Electrical Conductance of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ Melts

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Electrical conductance values of $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melts are reported as functions of temperature and x. Electrical conductance, unlike viscosity, exhibits negative deviation from additivity. The temperature dependence of electrical conductance is described by the Vogel-Tammann-Fulcher (VTF) equation. Variation of the three VTF parameters, viz., A, B, and T_0, with x is found to be nonlinear. On the other hand, ln A and $1/B$ are empirically found to vary linearly with B/T_0 and T_0, respectively.

Introduction

Mixed alkali metal ion effect (MAE), which is a pronounced phenomenon in glass media (*1*, *2*), has been found to exist to a lesser extent in hydrate melt media also (*3-6*). 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-metal ion by another in a glass or melt. Recently we started investigating the occurrence of MAE in molten sodium thiosulfate pentahydrate medium (*7*). Since this molten solvent itself contains alkali-metal ion, it is considered to be different from other hydrate melt media like calcium nitrate tetrahydrate melt. MAE is therefore estimated in molten sodium thiosulfate pentahydrate medium by taking into consideration the alkali-metal ions of the added solutes only. In mixed alkali metal ion systems, both electrical conductance and viscosity are known to show generally negative deviations from additivity (*1*, *2*, *5-8*). On the contrary, the viscosity of $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melt is reported (*9*) to exhibit a positive deviation from additivity. It would be interesting to study the behavior of electrical conductance of this exceptional system also with respect to composition. Electrical conductances of molten $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ system are therefore reported here as functions of x and temperature, T.

Experimental Section

Details of purification of the salts, determination of the actual $\text{H}_2\text{O}/\text{Na}^+$ mole ratio in the sodium thiosulfate pentahydrate sample, and measurements of electrical conductance are given elsewhere (*6*, *7*, *9*).

Results and Discussion

The measured values of the electrical conductivity (κ) of the $0.3[x\text{NaSCN} + (1-x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melt as functions of temperature (in the range 25-65 °C) and x are given in Table I. These values of κ are found to be reproducible within ±1% accuracy. In the temperature range of this study, κ varies by factors of 3-4, and its slight non-Arrhenius-type temperature dependence is analyzed in terms of the Vogel-Tammann-Fulcher (VTF) equation of the form

$$\kappa = A \exp[-B/(T - T_0)] \qquad (1)$$

The least-squares fitted values of the three constant parameters, A, B, and T_0, are listed in Table II. The uncertainties in the values of A, B, and T_0 are estimated to be about ±0.3, ±70, and ±10, respectively (*7*). Within these uncertainty limits, changes in the values of A, B, and T_0 do not produce significant changes in the standard deviation.

In order to examine the effect of the presence of mixed-alkali-metal ions on conductance, we have plotted κ vs x in Figure 1. The amount of negative deviation decreases with an increase in temperature, and above 60 °C, the deviation becomes negligible, resulting in the linear variation of κ with x. This type of negative deviation of κ from additivity, which envisages the presence of MAE, is in accordance with the behavior observed in several other systems containing mixed-alkali-metal ions in hydrate melt (*5-7*) and glass media (*1*, *2*). Electrical conductivity, therefore, exhibits a normal behavior with respect to x in spite of the fact that the nature of the composition dependence of viscosity of this particular system is reported (*9*) to be different, as mentioned in the Introduction.

It may be noted that in the present system, although x varies from 0 to 1, the mole fraction $\text{K}^+/(\text{K}^+ + \text{Na}^+)$ actually varies from 0 to 0.18 only. It is not possible therefore to make a complete estimation of MAE using molten sodium thiosulfate pentahydrate medium. However, since the concentration of the medium is kept constant, the MAE is estimated in the present system as a function of x only and is equal to about 2-8% in the temperature range 328-298 K.

The deviation of κ from additivity may also be analyzed in light of the dependences of A, B, and T_0 on x, which are illustrated in Figure 2. The negative deviation of T_0 from additivity is similar to the trend reported in other systems (*4*, *7*) containing hydrate melts. However, such a variation of T_0 with x would cause a positive deviation of κ from additivity rather than a negative deviation. Similarly, the type of dependence of A on x (Figure 2) would also predict a positive deviation of κ from ideality. Therefore, the composition dependence of the B parameter appears to override the effect of the variations of T_0 and A with x and to govern the composition dependence of κ. It may be noted that B is directly related to the activation energy for conductance. A similar observation was also made in glasses containing mixed-alkali ions (*1*).

In order to correlate empirically the composition dependences of A, B, and T_0 parameters, we have plotted in Figure 3 ln A vs B/T_0 and $1/B$ vs T_0. It is interesting to notice the linearity of these plots. Such type of linear variations of ln A and $1/B$ with B/T_0 and T_0, respectively, are also observed in other similar mixed alkali systems, as evident from Figure 3. Therefore, empirical relations of the form

$$\ln A = A_0 + k_1 B/T_0 \qquad (2)$$

$$1/B = B_0 + k_2 T_0 \qquad (3)$$

seem to hold good in these mixed alkali metal ion systems. In eqs 2 and 3, A_0, B_0, k_1, and k_2 are all empirical constants.

