Viscosity and Molar Volume of Potassium Thiocyanate + Sodium Thiocyanate + Acetamide Melt Systems

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Density and viscosity of $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ melt systems were measured as functions of temperature ($293.15 \leq T/\text{K} \leq 343.15$) and mole fraction, $x = 0.0$ to 1.0. The temperature dependence of viscosity has been analyzed by using the Vogel−Tammann−Fulcher (VTF) equation. Molar volumes and intrinsic volume were found to be additive in nature. The existence of the mixed alkali effect (MAE) has been established by the significant negative deviation from the additivity in the ideal glass transition temperature and in the viscosity isotherms. The onset of the MAE in the present system has been explained by the mutual contribution of the polarization effect of SCN^- ion on the Na^+ ion and the presence of the rigid polymeric type structure, which decrease as the Na^+ ions are progressively replaced by the K^+ ions.

Introduction

In the scope of investigating the mixed alkali effect (Day, 1976; Moynihan, 1979; Ingram, 1987; Sangma et al., 1984; Mahiuddin, 1994, 1996a) in the ternary system, we reported earlier on the electrical conductivity of sodium + potassium thiocyanates in acetamide melt medium (Mahiuddin, 1996a). We observed a pronounced mixed alkali effect (MAE), i.e., both positive and negative deviation from the linearity in the electrical conductivity isotherms in the different temperature ranges of the study. In the mixed alkali metal ion systems, both electrical conductivity and viscosity isotherms generally exhibit either positive or negative deviation from linearity. In our earlier paper, we reported the electrical conductivity in an alternating electric field of 1.5 kHz (Mahiuddin, 1996a); perhaps the aggregates/rigid polymeric type solvated ions (Płowiec et al., 1985), which predominate below 333.15 K and in the Na⁺ ion rich region, practically do not move, and the conductivity is due to the jumps of the ions. As a result, we observed both maxima above 333.15 K and minima below 333.15 K in the electrical conductivity isotherms. However, the viscosity is governed by the movement of both the deformed aggregates according to the flux lines and the jumps of the ions. The two measured quantities (conductivity and viscosity) are different in nature in these systems. It would, therefore, be interesting to study the viscosity of the sodium + potassium thiocyanates in the acetamide melt medium. Accordingly, we report here the viscosity and molar volume of $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ systems as functions of temperature and composition to investigate the existence of the MAE in the viscosity isotherm.

Experimental Section

Materials and Equipment. Details of the purification of salts, preparation of samples, and the temperature control unit to maintain the temperature of the measurements to ±0.02 K are given elsewhere (Mahiuddin, 1996a,b)

Density Measurements. Densities (ρ) of all samples were measured by using a single-stem pycnometer as

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described earlier (Mahiuddin, 1996a). The reproducibility of densities of individual samples was within ±0.1%.

Viscosity Measurements. Viscosities (η) of all samples as functions of temperature and composition were measured with the help of a Schott-Geräte AVS 310 unit using Ubbelohde viscometers having cell constant 0.3127 mm² s⁻² and 0.5337 mm² s⁻², respectively. The experimental reproducibility between duplicate viscosity values of all samples was less than ±0.4%.

Results and Discussion

The density values of $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ systems are presented in Table 1 and are found to be a linear function of temperature (Table 2) at a fixed composition. The experimental density values of the present study are comparable within ±0.25% with the reported values (Mahiuddin, 1996a). The viscosities (η) and molar volumes (V) of the systems as functions of temperature and composition are listed in Table 3.

Viscosity values were found to exhibit non-Arrhenius variation with temperature ($\sim$4−6% deviation from the linearity in the $\ln \eta$ vs $1/T$ plots) and were analyzed by using the Vogel−Tammann−Fulcher equation (Vogel, 1921; Tammann and Hesse, 1926; Fulcher, 1925) of the form

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

The best-fit values of the parameters A, B, and the ideal glass transition temperature, T_0, with their uncertainties are presented and illustrated in Table 4 and Figure 1, respectively. T_0 values for the viscosity are slightly lower than the reported T_0 values (Mahiuddin, 1996a) for the electrical conductivity.

