 (208.00)	0.96 (0.91)
0.6	2.1352 (5.7198)	581.84 (665.67)	205.00 (206.28)	2.68 (0.73)
0.8	2.2609 (5.9787)	593.67 (680.60)	204.00 (205.40)	3.19 (4.72)
1.0	2.3100 (6.1088)	601.78 (683.02)	202.79 (204.61)	1.15 (0.79)

^aParameters for fluidity are within the parentheses. ^bStandard deviation in κ or ϕ .

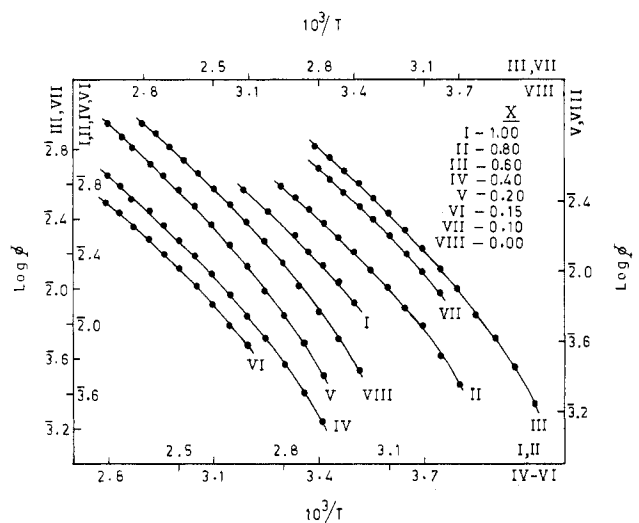


Figure 1. Arrhenius plots for fluidity of $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ melts.

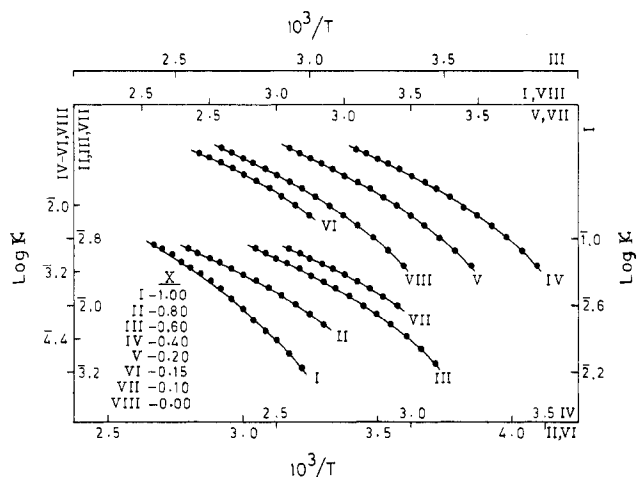


Figure 2. Arrhenius plots for conductivity of $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ melts.

and κ show non-Arrhenius temperature dependence. Such a temperature dependence of transport properties is typical of highly concentrated aqueous solutions. The conductivity and fluidity data were therefore least-squares fitted to the VTF equation of the form

$$Y(\phi, \kappa) = A_y \exp[-B_y/(T - T_{0y})] \quad (1)$$

where Y refers to either fluidity or conductivity. A_y , B_y , and T_{0y} are the three constant parameters. In eq 1 we have neglected the preexponential temperature term owing to its insignificant contribution to the temperature dependence of Y . The best-fit values of A_y , B_y , and T_{0y} are presented in Table III (supplementary material). A relatively high T_0 value has been obtained for the $0.3\text{NaSCN}-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ system. Similarly a high value for T_0 of the $\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ system was observed by Ingram et

