

Density and Electrical Conductance of Calcium Nitrate Tetrahydrate + Acetamide Melt

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Density and electrical conductance of the calcium nitrate tetrahydrate + acetamide melt were measured as functions of temperature and mole fraction of acetamide. On the basis of the additivity of molar volume, an alternative method has been suggested for estimating the densities of high- or low-melting anhydrous inorganic and organic salts using a suitable hydrate melt as solvent. Molar conductance data were analyzed by using the Vogel–Tammann–Fulcher equation. At ambient temperature the specific conductance of molten calcium nitrate tetrahydrate decreases by the addition of acetamide as was the case with the addition of KNO_3 .

Introduction

A considerable amount of research in the field of molten salt chemistry deals with the development of room temperature molten electrolytes which are important for use as electrolytes for high-voltage batteries and as media for carrying out chemical reactions.

Hydrate melts are one kind of room temperature molten electrolyte which possess remarkable chemical properties. Due to the presence of aquometal complexes, hydrate melts have high acidic behavior and their acidity can be controlled by the addition of a second salt (1–3). Acetamide is reported to have very interesting acid–base properties and has become in recent times a potential salt in room temperature molten salt chemistry (4, 5). We aim at investigating the physicochemical properties of mixtures of hydrate melt and acetamide. Reported here are the density and electrical conductivity data of a mixture of molten calcium nitrate tetrahydrate and acetamide as functions of temperature and composition.

Experimental Section

Calcium nitrate tetrahydrate (Merck) was used without further purification. Acetamide (Thomas Baker) was recrystallized from its ethanol solution and then stored in a vacuum desiccator. The methods of sample preparation and density measurements were the same as described elsewhere (6). Electrical conductivity measurements were made at 1 kHz frequency using a B905 Wayne Kerr automatic precision bridge and dip-type cell of cell constant 120.6 m^{-1} . A thermostated oil bath was used to regulate the temperature.

Results and Discussion

With the help of the density vs concentration isotherm of the $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ system (7), the actual $\text{H}_2\text{O}/\text{Ca}^{2+}$ mole ratio in the calcium nitrate tetrahydrate sample used was estimated to be 4.26 ± 0.01 .

The experimental values of the density, d , of molten $(1-x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ system (Table 1) vary linearly with temperature, t , and were therefore least-squares-fitted to the expression

$$d/(\text{kgm}^{-3}) = a - b(t/^\circ\text{C}) \quad (1)$$

The least-squares-fitted values of the constants a and b

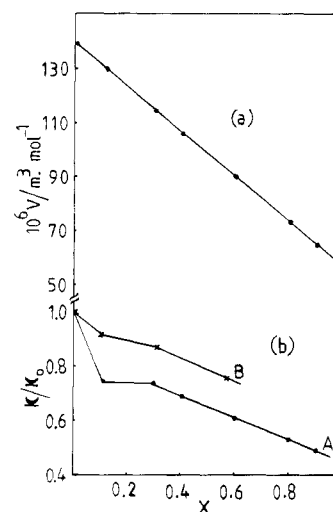


Figure 1. (a) Molar volume and (b, A) κ/κ_0 for $(1-x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ melts (\bullet) versus x . (b, B) κ/κ_0 for $(1-x) \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + x \text{KNO}_3$ melts (\times) versus x (from ref 12). κ_0 is the specific conductance of the hydrate melt medium.

for the melts of different x are given in Table 2. x denotes the mole fraction of acetamide.

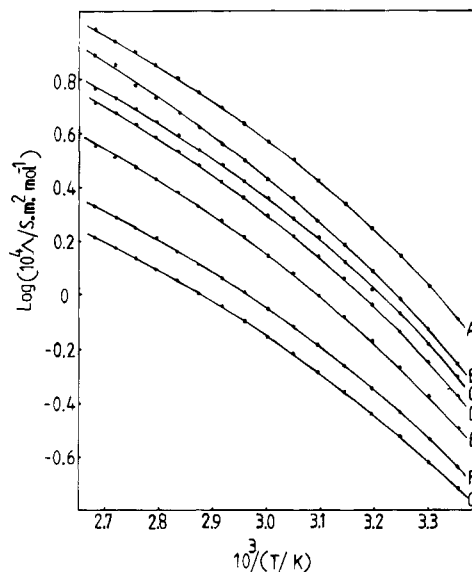
Although addition of acetamide to molten calcium nitrate tetrahydrate causes the density to decrease nonlinearly, the molar volume, V , decreases linearly with increasing x (Figure 1a). Similar behavior of d and V was reported in a molten mixture of calcium nitrate tetrahydrate and urea also (8). It may be noted that this type of variation of d and V with the mole fraction of solute is a general observation made in molten mixtures consisting of a hydrate melt as the solvent and an anhydrous inorganic salt as the solute (6, 9–11).

The observation made in the present and previous studies (6, 8–11) regarding the molar volume of binary mixtures consisting of a hydrate melt as one of the components indicates the possibility of employing an alternative method to estimate the densities of high- or low-melting anhydrous inorganic and organic salts. The proper choice of a hydrate melt as the solvent medium is what is most important in this method. This alternative method will be quite useful to measure indirectly the density of molten salts both above and below (supercooled) the melting points especially when the salts either decompose on melting or have high melting points.