Variation of T_0 versus mole fraction, x, for the viscosity (Figure 1) shows a negative deviation from the linearity, while for the electrical conductivity T_0 showed both negative and positive deviation (Mahiuddin, 1996a). The behavior of T_0 for the viscosity in the present study and for the electrical conductivity with x will be discussed in the subsequent section. However, the observed variation

Table 1. Values of the Density as Functions of the Temperature and Composition for the $0.25[xKSCN + (1 - x)NaSCN] + 0.75CH_3CONH_2$ Melt

T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}	T/K	ρ/kg m^{-3}
		$x = 0.0$			
323.75	1169.1	314.50	1176.8	306.35	1183.0
321.95	1170.6	312.35	1178.5	304.15	1184.2
320.20	1172.0	310.50	1180.2	302.05	1185.9
318.25	1173.5	308.40	1181.8	300.05	1187.4
316.40	1175.0				
		$x = 0.2$			
325.60	1171.8	316.20	1179.3	306.45	1187.2
324.25	1173.0	314.75	1180.6	304.85	1188.3
322.45	1174.4	313.20	1181.7	302.80	1189.7
320.95	1175.6	311.40	1183.2	301.25	1190.9
319.45	1177.0	309.85	1184.5	299.40	1192.3
317.90	1178.1	308.00	1185.8		
		$x = 0.4$			
323.65	1177.7	312.40	1186.5	304.05	1193.2
322.10	1178.9	310.85	1187.7	302.30	1194.3
318.85	1181.6	309.05	1189.2	300.55	1195.7
317.20	1182.9	307.60	1190.4	298.85	1197.0
315.55	1184.0	305.70	1191.8	297.10	1198.4
314.05	1185.3				
		$x = 0.6$			
334.55	1173.8	324.95	1181.3	314.95	1189.2
332.95	1174.9	323.45	1182.5	313.30	1190.3
331.35	1176.4	321.90	1183.7	311.60	1191.7
329.85	1177.6	320.05	1185.2	309.95	1192.9
328.20	1178.9	318.25	1186.4	308.25	1194.3
326.65	1180.0	316.65	1187.8		
		$x = 0.8$			
326.85	1184.0	318.45	1190.4	310.15	1196.8
325.15	1185.2	316.95	1191.6	308.35	1198.2
323.45	1186.7	315.25	1192.9	306.65	1199.6
321.75	1187.9	313.50	1194.1	304.75	1200.8
320.05	1189.3	311.85	1195.6		
		$x = 1.0$			
328.55	1187.0	318.15	1194.7	309.45	1201.3
326.75	1188.2	316.45	1195.9	307.55	1202.6
325.15	1189.7	314.85	1197.1	305.75	1203.8
323.35	1190.9	312.95	1198.6	303.95	1205.2
321.55	1192.3	311.25	1199.9	302.15	1206.4
319.95	1193.4				

Table 2. Least-Squares-Fitted Values of the Density Equation, $\rho = a - b(T - 273.15)$, for the $0.25[xKSCN + (1 - x)NaSCN] + 0.75CH_3CONH_2$ Melt

x	a/kg m^{-3}	b/kg m^{-3} K^{-1}	std. dev. in ρ/kg m^{-3}
0.0	1208.6 ± 0.5	0.7750 ± 0.0124	0.32
0.2	1213.0 ± 0.2	0.7819 ± 0.0042	0.13
0.4	1217.1 ± 0.1	0.7782 ± 0.0028	0.09
0.6	1221.6 ± 0.1	0.7774 ± 0.0026	0.08
0.8	1225.2 ± 0.2	0.7662 ± 0.0035	0.08
1.0	1227.9 ± 0.1	0.7380 ± 0.0029	0.09

of T_0 with x (Figure 1) reveals that the systems exhibit significant MAE.

Viscosities of the present systems also vary nonlinearly with the molar volumes and are analyzed by using the following equation, derived on the basis of the free volume model:

$$\eta = A' \exp[B'/(V - V_0)] \qquad (2)$$

where A' and B' are constant parameters and V_0 is the intrinsic volume. The best-fit values of A', B', and V_0 are presented and illustrated in Table 4 and Figure 2, respectively. The variation of molar volumes with x at 323.15 K is also shown in Figure 2. It has been reported that Na$^+$ ions in the acetamide melt medium form a polymeric type solvated ion (Płowiec et al., 1985). From Figure 2 it appears

