

Mixed alkali effect in $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems

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Density, electrical conductivity, and fluidity of $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems were measured as functions of temperature (363.15 to 428.15 K) and composition (0.0 to 1.0 mole fraction). Densities were linear functions of temperature. The temperature dependence of conductivity and fluidity has been analysed by using the Vogel–Tammann–Fulcher (VTF) equation. Deviation from additivity has been observed in the electrical conductivity, fluidity isotherms to a lesser extent, and in electrical conductivity under isofluidity condition. The onset of the mixed alkali effect (MAE) in the present system has been explained by the anion polarization model.

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On a mesuré les densités, les conductivités électriques et les fluidités des systèmes contenant $0,2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0,8\text{glycérol}$ en fonction de la température (de 363,15 à 428,15 K) et des fractions molaires (de 0,0 à 1,0). Les densités varient d'une façon linéaire avec la température. On a analysé la relation entre la température et les conductivités et les fluidités en faisant appel à l'équation de Vogel–Tammann–Fulcher (VTF). On a observé une déviation de l'additivité avec la conductivité électrique et, à un degré moindre, avec les isothermes de fluidité ainsi qu'avec la conductivité dans les conditions d'isofluidité. On explique le début de l'effet des métaux alcalins mixtes observé dans ce système en faisant appel au modèle de polarisation de l'anion.

[Traduit par la rédaction]

Introduction

When one alkali ion is replaced by another in an oxide glass and ionic melt several properties (preferably dynamic) vary as a function of composition in a highly non-additive fashion, a phenomenon usually referred to as mixed alkali effect (MAE). This phenomenon has been well documented by several authors (1–12) and is more pronounced in ionic and mass transport properties (2).

To date very few studies on the MAE using hydrate melt (6–12) as solvent have been made. Moynihan (6), in his studies using $x\text{NaNO}_3 + (0.2 - x)\text{KNO}_3 + 0.8\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ system failed to observe MAE in conductivity in the temperature range -5 to 70°C . But Ingram et al. (13) observed deviation in viscosity and conductivity while studying $x\text{K}_2\text{SiO}_3 + (1 - x)\text{Na}_2\text{SiO}_3 + 7\text{H}_2\text{O}$ systems in the temperature range -70 to 20°C . The observed shallow minima in conductivity and viscosity isotherms was considered an evidence for the onset of MAE. In earlier systems (9–12) containing hydrate melt as medium the MAE in fluidity and/or viscosity has been detected but to a lesser extent (ca. 4%). In all these systems MAE was found to depend on the temperature range of the study and the total alkali metal ion concentration. Moynihan (6) suggested that MAE may only be observed in systems with high viscosity and conductivity. On the other hand, based on their studies Eastal and Emson (7) suggested that MAE becomes significant when the total alkali metal ion concentration in the system is high.

Therefore, in this study we have made an attempt to find MAE by measuring the density, viscosity, and electrical conductivity of $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems due to the fact that glycerol is having inherent glass-forming tendency and high viscosity.

Experimental section

Both KNO_3 and NaNO_3 (BDH, LR grade) were recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator. Glycerol (EM, reagent grade) was used as solvent. Maximum water content in glycerol was found to be $<1\%$ when the observed density value was compared with the reported value (14) at 20°C .

KNO_3 was found to be soluble up to 20 mol% at about 100°C and the composition of the system in this study was chosen to be $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$. Accordingly six samples were prepared, keeping the total alkali ion concentration at 0.2 mole fraction. The densities of the systems were measured accurate to 0.01% by using a precalibrated single stem pycnometer. A suspended level Cannon–Ubbelohde viscometer of viscometer constant $1.243 \times 10^{-6} \text{ m}^2 \text{ s}^{-2}$ was used to measure the viscosity. Conductivity measurements (at 1 kHz) of all solutions were made by using a Philips PR9500 conductivity bridge and a dip-type cell of cell constant 198 m^{-1} . Viscosity and conductivity data were found to be reproducible to within $\pm 1\%$. Density, viscosity, and electrical conductivity were measured as functions of temperature (363.15 to 428.15 K) and composition, $x = 0.0$ to 1.0 mole fraction. All measurements were made in a thermostated oil bath (Ultra Thermostat type NBE) that maintained the temperature to $\pm 0.02 \text{ K}$.

