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117

Density and Viscosity of $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 Melt

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Density and viscosity of the molten $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 system were measured. Density varies linearly with temperature. Molar volume exhibits additivity. The system behaves like an ideal mixture of molten $Na_2S_2O_3 \cdot 5H_2O$ and hypothetical supercooled KNO_3. The study envisages a convenient alternative method for estimating the high-temperature densities of high melting anhydrous salts. Viscosity data are analyzed by using the Vogel-Tammann-Fulcher (VTF) equation.

Introduction

Molten hydrated salts form an interesting type of melts for physicochemical studies owing to their low melting points. After the first report made by Angell (1) on hydrate melts, several pure hydrate melts, binary mixtures of them, and solutions of anhydrous salts in hydrate melts have been studied. In most of the latter type of systems studied calcium nitrate tetrahydrate was used as the molten solvent. However, no study has yet been made using sodium thiosulfate pentahydrate as the molten solvent although transport properties of pure sodium thiosulfate pentahydrate were reported by Moynihan (2). Sodium thiosulfate pentahydrate is an interesting hydrated salt owing to the fact that continuous efforts are being made to use it as a material for thermal energy storage. Moreover, a report (3) has also been made on the electrical energy produced during the phase transformation of this particular hydrate melt. Therefore, it may be considered to be worthwhile to do some physicochemical studies on binary systems using sodium thiosulfate pentahydrate as the molten solvent. In the present work densities and viscosities of molten $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 system were measured as functions of temperature and composition.

Experimental Section

Sodium thiosulfate pentahydrate (S. Merck, GR grade) was used as solvent in the molten state without further purification. KNO_3 (BDH, LR grade) was recrystallized twice from distilled water and dried over P_2O_5 in a vacuum desiccator. The methods of sample preparation and density measurements were the same as described elsewhere (4). KNO_3 dissolves to the extent of 60 mol % in molten $Na_2S_2O_3 \cdot 5H_2O$ at about 50 °C. Viscosity measurements were made with a Hoppler viscometer Type BH-2. Using such a viscometer it is possible to prevent the loss of water from the hydrate melt at higher temperatures (5). However, this viscometer restricts the viscosity measurements to relatively higher temperatures owing to the crystallization of the melt initiated by the falling sphere. The NBE-type ultrathermostat (±0.02 °C) containing water as the bath liquid was used to regulate the temperature.

Results and Discussion

The measured densities of the $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 system were found to be a linear function of temperature. In Table I the least-squares fitted values of the two parameters of the

Table I. Parameters of the Density Equation, $\rho = a - bt$(°C), for $(1 - x)Na_2S_2O_3 \cdot 5H_2O$ + $xKNO_3$ Melts

x	a, g·cm⁻³	$b \times 10^4$, g·cm⁻³·°C⁻¹	$\sigma^a \times 10^4$	molar vol (50 °C), cm³·mol⁻¹
0.0	1.6958	7.7097	2.58	149.70
0.1	1.7029	6.3303	2.82	139.66
0.2	1.7244	7.4425	3.99	129.62
0.35	1.7491	6.9985	2.75	114.72
0.45	1.7843	8.1225	3.89	104.35
0.6	1.8259	7.1775	2.78	89.33

^{a} Standard deviation in ρ(g·cm⁻³).

Table II. Fluidity Data of $(1 - x)Na_2S_2O_3 \cdot 5H_2O$ + $xKNO_3$ Melts

T, K	ϕ, cP⁻¹					
	$x = 0.0$	$x = 0.1$	$x = 0.2$	$x = 0.35$	$x = 0.45$	$x = 0.6$
318.0		0.0415	0.0417	0.0391		
323.0	0.0483	0.0516	0.0510	0.0478	0.0422	
327.9			0.0604			
328.1	0.0584	0.0616		0.0579	0.0514	
333.0	0.0688	0.0738	0.0719	0.0673	0.0618	0.0521
338.0	0.0811	0.0862	0.0833	0.0785	0.0718	0.0615
343.0	0.0921	0.0981	0.0952	0.0908	0.0829	0.0682
348.0	0.1063	0.1125	0.1082	0.1028	0.0936	0.0808
353.0	0.1201	0.1243	0.1220	0.1227	0.1027	0.0959
358.0	0.1438	0.1443	0.1374		0.1183	0.1125
358.2				0.1377		

