J. Chem. Eng. Data **1984**, *29*, 14–16

Densities and Viscosities of Urea–Calcium Nitrate Tetrahydrate Melts

Surender K. Jain,* Niraj P. Kulshrestha,[†] and Vijay V. Singh

Hindu College, University of Delhi, Delhi—110 007, India

Densities and viscosities of urea-containing molten mixtures of calcium nitrate hydrate (n_{H_2O}/n_{salt} = 4.12) have been measured as a function of temperature and composition up to 80 mol % of urea. The molar volume varied linearly with temperature and composition. The thermal expansivity (α) of the system increased gradually with the urea content and attained a limiting value, nearly equal to that of pure water at higher urea content. The fluidity–temperature data exhibited non-Arrhenius behavior and least-squares fitted into the equation $\ln \phi = \ln \bar{A}_\phi - B_\phi/(T - T_{0,\phi})$

Introduction

Various reports (*1*–*19*) on the physicochemical studies of the molten hydrate of calcium nitrate and its mixtures with other hydrates and with monovalent inorganic nitrates have appeared in the past several years. However, solution properties of such liquids in which the Coulombic interactions are made weaker by adding some organic compound appear not to have been reported so far. Large solubility of urea in this melt and the subsequent increased supercooling tendencies of the system prompted us to report the results of the preliminary investigation of this system.

Experimental Section

The salts used were of AnalaR grade (BDH, India). The gravimetric analysis and comparison of the present density data with those of Ewing and Mikovsky (*20*) gave a H_2O:salt mole ratio of 4.12 ± 0.01 for the hydrate of calcium nitrate used in this study. The urea was desiccated for 24 h before use.

The densities were measured by using the modified manometric densitometer as described earlier (*13*). Viscosities were measured with an Ubbelhode type viscometer calibrated with aqueous solutions of sucrose and glycerol. The viscometer constant was 0.2009 cP s^{-1}. All measurements were made in a liquid paraffin bath (10 L), whose temperature was controlled and measured with a precision of ±0.1 °C. The reported density values are believed to be precise to ±0.05%. The viscosity values are estimated to be precise to ±0.5%.

Results and Discussion

Densities of the various mixtures studied in this work varied linearly with temperature and were expressed by equations of the type

$$\rho(\text{g cm}^{-3}) = a - bt(^\circ\text{C})$$

The linear density–temperature equations for various mixtures are presented in Table I. The density of the medium continues to fall with the increase in urea content in the system, the decrease being rather rapid at higher concentrations (Figure 1). The molar volumes (V_m) calculated through the relation

$$V_m = \{x_1M_1 + (1 - x_1)M_2\}/\rho \qquad (1)$$

also varied linearly with temperature and composition. The corresponding equations are presented in Tables I and II, respectively. The equations describing the temperature dependence of the partial molar volumes ($\bar{V}_m$) for both constituents of the system are recorded in Table III. The expansivity (α) calculated from the density data increased gradually with the urea content of the system and attained a limiting value at higher urea content, the value being nearly equal to that for water at the same temperature. It thus appears that there are some structural changes taking place in the medium but in a manner such that the volume–composition plot still remains linear over the composition range investigated.

The fluidity of the system shows a systematic increase with the urea content of the medium. The increase, however, is rapid beyond 50 mol % of urea in the system. The fluidity data showed non-Arrhenius temperature dependence. Such non-Arrhenius temperature dependence of transport properties of concentrated electrolytic solutions and molten systems has frequently been described (*1*–*8*, *11*, *16*, *18*) in terms of the equations

$$\phi = A_\phi T^{-1/2} \exp(-k_\phi/(T - T_{0,\phi})) \qquad (2)$$

$$\phi = \bar{A}_\phi \exp(-B_\phi/(T - T_{0,\phi})) \qquad (3)$$

respectively based upon the free volume model of Cohen and Turnbull (*21*) and the group cooperative rearrangement theory of Adam and Gibbs (*22*). Since, the basis for the presence of $T^{-1/2}$ in the preexponential term of eq 2 is not firmly established and as it has a very weak effect on the temperature dependence in comparison with the exponential term (cf. ref *4*), the present data have been fitted into the logarithmic form of eq 3, viz.

$$\ln \phi = \ln \bar{A}_\phi - B_\phi/(T - T_{0,\phi}) \qquad (4)$$

The least-squares parameters are presented in Table IV, and their dependence on the melt composition is shown in Figure 2. In view of the belief (*3*) that the most important parameter to influence $T_{0,\phi}$ is the electrostatic charge concentration of the medium, the trend reflected by the $T_{0,\phi}$ values (Figure 2) across the melt composition appears to be obvious. However, an attempt to describe the fluidity–charge concentration (N) data in terms of the equation

$$\phi = A_\phi \exp[-B_\phi'/(N_{0,\phi} - N)] \qquad (5)$$

did not yield any meaningful value of the parameter $N_{0,\phi}$.