Measured density data (ρ) of $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems are found to be linear functions of temperature and are presented in Table 1. Composition dependence of density isotherms at four temperatures are illustrated in Fig. 1. Density data were least-squares fitted to the polynomial equation in composition up to second degree and the maximum% deviation of ρ_{obs} from ρ_{cal} was found to be 0.56%. The interesting point to note from Fig. 1 is the deviation from additivity ($\approx 0.8\%$) at lower temperature (298.15 K) in the ρ vs. x plot (Fig. 1) and decreases at higher temperature and the density isotherm becomes linear at 398.15 K. Similar positive deviation from additivity ($\approx 0.7\%$) in density isotherm was found in the $(1 - x)\text{K}_2\text{O} + x\text{Li}_2\text{O} + 2\text{SiO}_2$ glass systems (2) at 293.15 K.

Results and discussion

The measured values of conductivity (κ) and fluidity ($\phi = 1/\eta$) of the systems under study are presented in Table 2 and Fig. 2 in the form of an Arrhenius plot. From Fig. 2 it is apparent that both κ and ϕ show a slight non-Arrhenius temperature dependence. Such a temperature dependence of transport properties (κ , ϕ) is an inherent nature of the concentrated electrolyte and

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TABLE 1. Least-squares fitted values of the density equation, $\rho = a - b(T - 273.15)$ for $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems

x	$a/10^3$ kg m^{-3}	$b/\text{kg m}^{-3}$ K^{-1}	Std. dev. in ρ
0.0	1.3750	0.6251	0.0006
0.2	1.3967	0.7688	0.0001
0.4	1.3834	0.6301	0.0001
0.6	1.3973	0.7221	0.0002
0.8	1.3865	0.6425	0.0001
1.0	1.3845	0.5520	0.0002

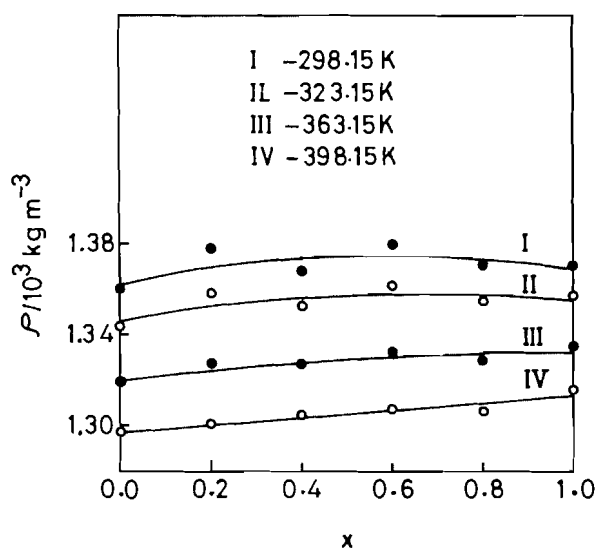


FIG. 1. Variation of density versus composition for $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems under isothermal condition (open and closed circles represent observed values and solid curves represent values calculated (from polynomial equation up to second degree), respectively).

ionic melt systems. The conductivity and fluidity values were, therefore, least-squares fitted to the Vogel–Tammann–Fulcher (VTF) equation of the form considering the insignificant contribution of the preexponential temperature term

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

where Y refers to either conductivity or fluidity, A_y and B_y are the adjustable parameters, and T_0 is the ideal glass transition temperature. The least-squares fitted values of A_y , B_y , and T_{0y} are presented in Table 3.

A relatively high T_{0y} value has been obtained for the present system. Similarly a high value for T_0 was observed by Sangma et al. (9) and Ingram et al. (13) while investigating MAE in ternary systems. On the other hand, similar high value for T_0 was also found for binary hydrate melts (15–17).

The presence of MAE in our system has been examined by plotting T_{0y} , A_y , and B_y versus x , $x = \text{K}^+ / (\text{K}^+ + \text{Na}^+)$ in Fig. 3. From Fig. 3 it is evident that the T_0 values for both κ and ϕ vary non-linearly. Such a positive deviation from additivity in T_0 vs. x (Fig. 3) may be attributed to the onset of MAE in the present system.