Table 3. Viscosity (η) and Molar Volume (V) Data for the $0.25[xKSCN + (1 - x)NaSCN] + 0.75CH_3CONH_2$ Melt

| T/K	η/(mPa s)	$10^6 V$/(m^3 mol^{-1})	T/K	η/(mPa s)	$10^6 V$/(m^3 mol^{-1})
		$x = 0.0$			
343.15	43.08	55.93	317.95	235.4	55.00
337.85	58.24	55.74	313.15	355.9	54.83
333.15	78.08	55.56	308.05	578.8	54.65
327.95	110.8	55.37	303.15	965.4	54.47
323.15	155.7	55.20			
		$x = 0.2$			
343.15	30.80	56.43	317.95	140.6	55.49
337.85	40.55	56.24	313.15	204.3	55.32
333.15	52.56	56.06	308.05	314.7	55.13
327.95	71.70	55.86	303.15	487.9	54.95
323.15	98.31	55.69	298.15	804.8	54.77
		$x = 0.4$			
343.15	23.27	56.92	313.15	126.3	55.80
337.85	29.78	56.72	308.05	187.2	55.62
333.15	37.58	56.54	303.15	276.1	55.44
327.95	49.59	56.35	298.15	433.0	55.26
323.15	65.10	56.17	293.25	700.4	55.08
317.95	90.43	55.98			
		$x = 0.6$			
343.15	18.81	57.38	313.15	87.27	56.26
337.85	23.51	57.18	308.05	125.8	56.08
333.15	29.02	57.01	303.15	178.5	55.90
327.95	37.32	56.81	298.15	270.0	55.71
323.15	47.71	56.63	295.15	350.6	55.61
317.95	64.19	56.44			
		$x = 0.8$			
343.15	16.08	57.87	313.15	63.83	56.75
337.85	19.62	57.66	308.05	87.73	56.57
333.15	23.79	57.49	303.15	120.6	56.39
327.95	29.94	57.29	298.15	174.0	56.21
323.15	37.43	57.12	293.55	256.7	56.05
317.95	49.01	56.93			
		$x = 1.0$			
343.15	14.35	58.31	313.15	48.85	57.24
337.85	17.14	58.12	307.95	65.06	57.06
333.15	20.48	57.96	303.15	86.50	56.89
327.95	24.61	57.77	298.15	120.3	56.71
323.15	30.20	57.59	296.15	138.7	56.64
317.95	38.58	57.41			

Table 4. Best-Fit Values of the Parameters of Eqs 1 and 2 for the $0.25[xKSCN + (1 - x)NaSCN] + 0.75CH_3CONH_2$ Melt^a

| x	A/mPa s (A'/mPa s)	B/K ($10^5 B'$/ m^3 mol^{-1})	T_0/K ($10^6 V_0$/ m^3 mol^{-1})	std. dev. in ln η
0.0	0.0239 ± 0.0026	1022.9 ± 23.3	206.7 ± 1.3	0.002
	(0.0206 ± 0.0059)	(3.857 ± 0.168)	(50.88 ± 0.06)	(0.011)
0.2	0.0224 ± 0.0031	1044.7 ± 35.6	198.6 ± 2.0	0.004
	(0.0346 ± 0.0068)	(3.479 ± 0.150)	(51.31 ± 0.09)	(0.009)
0.4	0.0360 ± 0.0055	935.2 ± 39.4	198.6 ± 2.4	0.006
	(0.0543 ± 0.0067)	(3.089 ± 0.109)	(51.82 ± 0.07)	(0.009)
0.6	0.0610 ± 0.0065	812.1 ± 26.1	201.4 ± 1.8	0.007
	(0.0874 ± 0.0084)	(2.696 ± 0.083)	(52.36 ± 0.06)	(0.011)
0.8	0.0934 ± 0.0036	731.5 ± 9.2	201.1 ± 0.7	0.004
	(0.1489 ± 0.0197)	(2.293 ± 0.096)	(52.97 ± 0.08)	(0.008)
1.0	0.1619 ± 0.0167	627.8 ± 25.0	203.2 ± 2.2	0.005
	(0.1842 ± 0.0189)	(2.127 ± 0.076)	(53.43 ± 0.07)	(0.008)

^{a} Values of the parameters for eq 2 are given in parentheses.

that the polymeric type solvated ion does not cause detectable deviation in the molar and intrinsic volume. The intrinsic volume, V_0, predominantly governs the linear variation of molar volume with mole fraction.