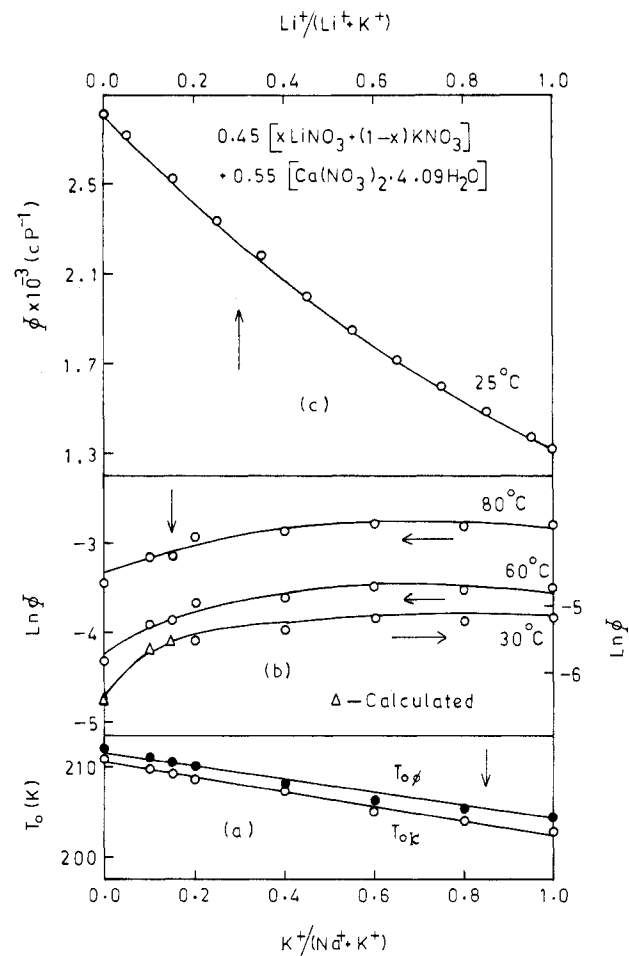


Figure 3. Plots of (a) T_0 and (b) $\ln \phi$ vs. x for $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ melts and (c) of ϕ vs. x for $0.45[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}(\text{NO}_3)_2\cdot 4.09\text{H}_2\text{O}$ melts (ref 14). In parts b and c open circles and solid curves represent observed and calculated (from eq 2, Table VI) values, respectively.

al.¹⁰ while investigating the MAE in supercooled $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ mixtures. From Table III it may be seen that there is no regular trend in the variation of T_0 with composition. An irregular trend in the variation of T_0 with composition was also observed in binary melts containing hydrated salts.^{15,16} In such cases an alternative method suggested by Moynihan et al.¹⁶ is normally adopted for the data analysis. According to this method the data analysis is done by keeping in view the empirical facts that the B_y term is almost composition independent and $T_{0\kappa}$ is nearly equal to $T_{0\phi}$. The values obtained for A_y , B_y , and T_{0y} by using the above alternative method for data analysis are listed in Table IV. Approximately constant values for B_ϕ and B_κ were chosen in the light of the B_y values reported earlier for Ca-

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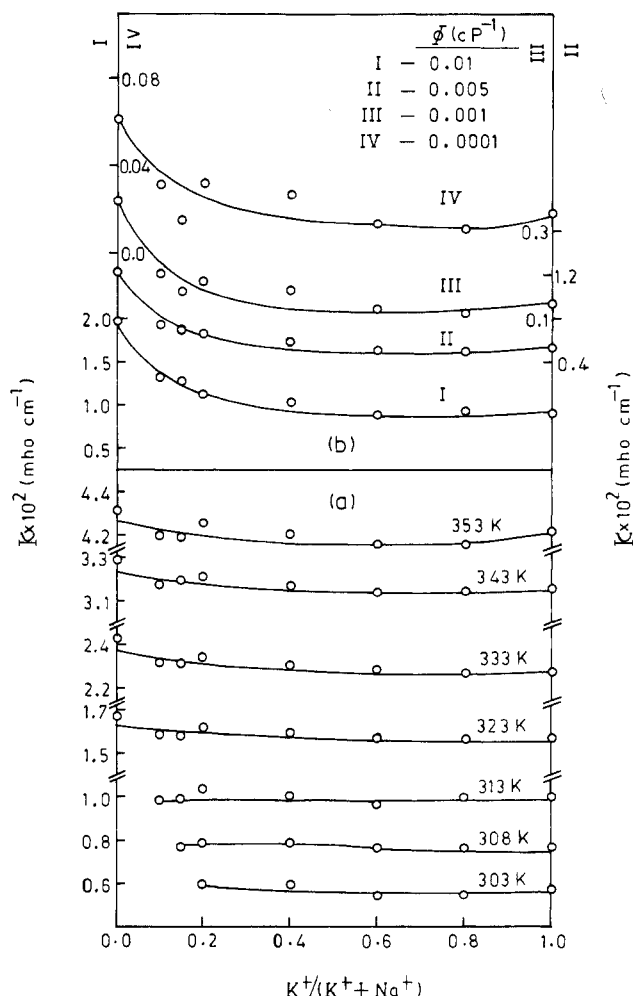


Figure 4. Plots of κ vs. x (a) under isothermal conditions (open circles and solid curves represent observed and calculated (from eq 2, Table VI) values, respectively) and (b) under isofluidity conditions for 0.3-[xKSCN-(1-x)NaSCN]-0.7Ca(NO₃)₂·4.06H₂O melts.