Although non-linear variations (generally negative deviation) in experimental glass transition temperature, T_g , and in ideal glass transition temperature, T_0 , with alkali ion concentration were reported for mixed alkali systems containing hydrate

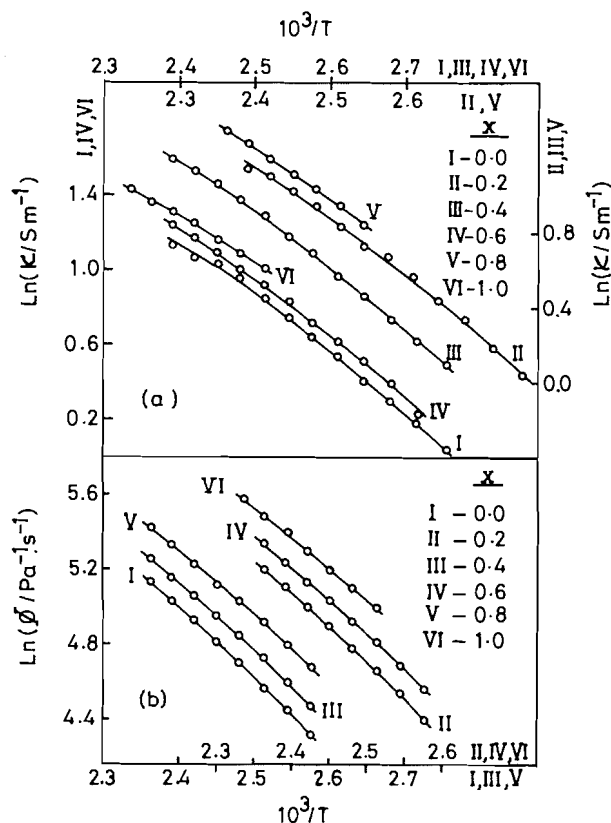


FIG. 2. Arrhenius plots for (a) conductivity and (b) fluidity of $0.2[x\text{KNO}_3 + (1 - x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems.

(6, 7, 10, 12) and anhydrous (18, 19) melts, to date no report on positive deviation in T_0 with composition in mixed alkali system has been made. On the other hand, T_0 was also reported to vary linearly with alkali ion fraction in $0.2[x\text{NaNO}_3 + (1 - x)\text{KNO}_3] + 0.8\text{Ca}(\text{NO}_3)_2 \cdot 4.09\text{H}_2\text{O}$ (6), $0.3[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.7\text{Ca}(\text{NO}_3)_2 \cdot 4.06\text{H}_2\text{O}$ (9), and in $x\text{K}_2\text{SiO}_3 + (1 - x)\text{Na}_2\text{SiO}_3 + 7\text{H}_2\text{O}$ (13) systems. In general, an irregular trend in T_0 vs. composition are reported for binary (15, 16) as well as ternary (9, 10) melts containing hydrated salts and in all such cases an alternative method suggested by Moynihan et al. (16) was normally adopted for data analysis. In our system, as a consequence, the positive deviation in the T_0 vs. x plot in Fig. 3 could be illusory. One of the reasons may be pointed out that in the temperature ranges of the study the conductivity and fluidity data in the present system vary by factors of 1.5 to 3 and the computed values of T_0 parameter may not be precise.

The composition dependence of A_y and B_y parameters are illustrated in Fig. 3. From Fig. 3 it is apparent that both A_y and B_y parameters vary non-linearly with negative deviation. Similar negative deviation in A_y vs. x plot was found in $0.3[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3 \cdot 5.1\text{H}_2\text{O}$ system (11). However, we observed that the variations of the VTF parameters (A_y , B_y , and T_{0y}) with composition (9–11) are interrelated.