To examine the existence of MAE, we illustrated the viscosity isotherms in Figure 3. The following semiempirical equation (Mahiuddin, 1996a) has been used for the concentration dependence of the viscosity:
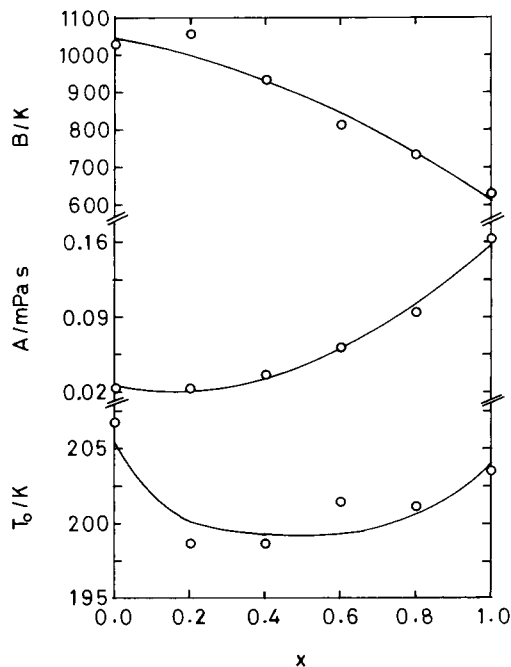
Figure 1. Variation of the ideal glass transition temperature, $T_0/$K, and $A/$mPa s and $B/$K parameters with mole fraction, x, for the $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ melt systems (circles and solid curves represent observed and calculated (from the polynomial equation up to second degree) values, respectively).
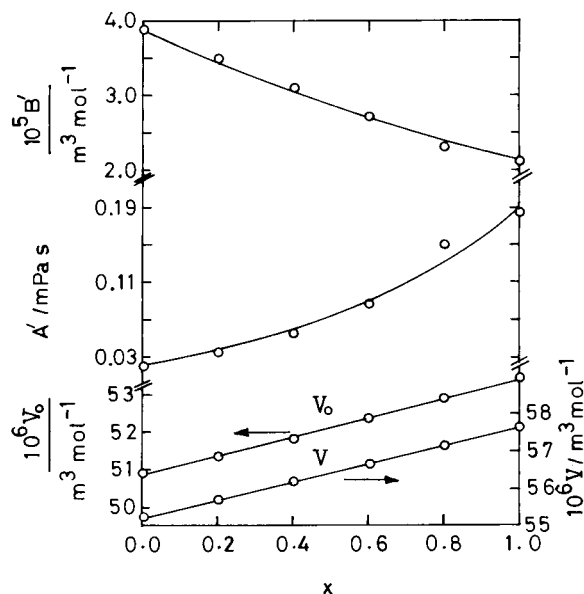

Figure 2. Variation of $V_0/\text{m}^3 \text{ mol}^{-1}$, $A'/$mPa s, $B'/\text{m}^3 \text{ mol}^{-1}$, and molar volume, $V/\text{m}^3 \text{ mol}^{-1}$, with mole fraction, x, for the 0.25-$[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ melt systems (circles and solid curves and lines represent observed and calculated (from the polynomial equation up to second degree and linear equation) values, respectively).

$$\eta = a_1 \exp(b_1 x + c_1 x^2) \tag{3}$$

The computed values of the constant parameters a_1, b_1, and c_1 are presented in Table 5. A reasonably good fit has been obtained (Table 5 and Figure 3).

The viscosity isotherms exhibit significant negative deviation ($\sim$27$-$55%) from the linearity in the viscosity vs x plots in the temperature range of the study (Figure 3). Electrical conductivity isotherms showed positive deviation from linearity above 333.15 K and negative deviation below
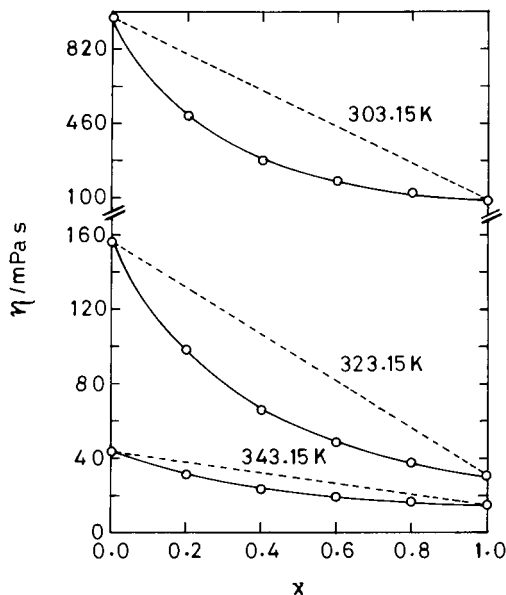
Figure 3. Plots of viscosity isotherms versus mole fraction, x, for the $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ melt systems (circles and solid curves represent observed and calculated (from eq 3) values, and the broken lines represent the additive property of viscosity, respectively).