(NO₃)₂·3.99H₂O-KSCN melts.¹⁵ It may be noted from Tables III and IV that for some of the compositions the modified values of A_y , B_y , and T_{0y} are the same as their best-fit values. The new T_{0y} values (Table IV) increase linearly with the increase in Na⁺ ion fraction (Figure 3a) as was the case in $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ ¹⁰ and $0.2[x\text{NaNO}_3-(1-x)\text{KNO}_3]-0.8\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ ¹¹ systems also.

In order to examine the presence of the MAE in the present system under investigation we plotted $\ln \phi$ vs. concentration, $x = K^+ / (Na^+ + K^+)$, at different temperatures (Figure 3b). Deviation of ϕ from additivity is observed even at 80 °C (Figure 3b), which therefore indicates the presence of the MAE for fluidity in the 0.3[xKSCN-(1-x)NaSCN]-0.7Ca(NO₃)₂·4.06H₂O system. Similar deviations of ϕ from additivity were reported in other ternary systems^{10,14} also. From Figure 4a it is evident that the MAE also exists for electrical conductivity at such a high temperature as 80 °C. This is contrary to what was observed in 0.2[xNaNO₃-(1-x)KNO₃]-0.8Ca(NO₃)₂·4.09H₂O¹¹ and $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ ¹⁰ melts wherein such a MAE was not detected even up to a very low temperature. Moreover, in the present system under study, unlike the trend observed in other ternary molten systems containing water molecules, the conductivity at a particular temperature is found to decrease initially by the replacement of Na⁺ by K⁺ ion. Among the anhydrous mixed-alkali systems also there are reports^{9,17} of some systems which show under isothermal conditions such an initial

TABLE V: r_κ Values for 0.3[xKSCN-(1-x)NaSCN]-0.7Ca(NO₃)₂·4.06H₂O Melts under Isothermal Conditions

x	r_κ			
	353.0 K	343.0 K	333.0 K	323.0 K
0.1	1.022	1.031	1.045	1.046
0.15	1.026	1.023	1.041	1.044
0.2	1.009	1.014	1.025	1.017
0.4	1.016	1.019	1.028	1.016
0.6	1.022	1.019	1.023	1.017
0.8	1.018	1.010	1.013	1.004

decrease in κ by the addition of an alkali ion of larger size. It, therefore, appears that the anion framework of the mixed-alkali system also plays a significant role in determining the MAE.

Although plots of conductivity isotherms detect the MAE, sometimes they fail to do so. A somewhat more sensitive detector of the electrical MAE is the deviation from additivity of the κ isotherms represented by the ratio $r_\kappa = \kappa_{\text{add}} / \kappa_{\text{obsd}}$ as suggested by Moynihan.¹¹ For instance, in $x\text{NaNO}_3-(0.2-x)\text{TlNO}_3-0.8\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ melt¹¹ the plot of the conductivity isotherm at -5 °C was found to be linear whereas the estimation of the r_κ value for this melt revealed the presence of the MAE at that temperature. Therefore, we calculated the r_κ values at different temperatures for the system under study and these values are listed in Table V. However, r_κ values at lower temperatures (<50 °C) could not be estimated since conductivity measurements of the 0.3NaSCN-0.7Ca(NO₃)₂·4.06H₂O melt could not be made below 50 °C due to crystallization of this melt. In view of experimental uncertainties the r_κ values may be claimed to be accurate up to ± 0.005 . From Table V it is interesting to note that in terms of r_κ also the MAE exists for electrical conductivity at 80 °C and below. The MAE seems to be more in the concentration region from 0.0 to 0.2x and beyond 0.2x it is relatively less. Furthermore, the r_κ values do not appear to exhibit any regular trend in the dependence of electrical MAE on temperature except for the melt of composition 0.1x, in which case the MAE increases with decrease in temperature. This seems to envisage that the isothermal condition is not a satisfactory criterion for examining the presence of electrical MAE.