In mixed alkali metal ion systems in hydrate melt medium an interdependence between the three VTF parameters was recently observed (12), as represented by empirical relationships of the type

$$[2] \quad \ln A_y = A_{1y} + A_{2y} [B_y / T_{0y}]$$

$$[3] \quad 1/B_y = B_{1y} + B_{2y} T_{0y}$$

TABLE 2. Electrical conductivity and fluidity^a data for 0.2[xKNO₃ + (1 - x)NaNO₃] + 0.8glycerol systems

T/K	$\kappa/S\ m^{-1}$ and $\phi/Pa^{-1}\ s^{-1}$					
	x = 0.0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1.0
363.15	1.02	1.05	1.10			
368.15	1.20	1.21	1.25	1.25		
373.15	1.36	1.40	1.40	1.48		
378.15	1.51	1.55	1.59	1.68		
383.15	1.72	1.76	1.78	1.86		
388.15	1.91	1.95	2.00	2.05		
	(75.1)	(81.8)	(87.6)	(96.2)	(108.2)	
393.15	2.10	2.08	2.18	2.30	2.32	
	(85.7)	(93.8)	(99.7)	(108.9)	(122.2)	
398.15	2.33	2.30	2.40	2.50	2.58	2.75
	(96.4)	(106.1)	(113.1)	(123.2)	(137.1)	(148.6)
403.15	2.60	2.55	2.64	2.74	2.82	2.98
	(110.3)	(119.5)	(126.9)	(137.7)	(153.4)	(164.2)
408.15	2.80	2.78	2.89	2.98	3.05	3.20
	(123.3)	(134.3)	(142.2)	(153.8)	(170.3)	(180.9)
413.15	2.90	3.00	3.10	3.22	3.31	3.50
	(138.1)	(149.3)	(157.5)	(169.9)	(187.8)	(200.4)
418.15	3.08	3.12	3.30	3.45	3.59	3.72
	(153.1)	(165.9)	(174.7)	(188.1)	(207.3)	(220.5)
423.15					3.82	4.00
	(169.6)	(182.4)	(192.8)	(207.8)	(227.0)	(241.3)
428.15						4.20
						(265.8)

^aFluidity data in parentheses.TABLE 3. Least-squares fitted values of the parameters of eq [1] for conductivity ($S\ m^{-1}$) and fluidity ($Pa^{-1}\ s^{-1}$) for 0.2[xKNO₃ + (1 - x)NaNO₃] + 0.8glycerol systems^a

x	$A_{\kappa}/10^2\ S\ m^{-1}$ $A_{\phi}/10^3\ Pa^{-1}\ s^{-1}$	B_y/K	T_{0y}/K	Std. dev. in ln Y
0.0	0.5951 ± 0.48 (25.59 ± 3.2)	725.7 ± 140 (1252.9 ± 340)	180.4 ± 9 (173.4 ± 7)	0.089 (0.004)
0.2	0.3142 ± 0.08 (9.92 ± 1.4)	389.2 ± 40 (836.1 ± 191)	248.6 ± 8 (213.9 ± 9)	0.013 (0.001)
0.4	0.3890 ± 0.1 (12.97 ± 1.4)	387.4 ± 38 (935.1 ± 203)	250.0 ± 8 (201.1 ± 9)	0.012 (0.002)
0.6	0.2994 ± 0.04 (20.43 ± 2.4)	342.3 ± 30 (1121.5 ± 349)	259.9 ± 5 (178.9 ± 9)	0.009 (0.002)
0.8	0.2887 ± 0.1 (13.93 ± 1.4)	408.8 ± 70 (944.7 ± 151)	224.4 ± 9 (193.7 ± 7)	0.049 (0.001)
1.0	0.3088 ± 0.15 (32.35 ± 8.9)	512.4 ± 80 (1337.3 ± 470)	170.8 ± 9 (150.0 ± 8)	0.094 (0.005)

^aValue of parameter for fluidity in parentheses.

where A_{1y} , A_{2y} , B_{1y} , and B_{2y} are all empirical constants. The above empirical relationships between A_y , B_y , and T_{0y} are found to hold reasonably well in the present system as is evident from Fig. 4. The validity of such empirical relationships actually indicates that the composition dependence of the T_{0y} parameter alone can fully govern the composition dependence of transport properties of mixed alkali metal ion system in a hydrate melt medium.