The variation of the preexponential coefficient ($\bar{A}_\phi$) with the melt composition appears to contradict the $rm^{-1/2}$ dependence of this parameter as predicted by the theory (*21*), r and m being the radius and the mass of the species involved in the mass transport.

The decrease in the B_ϕ values with the urea content of the melt may be a reflection of the lowering of the restricting potential opposing the viscous flow in the medium. The ratio $B_\phi/T_{0,\phi}$ however appears to be nearly constant at 2.6 ± 0.3.

The changes in the parameters $\bar{A}_\phi$, B_ϕ, and $T_{0,\phi}$ with composition when seen concomitantly with the changes in the density and fluidity of the medium indicate that urea molecules

---

[†] Presently at the Department of Chemistry, University of Louisville, Louisville, KY.

0021-9568/84/1729-0014$01.50/0

Table I. Density–Temperature and Molar Volume–Temperature Equations for Urea-Containing Melts of Calcium Nitrate Tetrahydrate

[urea], mol %	data points	temp range, °C	ρ(g cm^{-3}) = $a - bt$(°C)			V_m(cm^3 mol^{-1}) = $A + Bt$(°C)			$10^4\alpha$,[a] deg^{-1}
			a	10^4b	10^3(SE)	A	10^2B	SE	
0.0	10	27-71	1.7604	8.41	0.21	135.29	6.79	0.01	4.87
11.0	13	13-72	1.7381	8.12	0.31	125.78	6.12	0.03	4.73
20.4	9	24-67	1.7207	8.46	0.35	117.25	6.04	0.03	4.99
30.3	15	11-70	1.6974	8.25	0.26	108.50	5.49	0.02	4.91
40.5	14	12-72	1.6716	8.44	0.45	99.29	5.24	0.03	5.11
50.6	17	15-72	1.6365	8.35	0.50	90.40	4.82	0.03	5.17
60.3	12	26-76	1.5963	8.51	0.64	81.81	4.61	0.04	5.45
70.2	12	27-76	1.5499	8.35	0.27	72.87	4.16	0.02	5.52
80.1	11	28-74	1.4881	8.12	0.17	64.10	3.70	0.01	5.58

[a] At 60 °C.

Table II. Molar Volume–Composition Isotherms for Urea-Containing Melts of Calcium Nitrate Tetrahydrate

temp, °C	x_{urea}[a]	V_m(cm^3 mol^{-1}) = $A' - B'x$			$\overline{V}_m$(urea)
		A'	B'	SE	
60	0-0.8	139.43	91.20	0.07	48.23
40	0-0.8	138.10	90.49	0.07	47.61
20	0-0.8	136.75	89.71	0.07	47.04

[a] Composition range of urea (mol fraction).

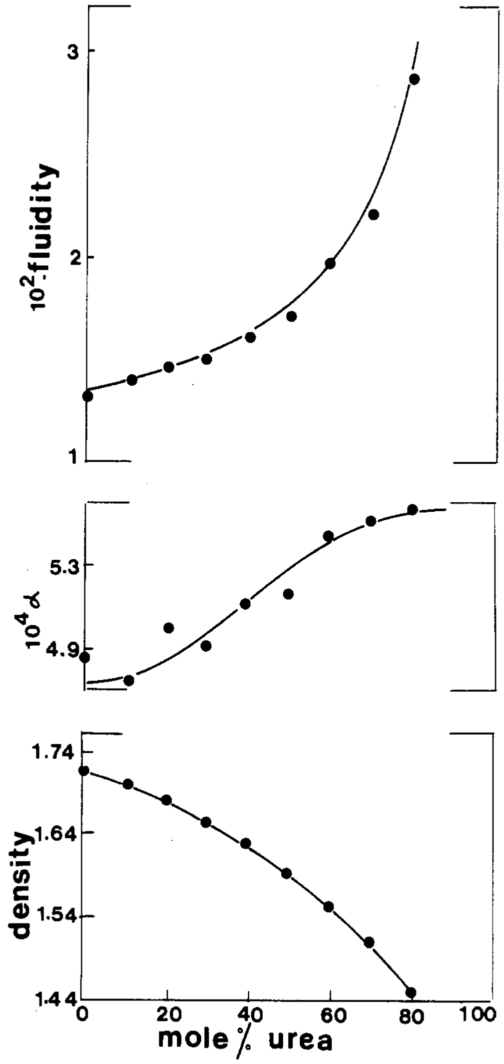

Figure 1. Composition dependence of density (g cm^{-3}), expansivity (K^{-1}), and fluidity (P^{-1}) for urea-containing melts of calcium nitrate tetrahydrate, at 60 °C.

might squeeze out water molecules from the coordination of calcium ion, with an increased possibility of cation–anion in-

Table III. Partial Molar Volume–Temperature Equation for Molten Urea and Calcium Nitrate Tetrahydrate

salt	temp range, °C	$\overline{V}_m$(cm^3 mol^{-1}) = $A'' + B''t$(°C)		
		A''	$10^2B''$	10^2 × (SE)
$Ca(NO_3)_2 \cdot xH_2O$[a]	20-60	135.41	6.70	0.82
NH_2CONH_2	20-60	46.43	2.97	2.0

[a] $x = 4.12$.