density equation are listed. The actual $H_2O/2Na^+$ mole ratio in pure sodium thiosulfate pentahydrate melt was estimated by using the density vs. concentration isotherm of $Na_2S_2O_3$ + H_2O system (6) and it was found to be equal to 5.00 ± 0.01. The present density value of pure $Na_2S_2O_3 \cdot 5H_2O$ melt is about 0.1% higher than the density value reported by Moynihan (2) for this melt. Therefore a slight difference in the water of hydration of the sodium thiosulfate samples used by us and Moynihan may be expected. The molar volumes of $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 system calculated at 50 °C are also given in Table I. The interesting point to note is the linear variation of molar volume with the mole fraction of KNO_3 at all temperatures. Moreover, the extrapolation of the molar volume isotherm of the present system under investigation provided a value 49.11 cm³·mol⁻¹ for the molar volume of pure KNO_3 at 50 °C. This extrapolated value agrees within 0.67% with the value 48.78 cm³·mol⁻¹ for the molar volume of KNO_3 at 50 °C calculated from the high-temperature density data of molten KNO_3 (7). Similar observation regarding the additivity of molar volume was earlier made in the $Ca(NO_3)_2 \cdot 4H_2O$ + KNO_3 (8) and $Ca(NO_3)_2 \cdot 4H_2O$ + $KSCN$ (4, 9) molten systems also. The additivity of molar volume may be attributed to the fact that in $Na_2S_2O_3 \cdot 5H_2O$ + KNO_3 molten mixture all the water molecules may be present in the hydration sphere of the sodium ion, since K^+ ion has a smaller charge to radius ratio than Na^+ ion. In view of the present and earlier (4, 8, 9) observations it may therefore be suggested that a binary mixture containing a hydrate melt and an anhydrous solute with common or different anions behaves ideally with respect to molar volume if the solute is not capable of displacing water from the coordinating sphere of the cation of the hydrate melt. Such a system therefore appears to be an ideal mixture of hydrate melt and hypothetical supercooled solute. This interesting property of such binary mixtures may therefore
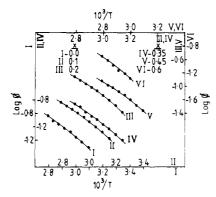
Figure 1. Arrhenius plot for fluidity of $(1 - x)Na_2S_2O_3 \cdot 5H_2O + xKNO_3$ melts.

Table III. Least-Squares Fitted Values of the Parameters of Eq 1 for Fluidity of $(1 - x)Na_2S_2O_3 \cdot 5H_2O + xKNO_3$ Melts

x	A	B	T_0, K	std dev in $\ln \phi$
0.0	5.7057	586.46	200.27	0.018
0.1	5.4083	575.99	199.32	0.013
0.2	4.6221	558.62	199.06	0.006
0.35	5.3893	590.86	197.95	0.016
0.45	4.5169	585.83	197.08	0.017
0.6	5.3599	594.25	205.45	0.031

be successfully employed to estimate the high-temperature (above the melting point) densities of high melting anhydrous salts by the proper choice of a molten hydrated salt as the solvent medium.

The measured viscosities of $Na_2S_2O_3 \cdot 5H_2O + KNO_3$ melt are listed in Table II. The viscosity of pure $Na_2S_2O_3 \cdot 5H_2O$ is found to be about 5% higher than that reported by Moynihan (2). This difference in the viscosity values may be attributed to a possible difference, as also expected above from the density value, in the water of hydration of the sodium thiosulfate samples used by us and Moynihan. For example, in calcium nitrate tetrahydrate melt Moynihan et al. (10) suggested about 0.03% and 2% changes in density and viscosity values, respectively, for every 0.01 change in the H_2O/Ca mole ratio. In Figure 1 the temperature dependence of fluidity of the system under study is illustrated in the form of Arrhenius plots. The temperature dependence of fluidity is seen to be non-Arrhenius as is nor-

mally the case with similar kind of systems. However, the non-Arrhenius behavior is less pronounced in the present case which is due to the narrow temperature range of viscosity measurement. The temperature dependence of fluidity, ϕ, of the system under investigation is therefore analyzed by least-squares fitting the fluidity data to the VTF equation of the form

$$\phi = A \exp(-B/(T - T_0)) \qquad (1)$$

where A, B, and T_0 are constant parameters. T_0 is the ideal glass transition temperature at which the viscosity of the system becomes of the order of $(10^{11}-10^{13})P$. In eq 1 we have neglected the preexponential temperature term owing to its insignificant contribution to the temperature dependence of ϕ. The data fitting has been done by using the same procedure described elsewhere (4, 10). The values of A, B, and T_0 computed in this fashion are listed in Table III. The value of T_0 for pure $Na_2S_2O_3 \cdot 5H_2O$ melt is in good agreement with the value reported by Moynihan (2). However, in the present system of study, unlike the case with other similar systems, the value of T_0 does not vary monotonously or linearly with composition. Initially the value of T_0 appears to decrease slightly by the addition of KNO_3, and as the system becomes saturated with KNO_3 it starts increasing. Such a nonlinear variation of T_0 with composition may be due to the presence of two different alkali ions in the present system of investigation which may be causing a mixed alkali effect (11).

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