Mixed alkali effect in sodium thiosulfate pentahydrate melt

SHAKIRA S. ISLAM AND KOCHI ISMAIL[1]

Department of Chemistry, North-Eastern Hill University, Bijni Campus, Laitumkhrah, Shillong – 793003, India

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Density and electrical conductance measurements of $0.35[X\mathrm{NaNO_3} + (1 - X)\mathrm{KNO_3}] + 0.65\mathrm{Na_2S_2O_3.5H_2O}$ melt were made as functions of temperature and X. Molar volume, V, is found to be additive. The percent deviation of V_{ext} (extrapolated V of the pure solute from the plot of V vs. total added alkali ion fraction) from V_{cal} (calculated V of the pure solute from its high temperature density data) increases monotonically as the amount of $NaNO_3$ in the hydrate melt increases, thereby manifesting a "structure-forming" tendency of $NaNO_3$. The non-Arrhenius temperature dependence of molar conductance, Λ is analyzed in terms of the Vogel–Tammann–Fulcher (VTF) equation. Mixed alkali effect (MAE) has been observed on Λ and T_0 (ideal glass transition temperature). A competitive polarization model has been used to explain the MAE on Λ.

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On a effectué des mesures de densité et de conductivité électrique sur des mélanges fondus de $0{,}35[X\mathrm{NaNO_3} + (1 - X)\mathrm{KNO_3}] + 0{,}65\mathrm{Na_2S_2O_3.5H_2O}$, en fonction de la température et de la valeur de X. On a trouvé que le volume molaire, V, est une propriété additive. Le pourcentage de déviation de la valeur V_{ext} (la valeur de V du soluté pur extrapolée à l'aide du courbe de V en fonction de la fraction totale des ions alcalins ajoutés) par rapport à la valeur V_{cal} (la valeur V calculée du soluté pur obtenue à partir de ses données de densité à haute température) augmente d'une façon monotone avec l'augmentation de la quantité de $NaNO_3$ dans la phase hydratée fondue; ces résultats suggèrent que le $NaNO_3$ a tendance à former des structures. La relation entre conductivité molaire, Λ, et la température ne suit pas la loi d'Arrhénius; on analyse ce fait en fonction de l'équation de Vogel–Tamman–Fulcher (VTF). On a observé l'effet des sels alcalins mixtes (EAM) sur Λ et sur T_0 (température de transition vitreuse idéale). On a utilisé un modèle de polarisation compétitive pour expliquer l'EAM sur Λ.

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Introduction

The mixed alkali effect (MAE) is an established phenomenon which has long been known to occur in a glassy or molten medium (1–6). It 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. Normally the MAE is most pronounced for properties related to ionic transport. 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 MAE mainly because of the following reasons. Firstly, it has a direct relevance to glass industry (5, 7). 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 (2–4, 8–11). Thirdly, curiosity has recently arisen among workers to look for MAE in media other than glass or melt of rigid network structure. One such convenient medium for testing the existence of MAE is hydrate melt. A few reports (11–14) have been made on the study of MAE in hydrate melts. In all these studies made up till now only calcium nitrate tetrahydrate has been used as the medium.

Recently we have reported (15) the feasibility of using $Na_2S_2O_3.5H_2O$ melt as a molten solvent for physicochemical studies. This melt has been found to dissolve about 60 mol% of KNO_3. Therefore in the present study we have made an attempt to look for MAE in molten sodium thiosulfate pentahydrate medium by measuring the density and electrical conductance of $0.35[X\mathrm{NaNO_3} + (1 - X)\mathrm{KNO_3}] + 0.65\mathrm{Na_2S_2O_3.5H_2O}$ system.

Experimental section

The solutes, $NaNO_3$ and KNO_3 (BDH, LR grade), were recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator for several days before use. Sodium thiosulfate pentahydrate (SMerck, GR grade) was used as molten solvent without further purification. The actual H_2O/Na^+ mole ratio in the sodium thiosulfate pentahydrate sample used was determined to be 5 ± 0.01 (0.2% error on the molality scale) from iodometric titration.

Although sodium thiosulfate pentahydrate melt dissolves ~60% mol% of KNO_3, it dissolves only ~35 mol% of $NaNO_3$. Therefore the total solute alkali ion concentration in the samples was kept constant at 0.35 mole fraction. The crystallization temperature of the melt increased with increase in the amount of $NaNO_3$.

