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Viscosity of a Mixture of NaSCN and KSCN in Molten Sodium Thiosulfate Pentahydrate. A Case of Positive Deviation from Additivity

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Density and viscosity data of the molten $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot 5.1\text{H}_2\text{O}$ system are reported as functions of temperature and x. The temperature dependence of viscosity has been described by the Vogel–Tammann–Fulcher equation. A positive deviation of viscosity from additivity has been observed unlike the case with other systems containing mixed alkali-metal ions.

Introduction

In recent years there have been attempts to examine the presence of the mixed alkali effect (MAE) in hydrate melt media (*1–4*). Both electrical conductance and viscosity of mixed alkali systems are found to show, without exception, negative deviation from additivity (*3–7*). However, during our attempt to examine the MAE in the sodium thiosulfate pentahydrate melt we surprisingly observed that in this molten solvent a mixture of sodium and potassium thiocyanates exhibits a positive deviation of viscosity from additivity rather than a negative deviation. Therefore, reported here are the viscosity as well as density data of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot 5.1\text{H}_2\text{O}$ melt as functions of temperature and x.

Experimental Section

Both NaSCN and KSCN (SD, reagent grade) were recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator. Sodium thiosulfate pentahydrate (S. Merck, GR grade) was used as the solvent in the molten state without further purification. The actual H_2O/Na^+ mole ratio in the sodium thiosulfate pentahydrate sample used was determined to be 5.1 ± 0.01 from iodometric titration. Density and viscosity measurements were made, as described earlier (*8*), in a thermostated water bath. The viscometer constant of the Cannon–Ubbelohde viscometer used in the present work was determined to be 1.294×10^{-3} cm^2·s^{-2}.

Results and Discussion

The measured values of the density are presented in Table I in the form of a linear function of temperature. The experimental values of the viscosity (η) are given in Table II. The non-Arrhenius-type temperature dependence of viscosity was analyzed in terms of the Vogel–Tammann–Fulcher equation of the form

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

Table I. Parameters of the Density Equation, $\rho = a - bt$ (°C), for $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\bullet 5.1\text{H}_2\text{O}$ Melts

x	a, g·cm^{-3}	10^4b, g·cm^{-3} °C^{-1}	correln coeff
0.0	1.6518	7.2052	−0.987
0.1	1.6509	6.2715	−0.994
0.2	1.6525	6.5545	−0.995
0.4	1.6632	7.4348	−0.998
0.7	1.6586	6.9441	−0.993
0.9	1.6546	6.6019	−0.992
1.0	1.6634	7.1549	−0.995

Table II. Viscosity Data of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\bullet 5.1\text{H}_2\text{O}$ Melts

	η, cP						
T, K	x = 0.0	x = 0.1	x = 0.2	x = 0.4	x = 0.7	x = 0.9	x = 1.0
294	39.213						
298	31.110		36.986	43.380	42.820	51.933	
303	24.565	27.033	28.185	33.116	36.299	38.977	
308	19.438	21.795	22.563	25.790	28.514	30.126	30.265
313	15.604	17.609	18.140	20.491	22.603	23.281	23.841
318	13.097	14.216	14.859	16.777	18.419	18.924	19.145
323	10.893	11.725	12.041	13.500	14.961	15.255	15.543
328	9.430	9.977	10.271	11.203	12.298	12.711	13.092
333	8.118	8.674	8.809	9.608	10.461	10.804	11.177
338	6.999	7.563	7.583	8.248	9.134	9.229	9.520

Table III. Best-Fit Values of the Parameters of Eq 1 for Viscosity of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\bullet 5.1\text{H}_2\text{O}$ Melts

x	A, cP	B, K	T_0, K	std dev in ln η
0.0	0.2031	478.68	203.0	0.007
0.1	0.2012	481.35	205.0	0.010
0.2	0.1179	603.49	193.0	0.008
0.4	0.0943	656.41	191.0	0.007
0.7	0.0955	677.47	189.0	0.009
0.9	0.1558	546.48	204.0	0.006
1.0	0.2988	415.76	218.0	0.004

The best-fit values of the three constant parameters, A, B, and T_0, are listed in Table III.