An attempt has been made to describe the observed nature of the concentration dependence of ϕ and κ (Figures 3b and 4a) by least-squares fitting the ϕ and κ data for the system under study to an isothermal equation of the form

$$Y(\phi, \kappa) = a_{0y} \exp(b_{0y}x + c_{0y}x^2) \quad (2)$$

where a_{0y} , b_{0y} , and c_{0y} are empirical constants. This equation may be derived from the VTF equation by inserting the empirically observed linear variation of T_{0y} with x (Figure 3a) and presuming that A_y and B_y are nearly concentration independent. However, it may be pointed out that there is evidence for nonlinear variation of the glass transition temperature with composition.^{12,14,18} In such cases eq 2 may be considered at the moment simply as an expression of empirical origin.

The least-squares-fitted values of the three parameters of eq 2 for fluidity and conductivity of the molten 0.3[xKSCN-(1-x)NaSCN]-0.7Ca(NO₃)₂·4.06H₂O system are given in Table VI. A reasonably good fit has been obtained, as apparent from Figures 3b and 4a also.

In order to establish further the success of eq 2 in representing the electrical conductivity data, we also made an attempt to least-squares fit the reported κ data for $x\text{K}_2\text{O}-(1-x)\text{Na}_2\text{O}-3\text{SiO}_2$ ^{11,17} mixtures, an exemplary system which exhibits pronounced MAE. It is interesting to note from Table VI as well as from Figure 5a that eq 2 satisfactorily fits the conductivity data for the above system in spite of the fact that its conductivity passes through a deep minimum. Equation 2 has been found to fit the reported fluidity and electrical conductivity data for the 0.45-

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TABLE VI: Least-Squares-Fitted Values of the Parameters of Eq 2 for Conductivity ($\text{mho}\cdot\text{cm}^{-1}$) and Fluidity (cP^{-1}) of Different Mixed-Alkali Systems^a

T, K	$\ln a_{0y}$	b_{0y}	c_{0y}	SD in $\ln Y$
0.3[xKSCN-(1-x)NaSCN]-0.7Ca(NO ₃) ₂ ·4.06H ₂ O				
303.0	-5.0609 (-5.5594)	-0.2543 (0.9327)	0.1500 (-0.5178)	0.011 (0.031)
308.0	-4.8628 (-5.1929)	0.0326 (0.8254)	-0.0537 (-0.4444)	0.017 (0.037)
313.0	-4.6087 (-5.0134)	-0.0236 (1.2666)	0.0206 (-0.7699)	0.022 (0.050)
323.0	-4.1164 (-4.4908)	-0.0883 (1.3941)	0.0486 (-0.8842)	0.014 (0.053)
333.0	-3.7356 (-4.1856)	-0.1356 (2.1044)	0.0897 (-1.4945)	0.012 (0.095)
343.0	-3.4278 (-3.6981)	-0.0936 (1.8090)	0.0653 (-1.3148)	0.008 (0.103)
353.0	-3.1521 (-3.3370)	-0.0903 (1.7112)	0.0755 (-1.2260)	0.007 (0.082)
xK ₂ O-(1-x)Na ₂ O-3SiO ₂				
323.0	-18.5341	-42.0013	39.7617	0.482
373.0	-15.4593	-34.3287	32.1873	0.435
423.0	-13.1845	-28.2858	26.3478	0.392
473.0	-11.3487	-24.0394	22.2172	0.346
523.0	-9.7431	-20.4513	18.5366	0.337
0.45[xLiNO ₃ -(1-x)KNO ₃]-0.55Ca(NO ₃) ₂ ·4.09H ₂ O ^b				
298.15	-5.2775 (-0.9644)	-0.7457 (0.7633)	0.3412 (-0.0071)	0.013 (0.002)

^a Parameters for fluidity are within the parentheses. ^b In this system fluidity is ($\text{Pa}\cdot\text{s}$)⁻¹.