Methods of density and conductance (at 1 kHz) measurements are the same as described earlier (14, 16). For the conductivity measurement the samples were taken in a closed Corning glass container attached with the conductivity cell to prevent water loss. The temperature control of the thermostat was improved ($< \pm 0.02$°C) by connecting an additional voltage divider to the heating element of the NBE Type Ultra Thermostat.

Results and discussion

Volumetric property

Measured density of the system under study is a linear function of temperature and is presented in Table 1. Composition dependence of molar volumes of systems containing hydrate melts is rather more interesting. Previous studies (15–18) on the composition dependence of molar volumes of binary systems containing anhydrous solute and hydrate melt have led to treat these systems as a mixture of hydrate melt and hypothetical supercooled solute. This general feature of such binary melts is, however, expected only in systems containing anhydrous solutes whose cations do not get hydrated by the water molecules of the hydrate melt. The water–anion interaction is normally not taken into consideration.

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[1] To whom correspondence should be addressed.

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TABLE 1. Parameters for the density equation, $\rho = a - bt(°C)$ for $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ melt

X	$a/(\text{g cm}^{-3})$	$b \times 10^4/$ $(\text{g cm}^{-3}\text{deg}^{-1})$	rms dev., $\sigma \times 10^4$
0.0	1.7509	7.4642	4.05
0.2	1.7529	7.6771	3.41
0.4	1.7517	7.3176	3.69
0.6	1.7519	7.4392	2.04
0.8	1.7554	7.9281	3.39
1.0	1.7499	7.1504	3.21

$\rho(\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}) = 1.6958 - 7.7097 \times 10^{-4}t$ $(\sigma \times 10^4 = 2.58)$

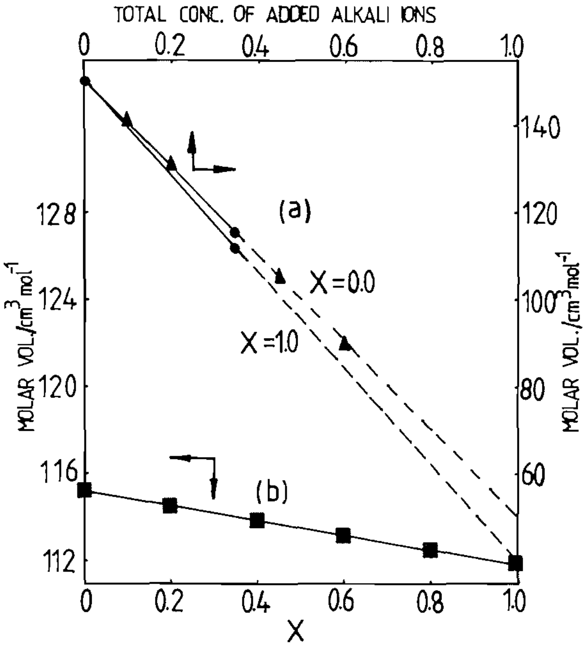

FIG. 1. Plots of molar volume of $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ melt as functions of (*a*) total concentration of added alkali ion and (*b*) X. (▲: data from ref. 15).

In the present system of interest there is an opportunity to examine the above aspect for the two types of solutes, viz., one having cation which competes and the other having cation which does not compete for the water of hydration of the solvent molecule. Although we have here only two concentration points (0 and 0.35 mole fraction of solute) to draw the molar volume vs. mole fraction isotherms, an attempt to draw such isotherms and then to extrapolate them to the pure solute concentration is justifiable in view of the fact that the linearity of this type of isotherms is already established for $\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O} + \text{KNO}_3$ system (15). Two such exemplary plots at 60°C are illustrated in Fig. 1. It may be noted that in those systems containing both NaNO_3 and KNO_3 the mixture of these two with the respective proportion is considered to be the solute of 0.35 mole fraction. The molar volumes, V_{ext}, of the pure solutes at 60°C obtained by extrapolating the plots of the type shown in Fig. 1 are listed in Table 2 along with the corresponding values of the molar volume, V_{cal}, evaluated from the high temperature density data (19) of these molten solutes. The interesting point to note from Table 2 is the % deviation of V_{ext} from V_{cal}. This deviation is minimum (0.87%) for the case of pure KNO_3 which is in accordance with our earlier result (15). The % deviation monotonically increases as the solute contains more and more amounts of NaNO_3 and is maximum (4.45%) for the case of pure NaNO_3. Similar trend in the % deviation was observed at other ambient temperature also. Since the experimental uncertainties involved are the same at all compositions, such a monotonic increase in the % deviation of V_{ext} from V_{cal} with increase in the amount of NaNO_3 is not attributable to experimental errors. Another possible source of error is the uncertainty in the high temperature density data from which V_{cal} is evaluated. We found that the monotonic increase in the % deviation exists even after accounting for the uncertainty (0.5%) in the high temperature density data (19).