Table IV. Least-Squares Fit of Fluidity Data for Melts Containing Urea and Tetrahydrate of Calcium Nitrate

[urea], mol %	temp range, °C	$\ln \phi(P^{-1}) = \ln \overline{A}_\phi - B_\phi/(T - T_{0,\phi})$			
		$\ln \overline{A}_\phi$	B_ϕ	$T_{0,\phi}$	SE
0.0	27-71	0.831	599.5	207	0.006
11.0	6-72	0.495	530.7	212	0.024
20.4	11-70	0.772	581.1	207	0.011
30.3	8-70	0.591	546.8	209	0.009
40.5	8-72	0.556	535.6	209	0.006
50.6	8-72	0.743	567.8	205	0.017
60.3	9-76	0.528	512.6	208	0.004
70.2	8-76	0.596	513.5	207	0.034
80.1	10-74	0.678	513.1	202	0.009

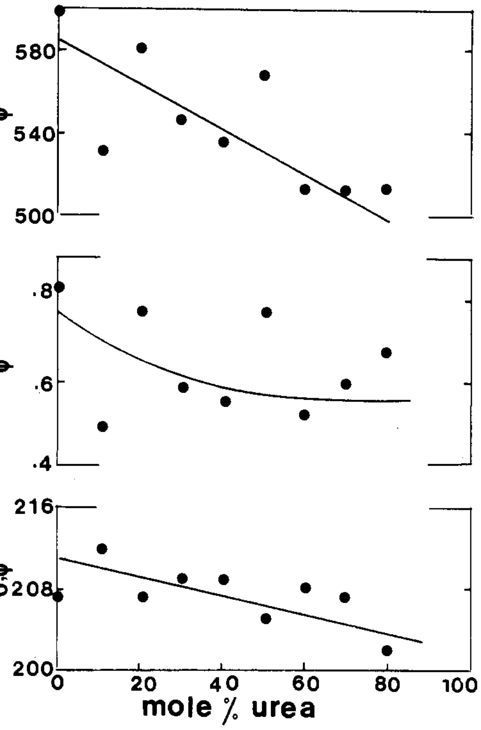

Figure 2. Variation of the parameters $\overline{A}_\phi$, B_ϕ, and $T_{0,\phi}$ with composition for urea-containing melts of calcium nitrate tetrahydrate.

teraction leading to a partial neutralization of the cationic charge.

Registry No. Calcium nitrate tetrahydrate, 10022-68-1; urea, 57-13-6.

Literature Cited

(1) Angell, C. A. *J. Electrochem. Soc.* **1965**, *112*, 1224.
(2) Angell, C. A. *J. Phys. Chem.* **1965**, *69*, 2137.
(3) Angell, C. A. *J. Phys. Chem.* **1966**, *70*, 3988.
(4) Angell, C. A. *J. Chem. Phys.* **1967**, *46*, 4673.
(5) Angell, C. A.; Bressel, R. D. *J. Phys. Chem.* **1972**, *76*, 3244.
(6) Ambrus, J. H.; Moynihan, C. T.; Macedo, P. B. *J. Electrochem. Soc.* **1972**, *119*, 192.
(7) Moynihan, C. T.; Smalley, C. R.; Angell, C. A.; Sare, E. J. *J. Phys. Chem.* **1969**, *73*, 2287.
(8) Braunstein, J.; Orr, L.; Alvarez-Funes, A. R.; Braunstein, H. *J. Electroanal. Chem.* **1966**, *15*, 337.
(9) Braunstein, J.; Orr, L.; MacDonald, W. *J. Chem. Eng. Data* **1967**, *12*, 415.
(10) Braunstein, J.; Alvarez-Funes, A. R.; Braunstein, H. *J. Phys. Chem.* **1966**, *70*, 2734.
(11) Moynihan, C. T. *J. Phys. Chem.* **1966**, *70*, 3399.
(12) Moynihan, C. T.; Fratiello, A. *J. Am. Chem. Soc.* **1967**, *89*, 5546.
(13) Jain, S. K. *J. Chem. Eng. Data* **1973**, *18*, 397.
(14) Jain, S. K. *J. Chem. Eng. Data* **1977**, *22*, 383.
(15) Jain, S. K. *J. Chem. Eng. Data* **1978**, *23*, 170, 216, 266.
(16) Jain, S. K. *J. Phys. Chem.* **1978**, *82*, 1272.
(17) Jain, S. K.; Tamamushi, R. *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn*). **1980**, *74*, 73.
(18) Jain, S. K.; Tamamushi, R. *Can. J. Chem.* **1980**, *58*, 1697.
(19) Jain, S. K.; Singh, V. V. *J. Chem. Eng. Data* **1982**, *27*, 84.
(20) Ewing, W. W.; Mikovsky, R. J. *J. Am. Chem. Soc.* **1950**, *72*, 1390.
(21) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(22) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.