The dependence of η on x is illustrated in Figure 1. From this figure it is apparent that at 308 K there is about 8% positive deviation of η from additivity and the amount of deviation decreases with increase in temperature. At about 338 K and above the viscosity seems to become additive. The deviation of viscosity from additivity, in turn, reveals the existence of MAE. The noteworthy behavior of the present system under study is the positive deviation of η from additivity which is unlike the case observed in all other systems containing mixed alkali-metal

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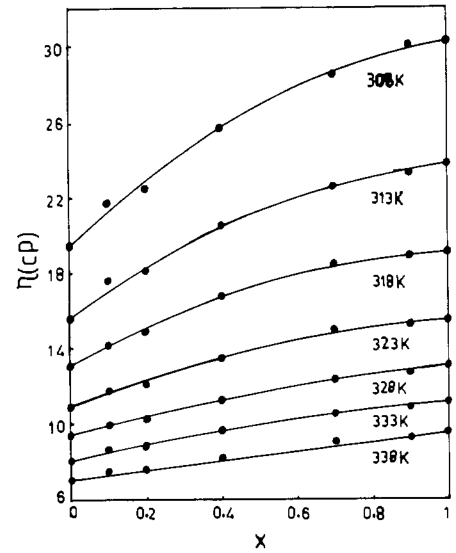

Figure 1. Variation of viscosity of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melt with composition.

ions studied to date. In binary melts also normally a negative deviation of η from additivity is observed (*9*).

It has been reported (*10*) recently that when Na^+ and K^+ ions are added to the molten sodium thiosulfate pentahydrate only the Na^+ ions compete for the water of hydration of the hydrate melt. Probably, this particular interaction between the Na^+ ions of the solute and the water of hydration of the molten solvent which is absent in other similar type of mixed alkali systems studied earlier may be causing in the present case the unusual positive deviation of η from additivity. A comparative study, however, reveals that positive deviations of η from additivity are noticed in binary mixtures containing organic salts (*11*, *12*). By looking into the nature of the dependences of A, B, and T_0 on x, it is realized that the B parameter seems to govern the variation of η with x. Finally, it may be commented that in the system under study, although x varies from 0 to 1, the mole fraction, $K^+/(Na^+ + K^+)$, varies from 0 to 0.18 only.

Registry No. NaSCN, 540-72-7; KSCN, 333-20-0; $Na_2S_2O_3\cdot5H_2O$, 10102-17-7.

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Surface Tensions of Mixtures at Their Boiling Points

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The surface tensions at the boiling points of four binary mixtures and one ternary system are reported. The mixtures studied were methanol/water, ethanol/water, 1-propanol/water, methanol/1-propanol, and methanol/1-propanol/water. The apparatus used in these experimental measurements is simple and easy to use in this application. It uses the principle of bubble detachment pressures from two capillaries in a boiling liquid. Good agreement with previous values for pure components was achieved, and surface tension/composition data for all five systems are reported. Correlations of the data from the four binary mixtures are given.

The measurements of surface tension described in this paper were made in connection with a project to study the effect of surface phenomena on distillation efficiencies.

The "Marangoni" effect has been attracting increased attention because of its influence on mass transfer in the field of distillation (*1*–*6*) humidification, absorption of gases, and liquid–liquid extraction (*7*). It has been shown to occur in many systems of commercial interest, affecting interfacial turbulence and droplet–droplet coalescence rates, froth formation and droplet size, thus altering the interfacial area available for mass transfer. Marangoni effects occur in mixtures when large surface tension differences exist between the components, and they are intensified by large mass-transfer driving forces. Examples of such systems are alcohol–water mixtures, and considerable efforts have been made in the past to develop suitable correlations to describe the surface tension behavior of these systems (*8*, *9*). Due to the highly nonlinear nature of these systems, arising from the complexity of the structure of the hydrogen bonding of water, the correlations have not been very successful. In the field of distillation the surface tension/composition relationship at the boiling point is of interest, and most of the measurement techniques, such as capillary rise, cannot be used. Sugden (*10*, *11*) gave details of a tensiometer which was reported by Adam (*12*) to "combine the advantages of speed, simplicity and accuracy to a greater extent than any other method". Although the apparatus was originally designed for room temperature determinations, with some modification it was used successfully for measurements at the boiling point by Catchpole (*13*) and Biddulph (*2*).

By use of this equipment the surface tensions of some binary and ternary alcohol–water mixtures were measured. In addition, the surface tension of the system MeOH/1-PrOH was also

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