Since the K^+ ion has a smaller ionic potential than the Na^+ ion, it does not compete with the Na^+ ion of the solvent for the water of hydration. Therefore KNO_3 appears to behave like an inert solute in molten sodium thiosulfate pentahydrate. On the other hand, as K^+ ions are replaced by Na^+ ions, these added Na^+ ions also compete with the solvent Na^+ ion for the water of hydration. This "structure-forming" tendency of the Na^+ ion added to molten sodium thiosulfate pentahydrate appears to cause a decrease in the volume of the system and may thereby account for the increase in the % deviation of V_{ext} from V_{cal} with increase in the amount of NaNO_3. In Fig. 1 we have also plotted the molar volume (at 60°C) of the system of interest against X. This plot is linear as is the case with other similar systems (13, 14). The linearity of this particular plot reveals that the above referred "structure-forming" tendency of the added Na^+ ion does not seem to cause an observable amount of non-ideality in the molar volume of the system.

Conductance property

The measured values of Λ in the temperature range 20–90°C are represented in Fig. 2 in the form of Arrhenius plots. From Fig. 2 it is apparent that the temperature dependence of Λ is non-Arrhenius which is normally the case with systems containing hydrate melts. The molar conductances are therefore least-squares fitted using an iterative least-squares method to the VTF equation of the form

$$[1] \quad \ln \Lambda = A - B/(T - T_0)$$

A, B, and T_0 are temperature independent parameters. The best-fit values of A, B, and T_0 obtained thus are listed in Table 3. It is interesting to note the variation in T_0 with the concentration of one of the added alkali ions. The plot (Fig. 3) of T_0 vs. X passes through a minimum around $X = 0.5$. Such a behaviour of T_0 with X may be attributed to the MAE. Although similar trends in the variation of experimental glass transition temperature, T_g with the ion fraction of either of the alkali ions were reported for mixed alkali systems in hydrate (12, 13) as well as anhydrous melts (2, 20), to date no report of T_0 of mixed alkali system varying in this fashion with composition has been made. However, it may be pointed out that since in the temperature ranges of this study the conductance varies by only factors of 3 to 6 the computed values of the T_0 parameter may not be very precise. As a consequence the minimum in the T_0 vs. X plot in Fig. 3 could be illusory. Therefore, in order to assess the uncertainties in T_0 we also analyzed the conductance data using the procedure adopted by Moynihan (21). The best-fit values (corresponding to minimum average |% dev.| in Λ) of A, B, and T_0 thus obtained are found to be in agreement with the values given in Table 3. In the light of the percent deviations of

TABLE 2. Molar volumes of $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ melts (V) and of pure solutes (V_{ext} and V_{cal}) at 60°C

X	Solute	$V/(\text{cm}^3\ \text{mol}^{-1})$	$V_{\text{ext}}/(\text{cm}^3\ \text{mol}^{-1})$	$V_{\text{cal}}/(\text{cm}^3\ \text{mol}^{-1})$	% dev. between V_{ext} and V_{cal}
0.0	KNO_3	115.30	49.98	50.42	0.87
0.2	$0.8KNO_3 + 0.2NaNO_3$	114.59	47.96	48.78	1.68
0.4	$0.6KNO_3 + 0.4NaNO_3$	113.87	45.90	47.15	2.65
0.6	$0.4KNO_3 + 0.6NaNO_3$	113.24	44.10	45.51	3.10
0.8	$0.2KNO_3 + 0.8NaNO_3$	112.54	42.13	43.88	3.99
1.0	$NaNO_3$	111.94	40.38	42.26	4.45
$V(\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}) = 150.47$					