An attempt has been made to describe the observed nature of the composition dependence of both κ and ϕ on x (Fig. 5) by least-squares fitting the κ and ϕ data for the present system to an empirical equation of the form

$$[4] \quad Y(\kappa, \phi) = a_y \exp(b_y x + c_y x^2)$$

where a_y , b_y , and c_y are empirical constants. Equation [4] was successfully used by Sangma et al. (9) to explain the composition dependence of observed conductivity and/or fluidity data for 0.3[xKSCN + (1 - x)NaSCN] + 0.7Ca(NO₃)₂·4.06H₂O, and the reported data for $xK_2O + (1 - x)Na_2O + 3SiO_2$ (6) and 0.45[xLiNO₃ + (1 - x)KNO₃] + 0.55Ca(NO₃)₂·4.09H₂O (8) systems and a reasonably good fit was obtained. The least-squares fitted values of the parameters of eq. [4] for the conductivity and fluidity for the present system are given in Table 4. A reasonably good fit has been obtained as is apparent from Fig.

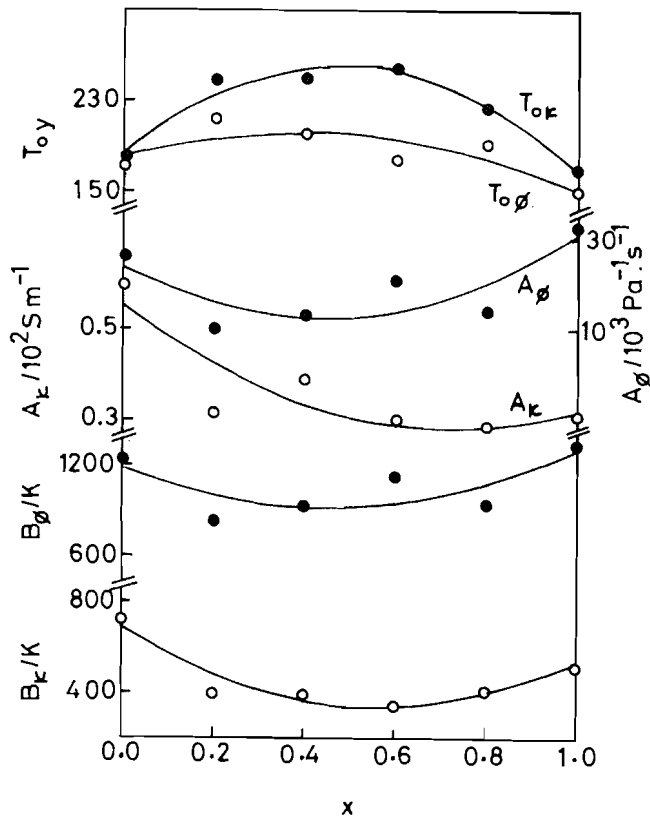


FIG. 3. Variation of T_{0y} , A_y , and B_y with composition for $0.2[x\text{KNO}_3 + (1-x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems.

TABLE 4. Least-squares fitted values of the parameters of eq. [4] for conductivity (S m^{-1}) and fluidity ($\text{Pa}^{-1} \text{s}^{-1}$) of $0.2[x\text{KNO}_3 + (1-x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems^a

T/K	$\ln a_y$	b_y	c_y	Std. dev. in $\ln Y$
398.15	0.8385 (4.5729)	0.0218 (0.3886)	0.1516 (0.0426)	0.011 (0.010)
408.15	1.0236 (4.8170)	0.0442 (0.3628)	0.0953 (0.0239)	0.009 (0.011)
418.15	1.1167 (5.0341)	0.1798 (0.3268)	0.0215 (0.0398)	0.010 (0.010)

^aParameters for fluidity in parentheses.

5. It is evident from Fig. 5 that in the temperature range of the study κ exhibits negative deviation from additivity whereas ϕ shows slightly narrow deviation from additivity. The maximum deviation from additivity was estimated to be $\approx 4\%$ for conductivity and $\approx 3.5\%$ in the case of fluidity at 398.15 K which is more than the uncertainty involved in the measured data. The deviation from additivity both in κ and ϕ isotherms decreases at higher temperatures.