Table 5. Best-Fit Values of the Parameters of Eq 3 for the $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ Melt

| $T/$K	$a_1/$mPa s	b_1	c_1	std. dev. in $\ln \eta$
303.15	964.5 ± 4.7	-3.630 ± 0.056	1.269 ± 0.082	0.021
323.15	155.8 ± 0.7	-2.499 ± 0.036	0.8697 ± 0.0454	0.012
343.15	43.07 ± 0.09	-1.821 ± 0.014	0.7272 ± 0.0163	0.004

333.15 K (Mahiuddin,1996a). The nature of the variation of the viscosity isotherms (Figure 3) in the present systems and of the conductivity isotherms (Mahiuddin, 1996a) has been reflected in the variation of T_0 vs x plots for the viscosity (Figure 1) and for the conductivity (Mahiuddin, 1996a) for the $0.25[x\text{KSCN} + (1 - x)\text{NaSCN}] + 0.75\text{CH}_3\text{CONH}_2$ melt systems. The above explanation governs the nature of variation of T_0 vs x (Figure 1).

The activation energy, E_η for the viscous flow has been calculated from the following relation

$$E_\eta = BR[T/(T - T_0)]^2 \tag{4}$$

and are presented in Figure 4 at different temperatures. Values of B and T_0 parameters have been taken from Table 4, and R is the gas constant. Activation energy decreases smoothly as the sodium ions are progressively replaced by the potassium ions. The activation energy for the viscous flow is higher than that for ion conduction (Mahiuddin,-1996a) although the T_0 values for the viscosity are lower than the T_0 for the electrical conductivity. The composition dependence of the B parameter, in fact, dominates over the nature of the variation of T_0 with x to govern the composition dependence of the activation energy.

From the nature of variation of T_0, η, and E_η vs x (Figures 1, 3, and 4), it may be concluded that the existence of the MAE in the present system is governed by the following two factors: the first, is the higher polarization effect (Moynihan and Laity, 1964; Moynihan, 1971) of SCN$^-$ ion on the Na$^+$ ion, which decreases as the Na$^+$ ions are progressively replaced by the K$^+$ ions, and the second is the breaking of rigid polymeric type structure that prevails
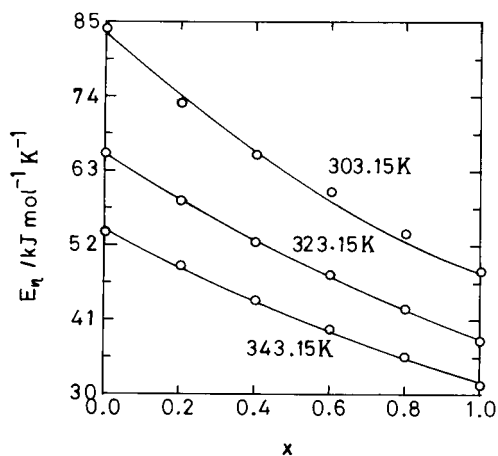
Figure 4. Plots of activation energy, E_η/kJ mol^{-1} K^{-1} for the viscous flow at different temperatures for the 0.25[xKSCN + (1 − x)NaSCN] + 0.75CH$_3$CONH$_2$ melt systems (circles and solid curves represent observed and calculated (from the polynomial equation up to second degree) values, respectively).

in the Na$^+$ ion rich region (Płowiec et al., 1985), as the Na$^+$ ions are progressively replaced by K$^+$ ions. Both these effects contribute toward the net negative deviation in the viscosity isotherms (Figure 3) in the present systems.

Acknowledgment

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