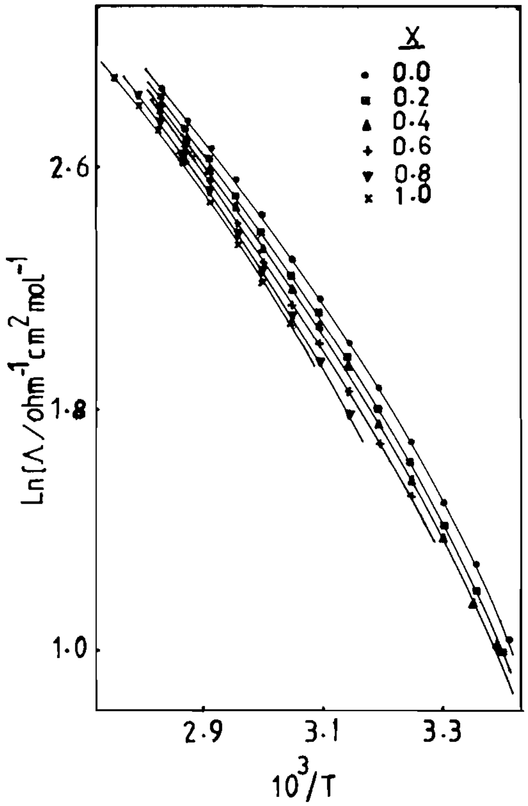

FIG. 2. Plots of $\ln \Lambda$ of $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ melt against $1/T$ for different X.

experimental values of the conductance from the least-squares curve for various values of T_0, the uncertainties involved in T_0 are estimated and are included in Table 3. For the T_0 values lying within the uncertainty range the least-squares fit of the conductance data is found to be very close to the best-fit. Since the uncertainties involved in the T_0 values are almost the same (6–8 K) for all the compositions, the nature of the T_0 vs. X plot (Fig. 3) does not seem to be very much affected.

The composition dependence of Λ is illustrated in Fig. 3. There is a negative deviation of Λ from additivity at temperatures below ~338 K. At temperatures higher than this Λ appears to approach additive behaviour. Increase in the amount of non-ideality of conductance with decreasing temperature is a general phenomenon observed in mixed alkali systems. The negative deviation of Λ from ideal behaviour therefore reveals the presence of MAE in the present system of study. The above referred "structure-forming" tendency of the Na^+ ion added to molten $Na_2S_2O_3.5H_2O$ may also be causing, superimposed on MAE, non-ideality of Λ of the present system.

TABLE 3. Best-fit parameters of eq. [1] for molar conductance of $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ melt

X	A	B	T_0/K	rms dev. in $\ln \Lambda$
0.0	5.6711∓0.2	427.48∓40	200.66∓6	0.0072
0.2	5.7729∓0.2	449.61∓45	200.00∓6	0.0086
0.4	6.1167∓0.2	545.37∓50	188.15∓6	0.0126
0.6	6.1504∓0.2	554.93∓60	188.68∓8	0.0112
0.8	6.1374±0.2	535.09∓60	195.14∓8	0.0107
1.0	5.7233∓0.2	434.81∓55	208.33∓8	0.0156

However, since the solvent used in this study contains also alkali ion, it is worthwhile to make a comment on the presence of MAE. It may be noted that in $0.35[X\text{NaNO}_3 + (1 - X)\text{KNO}_3] + 0.65\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ system although X varies from 0 to 1, the mole fraction, $K^+/(Na^+ + K^+)$ varies from 0 to 0.21 only unlike the case with other similar systems studied (11–14) containing solvent free from alkali ion. Consequently, for systems of the present type a complete estimation of MAE may not be possible. On the other hand, it is interesting to note that the maximum negative deviation of conductance from additivity observed in this study and that reported (14) in $0.3[X\text{KSCN} + (1 - X)\text{NaSCN}] + 0.7\text{Ca(NO}_3)_2.4.06\text{H}_2\text{O}$ are of the same order (~4% at 328 K). Therefore, in this work the presence of alkali ion in the solvent does not seem to affect the MAE significantly. A probable explanation to this may be that the hydration sheath around the Na^+ ions of the solvent makes the interaction with the K^+ ion very weak, thereby causing negligible MAE. This view is further supported by the above mentioned fact that the added K^+ ion does not compete for the water of hydration of the solvent. About 11% negative deviation from ideality is however reported (13) in $0.45[X\text{LiNO}_3 + (1 - X)\text{KNO}_3] + 0.55\text{Ca(NO}_3)_2.4.09\text{H}_2\text{O}$ at 298 K which is attributable to the higher alkali ion concentration, the lower temperature, and to the larger difference in the radii of the two alkali ions. The small amount of MAE generally observed in hydrate melts is attributed to the absence of rigid type structure in these melts.