In mixed alkali systems containing Na^+ and K^+ ions in hydrate melt medium the maximum negative deviation was found to be $\approx 4\%$ (9, 12) at 328 K. On the other hand, about 11% negative deviation from additivity was reported in the similar mixed alkali system containing Li^+ and K^+ ions (8). One of the key parameters for the significant MAE may be attributable to the large difference in the radii of the alkali ions in addition to the low temperature study and the higher alkali ion concentration in the mixed alkali systems. The small amount of MAE in

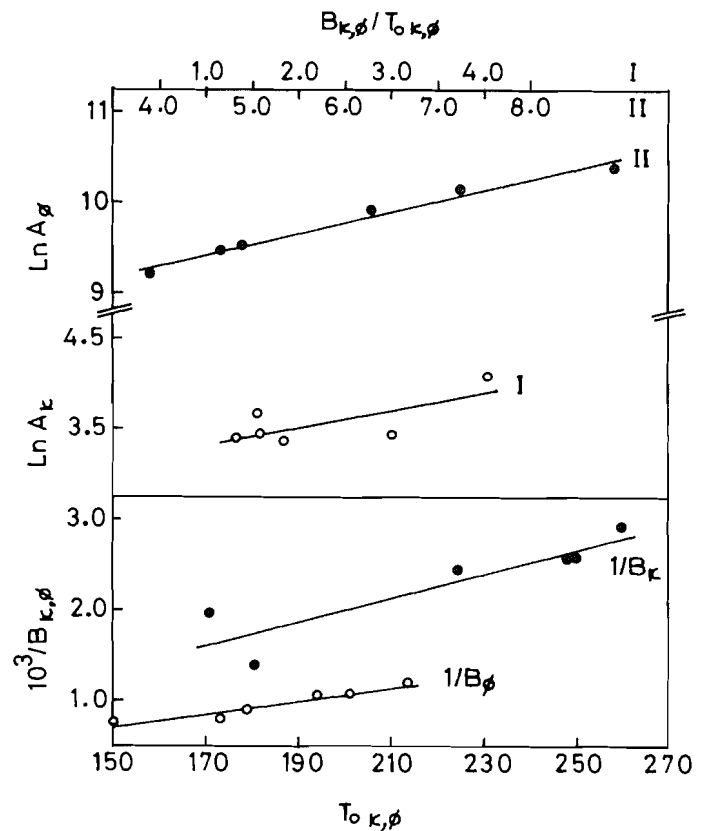


FIG. 4. Plots of $\ln A_{\kappa,\phi}$ vs. $B_{\kappa,\phi}/T_{0\kappa,\phi}$ and $1/B_{\kappa,\phi}$ vs. $T_{0\kappa,\phi}$ for $0.2[x\text{KNO}_3 + (1-x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems (open and closed circles represent observed values and solid lines represent values calculated (from eqs. [2] and [3]), respectively).

the present systems ($\approx 4\%$ negative deviation in κ and ϕ isotherms) may be due to the type of alkali ions ($\text{Na}^+ - \text{K}^+$) present with $\Delta F = 0.04$ (ΔF is the difference in field strength) (20) in comparison to $\Delta F = 0.10 - 0.14$ for $\text{Li}^+ - \text{K}^+$ ion (where maximum deviation of 11% was found (8)) resulted in non-rigid type structure in the present system.

According to the idea of solid-like conduction mechanism proposed by Moynihan (6) the structure of the mixed alkali system must be fixed. Therefore, based on the above argument isofluidity condition may be one of the important criteria to detect MAE in the electrical conductivity. Variation of κ with composition at different fluidity values are illustrated in Fig. 6. Electrical conductivity values at constant fluidity both within and outside the experimental ranges of fluidity required were calculated using eq. [1] and the least-squares fitted values of A_y , B_y , and T_{0y} parameters (Table 3). From Fig. 6 it is apparent that the percentage deviation from additivity in conductivity at low fluidity is higher, decreasing in value at higher fluidities, and becoming almost linear at $\phi = 100 \text{ Pa}^{-1} \text{ s}^{-1}$. Moynihan (6) suggested that the largest apparent deviation from linearity under low fluidity condition is due to the long time scale for the rearrangement of the local structure compared to that required for local diffusion of alkali cations from site to site. Similar explanation may also be used on the present system.