Received for review September 14, 1982. Accepted June 15, 1983. Financial assistance from the University Grants Commission, Delhi, is thankfully acknowledged.

Crystallization Curves for Binary Mixtures of Alkanes, Acids, and Alcohols

G. Gioia-Lobbia* and G. Vitali

Dipartimento di Scienze Chimiche, Università degli Studi, 62032 Camerino, Italy

The liquid–solid temperatures for the binary mixtures *n*-octacosane + hexadecanoic and dodecanoic acids, diphenyl + *n*-octacosane or *n*-tetracosane, cyclododecanol or cyclododecane + *n*-octacosane or *n*-tetracosane are measured by using a method previously described. The experimental cryoscopic lowering and thermodynamic values are discussed by comparison with literature data.

Introduction

In our laboratory we are at present studying (*1*, *2*) the use of group interaction theory in organic mixtures (*3*, *5*) and also parameters affecting the liquid–liquid equilibria (*6*–*8*). The statistical treatment of the systems previously studied (*1*) showed that, when there is high incidence of liquid–liquid equilibrium phenomena, a low coordination number is obtained (example, bicarboxylic acids + monocarboxylic acids, bicarboxylic acids + esters).

We plan to study extensively other binary systems which exhibit these features: a high coordination number (as was the case, in previous work (*1*), for mixtures with alkanes) and also differences in the polar character of the compounds. With this aim we report liquid–solid equilibrium temperatures for the following binary systems: *n*-octacosane + hexadecanoic and dodecanoic acids, diphenyl + *n*-octacosane or *n*-tetracosane, cyclododecanol or cyclododecane + *n*-octacosane or *n*-tetracosane.

Experimental Section

The experimental method employed has been widely described in previous papers (*10*, *11*). The initial crystallization temperature of the molten mixtures was determined with a chromel–alumel thermocouple (standardized with an NBS-certified Pt resistance thermometer) connected to a Leeds and Northrup type K-5 potentiometer. Pyrex tubes containing molten mixtures were put into a furnace where the temperature was controlled with a second thermocouple, connected to a Leeds and Northrup CAT control unit. If measurements had to be repeated, an auxiliary heater was used to ensure quick remelting.

A reliability of better than 0.3 K was expected, while a repeatability of within 0.06 K was obtained with a slow cooling rate (0.3 K/min).

The chemicals used were Fluka or Ega products of high purity and were not purified further before use. They were dried under dynamic vacuum.

Results and Discussion

Experimental values of the crystallization temperature are reported in Table I as a function of mole fraction and are shown in Figures 1–4. In Table II $\Delta T/m$ values extrapolated to $m = 0$ are reported. In Table III the coordinates of the eutectic point are given. When the enthalpy of fusion was available from the literature, a comparison between the experimental and thermodynamic cryoscopic constant was possible.

In *n*-tetracosane the solutes behaved regularly as shown by the agreement between K_T and $(\Delta T/m)_0$. In *n*-octacosane, monocarboxylic acids as solutes show $(\Delta T/m)_0$ values much lower than K_T. This behavior may be ascribed to dimer association as previously observed (*1*, *14*). Degrees of association of 0.74 and 0.60 may be calculated for dodecanoic and hexadecanoic acids, respectively, at low concentrations. The behavior of diphenyl–alkanes systems is more complicated. In fact, when diphenyl is the solvent, $(\Delta T/m)_0 \ll K_T$, contrary to when alkanes are solvents $(\Delta T/m)_0 \simeq K_T$. It is probable that formation of solid solutions occurs in the crystallization zone of diphenyl, while in the crystallization region of the alkane equilibrium occurs between liquid and pure solid alkane. For the alkane in hexadecanoic acid the cryoscopic behavior is regular. $(\Delta T/m)_0$ values for cyclododecane and cyclododecanol could not be used for critical analysis owing to the lack of thermodynamic fusion data. The $(\Delta T/m)_0$ value, concerning the systems with cyclododecane, predicts with reasonable accuracy

0021-9568/84/1729-0016$01.50/0