Numerous explanations have been proposed for the MAE on electrical conductivity. The structural/mechanistic theories appear to be more successful in systems of rigid network structure which exhibit normally large MAE. On the other hand,

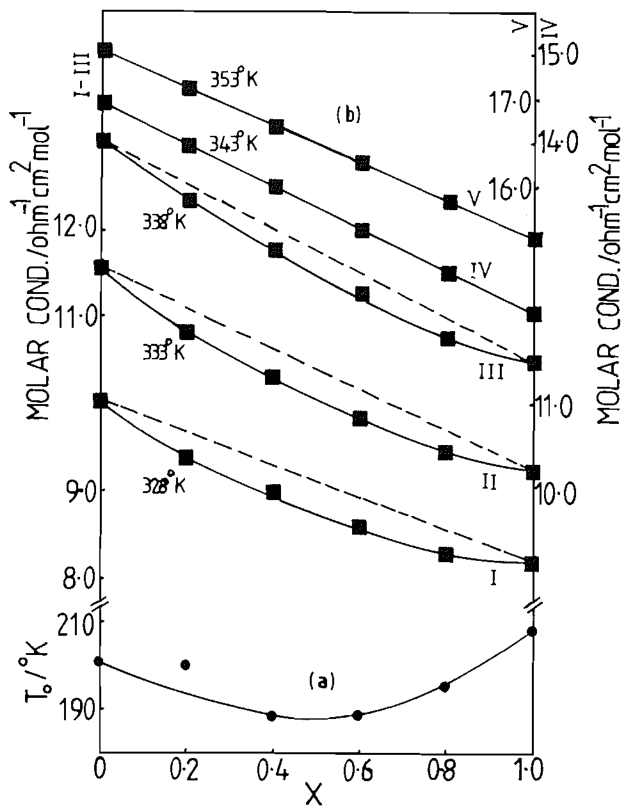

FIG. 3. Variation of (*a*) T_0 and (*b*) Λ of $0.35[X\mathrm{NaNO_3} + (1 - X)\mathrm{KNO_3}] + 0.65\mathrm{Na_2S_2O_3.5H_2O}$ melt with X.

in mixed alkali systems containing hydrate melts which do not show large MAE as seen above, the cationic interaction theories seem to be more appropriate.

Moynihan and Laity (22, 23) explained the negative deviations of conductance from additivity observed in molten binary systems like LiCl + KCl, $\mathrm{LiNO_3} + \mathrm{KNO_3}$, etc. in terms of an anion polarization model. Such a polarization model applicable to binary melts may also be employed to explain the MAE observed in the present system of interest. The following two factors seem to provide support to this view. (1) The $\mathrm{NaNO_3} + \mathrm{KNO_3}$ mixture behaves nearly like a hypothetical supercooled mixture in molten $\mathrm{Na_2S_2O_3.5H_2O}$ as mentioned above which is, of course, more true when the interactions between the added alkali ions and the water molecule of the hydrate melt are negligible. (2) Negative deviations of Λ from additivity are observed in the cases of both binary $\mathrm{NaNO_3} + \mathrm{KNO_3}$ melt (19) and the present system. Easteal (13) also made a similar attempt to compare the electrical conductance behaviour of $0.45[X\mathrm{LiNO_3} + (1 - X)\mathrm{KNO_3}] + 0.55\mathrm{Ca(NO_3)_2.4.09H_2O}$ with that of molten $(\mathrm{Na} + \mathrm{Tl})\mathrm{NO_3}$ system and then to use the anion polarization model to explain the MAE observed in the former molten system.