Several theories and model (21-24) have been proposed to account for the onset of MAE in ternary oxide glass and hydrate melt. The cation interaction theory seems to be more appropriate for the system not having such a rigid-network type structure. The anion polarization model (APM) proposed by

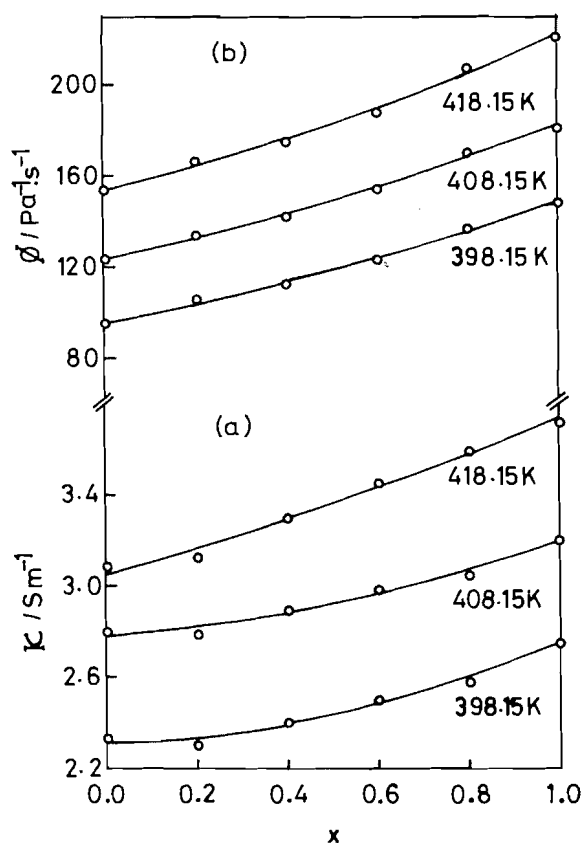


Fig. 5. Plots of (a) conductivity and (b) fluidity versus composition for $0.2[x\text{KNO}_3 + (1-x)\text{NaNO}_3] + 0.8\text{glycerol}$ systems under isothermal condition (open circles and solid curves represent observed and calculated values (from eq. [4], Table 4), respectively).

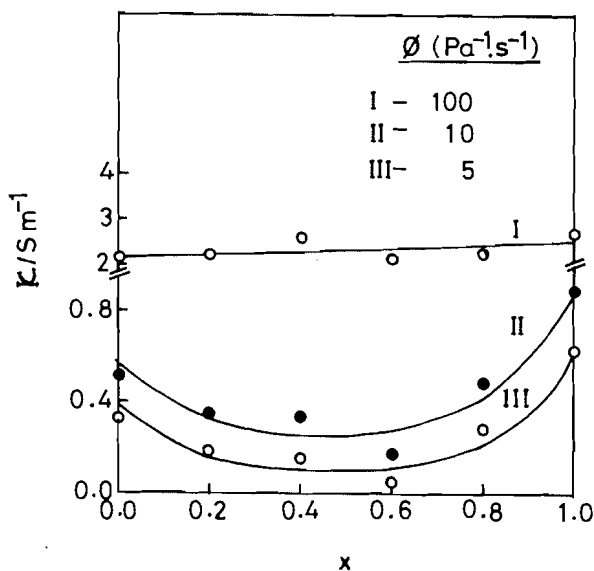


Fig. 6. Plots of conductivity versus composition under isofluidity condition (open and closed circles represent observed values and solid lines represent values calculated (from eq. [4]), respectively).

Moynihan and Laity (22, 25) is one such cation interaction theory. The APM has been used earlier to explain MAE on the electrical conductivity in hydrate melt medium (8, 10). The APM may, therefore, also be used to explain MAE in electrical conductivity and fluidity in a glycerol medium. According to this model, the NO_3^- ion experiences an average symmetrical field when the glycerol medium contains either NaNO_3 or KNO_3 . On the other hand, when the medium contains both Na^+ and K^+ ions, some of the NO_3^- ions find themselves between electrical fields of differing intensities. This results in a competitive polarization of the anion and generates an asymmetric electrical field around NO_3^- , causing the NO_3^- ion to be more polarized towards the Na^+ ion. As a result, the internal mobilities of Na^+ and K^+ ions are affected, thereby causing a net deviation from additivity.

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