Glossary

MAE	mixed alkali metal ion effect
VTF	Vogel-Tammann-Fulcher
κ	electrical conductivity

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Table I. Electrical Conductance of 0.3[xNaSCN + (1 − x)KSCN] + 0.7$Na_2S_2O_3 \cdot 5.1H_2O$ Melts as Functions of Temperature and x

T, K	$\kappa \pm 1\%$, S cm^{-1}							
	x = 0.0	x = 0.1	x = 0.2	x = 0.4	x = 0.5	x = 0.7	x = 0.9	x = 1.0
298.0	0.0433	0.0410	0.0390	0.0362	0.0350	0.0334	0.0324	0.0324
303.0	0.0520	0.0495	0.0474	0.0444	0.0440	0.0420	0.0410	0.0410
308.0	0.0613	0.0584	0.0571	0.0540	0.0530	0.0513	0.0500	0.0494
313.0	0.0702	0.0682	0.0670	0.0632	0.0621	0.0610	0.0594	0.0591
318.0	0.0822	0.0800	0.0780	0.0744	0.0732	0.0710	0.0694	0.0692
323.0	0.0950	0.0924	0.0910	0.0870	0.0860	0.0830	0.0810	0.0810
328.0	0.107	0.104	0.102	0.0970	0.0970	0.0944	0.0930	0.0920
333.0	0.122	0.120	0.118	0.115	0.113	0.110	0.108	0.107
338.0	0.135	0.134	0.133	0.131	0.129	0.127	0.125	0.124

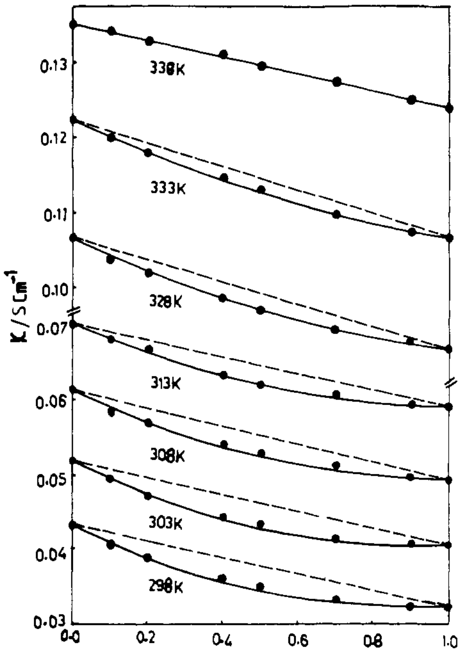

Figure 1. Variation of κ of the 0.3[xNaSCN + (1 − x)KSCN] + 0.7$Na_2S_2O_3 \cdot 5.1H_2O$ melt with x at different temperatures.

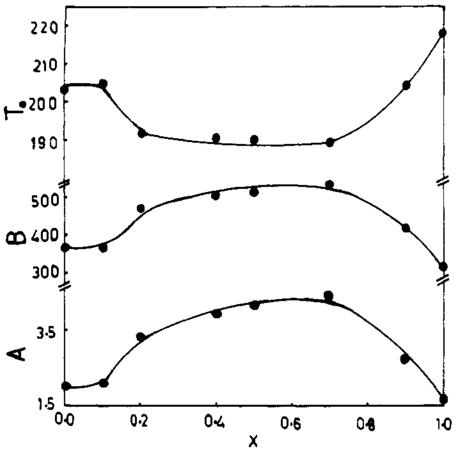

Figure 2. Variation of A, B, and T_0 of the 0.3[xNaSCN + (1−x)KSCN] + 0.7$Na_2S_2O_3 \cdot 5.1H_2O$ melt with x.

T	temperature, K
T_0	ideal glass transition temperature
A, B	constants
A_0	constant

Table II. Least-Squares Fitted Values of the Parameters of Equation 1

x	A, S cm^{-1}	B, K	T_0, K	std dev in ln κ
0.0	2.066	369.4	203.0	0.012
0.1	2.085	367.3	205.0	0.014
0.2	3.321	471.4	192.1	0.009
0.4	3.935	504.7	190.5	0.010
0.5	4.146	515.8	190.0	0.010
0.7	4.451	532.9	189.0	0.012
0.9	2.705	416.1	204.0	0.014
1.0	1.644	315.2	218.0	0.018

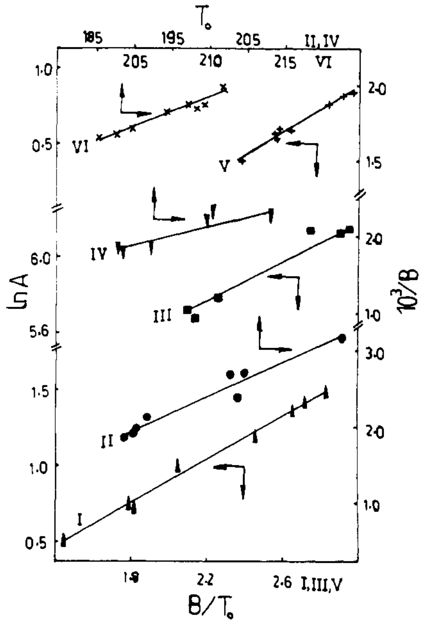

Figure 3. Plots of ln A vs B/T_0 and $1/B$ vs T_0 for different mixed alkali metal ion systems: (I, II) 0.3[xNaSCN + (1 − x)KSCN] + 0.7$Na_2S_2O_3 \cdot 5.1H_2O$; (III, IV) 0.35[xNaNO$_3$ + (1 − x)KNO$_3$] + 0.65$Na_2S_2O_3 \cdot 5H_2O$ (*7*); (V, VI) 0.3[xNaSCN + (1 − x)KSCN] + 0.7Ca(NO$_3$)$_2 \cdot 4.06H_2O$ (*6*).

B_0	constant
k_1, k_2	constants

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