According to the anion polarization model the $\mathrm{NO_3^-}$ ion is considered to experience an average symmetrical field when the hydrate melt medium contains either $\mathrm{NaNO_3}$ or $\mathrm{KNO_3}$. When $\mathrm{Na^+}$ ions are partially replaced by $\mathrm{K^+}$ ions, some of the $\mathrm{NO_3^-}$ ions find themselves between electric fields of differing intensities. Due to this a competitive polarization of the anion occurs and the $\mathrm{NO_3^-}$ ion gets more polarized towards the smaller ion, i.e., $\mathrm{Na^+}$. Consequently, in a hydrate melt medium addition of $\mathrm{KNO_3}$ to $\mathrm{NaNO_3}$ results in a decrease of the internal mobility of the $\mathrm{Na^+}$ ion whereas addition of $\mathrm{NaNO_3}$ to $\mathrm{KNO_3}$ increases the internal mobility of $\mathrm{K^+}$ ion. Presuming that the degrees of ionization of $\mathrm{NaNO_3}$ and $\mathrm{KNO_3}$ in the hydrate melt are equal and do not change with X we may write, $\Lambda = F[X|u_{\mathrm{Na^+}}| + (1 - X)|u_{\mathrm{K^+}}|]$, where F is the Faraday constant and the u terms refer to the internal mobilities of cations with respect to the $\mathrm{NO_3^-}$ ion. Therefore, the observed negative deviation of Λ from additivity implies that in the hydrate melt when both $\mathrm{NaNO_3}$ and $\mathrm{KNO_3}$ are present the decrease caused in $|u_{\mathrm{Na^+}}|$ is always greater than the increase in $|u_{\mathrm{K^+}}|$. Considering linear composition dependences of cationic internal mobilities it is possible to write the excess molar conductance as $\Delta\Lambda = KX(1 - X)$, where $\Delta\Lambda = \Lambda - \Lambda_{\mathrm{id}}$ and K is a constant. A similar equation for $\Delta\Lambda$ was reported by Timmermann (24). In the present case it has, however, been found that the plot of $\Delta\Lambda$ vs. X is not exactly a symmetric parabola in X thereby indicating that in the system under study the cationic mobilities vary non-linearly with composition as is the case with binary mixtures of molten nitrates (22).

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1. R. M. HAKIM and D. R. UHLMANN. Phys. Chem. Glasses, **8**, 174 (1967).
2. J. O. ISARD. J. Non-Cryst. Solids, **1**, 235 (1969).
3. R. TERAI. J. Non-Cryst. Solids, **6**, 121 (1971).
4. D. E. DAY. J. Non-Cryst. Solids, **21**, 343 (1976).
5. J. E. SHELBY. J. Appl. Phys. **46**, 193 (1975).
6. A. A. AHMED and A. F. ABBAS. J. Non-Cryst. Solids, **80**, 371 (1986).
7. S. YUZHEN, S. YOUAN, and H. BAOYE. J. Non-Cryst. Solids, **80**, 335 (1986).
8. W. M. RISEN, JR., G. B. ROUSE, and J. M. GORDON. *In* Non-crystalline solids. *Edited by* G. H. Frischat. Trans. Tech. Publ., Switzerland. 1977. p. 473.
9. M. D. INGRAM, C. T. MOYNIHAN, and A. V. LESIKAR. J. Non-Cryst. Solids, **38/39**, 371 (1980).
10. C. T. MOYNIHAN and A. V. LESIKAR. J. Am. Ceram. Soc. **64**, 40 (1981).
11. C. T. MOYNIHAN. J. Electrochem. Soc. **126**, 2144 (1979).
12. A. J. EASTEAL and M. C. EMSON. J. Phys. Chem. **84**, 3330 (1980).
13. A. J. EASTEAL. Aust. J. Chem. **34**, 1853 (1981).
14. P. SANGMA, S. MAHIUDDIN, and K. ISMAIL. J. Phys. Chem. **88**, 2378 (1984).
15. C. BHATTACHARJEE, S. ISMAIL, and K. ISMAIL. J. Chem. Eng. Data, **31**, 117 (1986).
16. N. ISLAM and K. ISMAIL. J. Phys. Chem. **79**, 2180 (1975).
17. J. BRAUNSTEIN, L. ORR, and W. MACDONALD. J. Chem. Eng. Data, **12**, 415 (1967).
18. S. MAHIUDDIN and K. ISMAIL. Bull. Chem. Soc. Jpn. **54**, 2525 (1981).
19. G. J. JANZ, U. KREBS, H. F. SIEGENTHALER, and R. P. T. TOMKINS. J. Phys. Chem. Ref. Data, **1**, 581 (1972).
20. C. T. MOYNIHAN, A. J. EASTEAL, D. C. TRAN, J. A. WILDER, and E. P. DONOVAN. J. Am. Ceram. Soc. **59**, 137 (1976).
21. C. T. MOYNIHAN. J. Phys. Chem. **70**, 3399 (1966).
22. C. T. MOYNIHAN and R. W. LAITY. J. Phys. Chem. **68**, 3312 (1964).
23. C. T. MOYNIHAN. *In* Ionic interactions. Vol. 1. *Edited by* S. Petrucci. Academic Press, New York. 1971. p. 261.
24. E. O. TIMMERMANN. Ber. Bunsenges. Phys. Chem. **83**, 263 (1979).