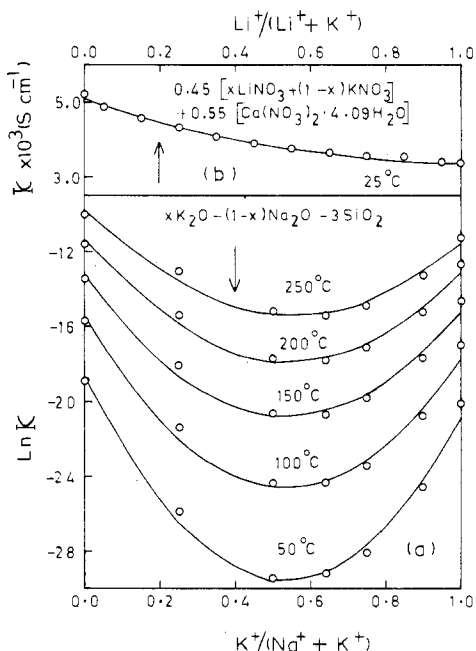


Figure 5. Plots of (a) $\ln \kappa$ vs. x for $x\text{K}_2\text{O}-(1-x)\text{Na}_2\text{O}-3\text{SiO}_2$ systems (ref 11) and (b) of κ vs. x for $0.45[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}(\text{NO}_3)_2\cdot 4.09\text{H}_2\text{O}$ melt (ref 14). Open circles and solid curves represent observed and calculated (from eq 2, Table VI) values, respectively.

$[x\text{LiNO}_3-(1-x)\text{KNO}_3]-0.55\text{Ca}(\text{NO}_3)_2\cdot 4.09\text{H}_2\text{O}$ ¹⁴ system also (Table VI and Figures 3c and 5b). In the absence of a satisfactory theoretical approach to account for the MAE, the success shown by the empirical isothermal eq 2 in representing the data on transport properties of mixed-alkali systems is worth registering.

Although the MAE is observed at constant temperatures in the present system under study, Moynihan's time-scale criterion¹¹ for detecting the MAE seems to be more rational. Moreover, the drawback in using the isothermal condition has been pointed out above. Moynihan¹¹ suggested that the MAE occurs in liquids or melts only when a solidlike conduction mechanism is operating and that the mobile cations can hop from one recognizable site to another before the anion framework has time to rearrange. According to this criterion the structure of the medium must be fixed for examining the presence of the MAE or, more precisely, the time scale for rearrangement of the local structure must be long compared to that required for the local diffusion of alkali cations (monovalent cations in general) from site to site. On the basis of this concept Ingram et al.¹⁰ estimated that the MAE might become detectable when $\kappa/\phi > 5$, κ in $\text{mho}\cdot\text{cm}^{-1}$ and ϕ in P^{-1} .

TABLE VII: r_κ Values for $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca}(\text{NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ Melts under Isofluidity Conditions

x	r_κ			
	0.01 cP^{-1}	0.005 cP^{-1}	0.001 cP^{-1}	0.0001 cP^{-1}
0.1	1.414	1.505	1.691	1.829
0.15	1.424	1.579	2.130	3.896
0.2	1.575	1.648	1.741	1.637
0.4	1.483	1.551	1.667	1.684
0.6	1.480	1.588	1.919	2.514
0.8	1.192	1.266	1.556	2.418

Therefore, for detecting the MAE an isofluidity condition is more appropriate than an isothermal condition. Accordingly, we plotted κ vs. x at constant fluidity values (Figure 4b). Conductivity values of the system under interest at constant fluidity values, both within and outside the experimental fluidity range, required for plotting were calculated from eq 1 using the best-fit values of the A_y , B_y , and T_{0y} parameters given in Table III. Estimation of the MAE in this fashion is, however, not exact owing to the uncertainties in the extrapolated values of κ , since it is known that extrapolation of κ data to lower temperatures using the VTF equation invariably leads to underestimates of κ . On the other hand, errors in the r_κ values (as they correspond to conductivity ratios) under isofluidity conditions are considerably smaller than those in the extrapolated κ values. This is because of the fact that the errors in the extrapolated values of κ for the different compositions of the melt under study should all be of the same sign. Therefore, almost the same maximum accuracy ($\sim \pm 0.005$) as that estimated above under isothermal conditions can be claimed for r_κ values under isofluidity conditions also. Consequently, we made an attempt to detect the MAE at constant fluidities by calculating the r_κ values (Table VII). From these r_κ values it is evident that the electrical MAE increases with decreasing fluidity of the melt. From Table VII and Figure 4b it may also be seen that the MAE exists even when the κ/ϕ ratio has a very low value much less than the value 5 suggested by Ingram et al.¹⁰ The present study therefore appears to reveal that it is not possible to have a universal time-scale criterion for detecting the MAE and the limit of the time scale may vary from system to system.

From Figure 4b it may further be noted that under isofluidity conditions the conductivity of the system decreases initially on replacing Na^+ by K^+ ion, which is similar to the observation made under isothermal conditions. Such a trend in the conductivity behavior under isofluidity conditions may be anticipated even after accounting for the uncertainties involved in the calculated κ values since, as mentioned above, the errors in the extrapolated values of κ for the present system at different compositions are of the same sign. In the $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ system¹⁰ also

a similar trend in the conductivity behavior under isofluidity conditions was noticed. Ingram et al.¹⁰ gave a mechanistic interpretation to such a conductivity behavior on the assumption that the paired cations form the mobile species in the $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ system. In the light of a similar structural interpretation it is also possible to explain the composition dependence of conductivity of the system under interest. In fact, such an attempt was made by Easteal¹⁴ to explain the MAE in $\text{Ca}(\text{NO}_3)_2 + (\text{Li},\text{K})\text{NO}_3$ hydrate melts. However, any similarity between the MAE in silicate melts and in hydrate melts of the present type is doubtful, since it is difficult to visualize a relatively rigid network structure (which exists in silicate, borate, germanate, and oxide melts and glasses) as existing in hydrate melts.

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Investigation on the Structure of Cadmium Nitrate Aqueous Solutions by X-ray Diffraction and Raman Spectroscopy

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X-ray scattering on a 4.54 M aqueous $\text{Cd}(\text{NO}_3)_2$ solution and the Raman spectra of five solutions from 1.04 to 4.54 M have been measured at 25 °C, together with the spectra of hydrated melt and solid. Both the spectral features and the X-ray pair-correlation function suggest the presence of anionic hydration shell and inner-sphere complex. Model interpretations of the X-ray data are discussed. As a result, two hydration shells around the cation and one composed of about nine water molecules around the anion are described. The presence of the complex of the mean formula $\text{Cd}(\text{H}_2\text{O})_5\text{ONO}_2^+$ is consistent with the X-ray data.

Introduction

The coordination of Cd^{2+} ions has been the subject of recent investigations in various aqueous solutions by X-ray diffraction. The presented structural models propose two possible coordination states for Cd^{2+} : either it is completely surrounded by six water molecules, as already found by Ohtaki et al.¹ in the $\text{Cd}(\text{ClO}_4)_2$ solution, or the anion enters into the first hydration shell of the cation. This was reported for the chloride, sulfate and phosphate solutions,²⁻⁵ where the anions act as monodentate ligands. For the completely hydrated Cd^{2+} ions, the existence of a second hydration shell was also described.³⁻⁵

As concerns the hydration of NO_3^- ion, the X-ray diffraction results show greater variety and are more uncertain than for the Cd^{2+} . In fact, sometimes the simple detection of the presence of the hydrating water molecules is difficult, while to assign to them an average geometry is almost hopeless. Here uncertainties arising from the physical nature of nitrate-water interactions concur with the difficulties in interpretation, as pointed out elsewhere.⁶

Although the NO_3^- ion has a tendency to create ion pairs with cations, no X-ray diffraction work examined this question up to now for the $\text{Cd}(\text{NO}_3)_2$ solutions. Only a dilute aqueous solution

(1 M) was studied by Bol et al.,⁷ and the $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ complex was found as the only species present. Evidence for complexation in aqueous solutions of cadmium nitrate was found in more recent conductivity, calorimetry, emf, and polarography measurements. These studies indicate the presence of a mononitratocadmium species. A dinitratocadmium species has also been proposed, but no higher complexes.⁸

Infrared and Raman spectroscopies have been extensively used in the studies of anion-solvent and cation-anion interactions in solutions containing NO_3^- ions.⁹⁻¹³ In fact, the vibrational spectrum of the unperturbed nitrate ion may be altered either by interaction with the solvent or by association. Then, in principle, it is possible to get information on the condition of nitrate ions in aqueous solutions through spectroscopic investigations.

The results show that the transition of the NO_3^- ion from an aqueous environment to the state of an ion in competition with water molecules for sites in the first coordination sphere of the cation should take place gradually, through states where the hydrated cations perturb the hydration sphere of NO_3^- ions.

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