Table 1. Experimental Values of the Density, d , of $(1 - x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ Melts

$t/^\circ\text{C}$	$10^{-3}d/(\text{kgm}^{-3})$	$t/^\circ\text{C}$	$10^{-3}d/(\text{kgm}^{-3})$	$t/^\circ\text{C}$	$10^{-3}d/(\text{kgm}^{-3})$
$x = 0.0$					
26.1	1.7283	53.2	1.7047	80.4	1.6825
30.0	1.7248	57.1	1.7016	84.3	1.6793
34.0	1.7214	61.0	1.6981	88.2	1.6761
37.9	1.7177	65.0	1.6951	92.1	1.6728
41.8	1.7145	68.8	1.6918	96.0	1.6696
45.6	1.7114	72.7	1.6888	99.9	1.6664
49.4	1.7079	76.5	1.6856		
$x = 0.111$					
33.6	1.6952	56.0	1.6762	79.3	1.6569
37.4	1.6918	59.8	1.6728	83.1	1.6538
41.2	1.6889	63.7	1.6697	86.9	1.6507
45.0	1.6857	67.6	1.6665	90.6	1.6476
48.7	1.6825	71.5	1.6633	94.4	1.6443
52.4	1.6794	75.4	1.6601	98.2	1.6411
$x = 0.300$					
34.6	1.6193	57.0	1.6004	79.3	1.5825
38.4	1.6161	60.7	1.5975	82.9	1.5796
42.2	1.6127	64.5	1.5942	86.6	1.5766
45.9	1.6096	68.3	1.5914	90.4	1.5736
49.6	1.6067	71.9	1.5883	94.1	1.5704
53.2	1.6035	75.6	1.5855	97.9	1.5675
$x = 0.401$					
21.7	1.5883	47.4	1.5665	76.2	1.5422
25.3	1.5851	51.1	1.5634	79.9	1.5395
28.8	1.5826	54.7	1.5601	83.6	1.5365
32.4	1.5791	62.0	1.5543	87.3	1.5338
36.4	1.5757	65.5	1.5512	91.0	1.5309
40.3	1.5724	69.0	1.5482	94.5	1.5280
44.2	1.5697	72.7	1.5454	98.2	1.5251
$x = 0.597$					
23.3	1.4704	50.9	1.4471	78.1	1.4252
26.4	1.4680	54.2	1.4444	81.5	1.4227
30.1	1.4648	57.6	1.4418	84.9	1.4201
33.8	1.4617	61.0	1.4389	88.2	1.4174
37.3	1.4586	64.5	1.4361	91.5	1.4147
40.5	1.4560	67.9	1.4335	94.9	1.4121
43.9	1.4531	71.3	1.4306	98.3	1.4092
47.4	1.4502	74.7	1.4281		
$x = 0.801$					
24.5	1.2987	52.6	1.2764	80.3	1.2547
27.6	1.2964	55.8	1.2737	83.3	1.2524
30.7	1.2938	59.0	1.2715	86.3	1.2500
33.9	1.2912	62.1	1.2690	89.5	1.2476
37.1	1.2885	65.2	1.2668	92.5	1.2452
40.2	1.2860	68.3	1.2644	95.6	1.2428
43.4	1.2837	71.4	1.2620	98.6	1.2405
46.5	1.2811	74.4	1.2596		
49.6	1.2787	77.4	1.2573		
$x = 0.900$					
25.7	1.1779	52.2	1.1574	77.6	1.1379
28.7	1.1756	55.2	1.1553	80.4	1.1358
31.7	1.1732	58.1	1.1530	83.2	1.1336
34.6	1.1707	61.0	1.1510	86.0	1.1314
37.5	1.1685	63.9	1.1489	88.9	1.1293
40.4	1.1664	66.7	1.1467	91.7	1.1271
43.4	1.1641	69.3	1.1446	94.4	1.1250
46.3	1.1618	71.9	1.1424	97.2	1.1229
49.3	1.1598	74.7	1.1401	100.0	1.1206
$x = 1.0$					
58.3	1.0163	70.2	1.0069	81.9	0.9975
60.8	1.0148	72.4	1.0050	84.1	0.9956
63.1	1.0125	74.9	1.0031	86.3	0.9938
65.5	1.0107	77.3	1.0012		
67.9	1.0088	79.5	0.9993		

The experimental values of the specific conductance, κ , of $(1 - x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ melts are given in Table 3 as functions of temperature t and x . The variation of the molar conductance, λ , with temperature T is non-Arrhenius and is illustrated in Figure 2. The molar conductance data were therefore least-squares-fitted to the

**Figure 2.** Arrhenius plots for the molar conductance of $(1 - x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ melts: A, $x = 0.0$; B, $x = 0.111$; C, $x = 0.300$; D, $x = 0.401$; E, $x = 0.597$; F, $x = 0.801$; G, $x = 0.900$.**Table 2. Parameters of Eq 1 for $(1 - x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ Melts**

x	$10^{-3}a$	b	corr coef
0.0	1.7495	-0.8340	-0.9999
0.111	1.7231	-0.8349	-0.9999
0.300	1.6471	-0.8152	-0.9999
0.401	1.6059	-0.8291	-0.9998
0.597	1.4890	-0.8140	-0.9999
0.801	1.3177	-0.7838	-0.9999
0.900	1.1978	-0.7678	-0.9999
1.0	1.0637	-0.8094	-0.9998

Table 3. Specific Conductance κ of $(1 - x) \text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ Melts

$t/^\circ\text{C}$	$10\kappa/(\text{S}\cdot\text{m}^{-1})$						
	$x = 0.0$	$x = 0.111$	$x = 0.300$	$x = 0.401$	$x = 0.597$	$x = 0.801$	$x = 0.900$
25.0	5.9193	4.3714	4.3976	4.0483	3.6102	3.1513	2.9369
30.0	7.8255	5.8092	5.8073	5.3603	4.7237	4.0049	3.6767
35.0	10.098	7.5614	7.5120	6.9007	6.0157	5.0137	4.5687
40.0	12.757	9.5763	9.3146	8.7540	7.4927	6.1350	5.5477
45.0	15.799	12.022	11.636	10.882	9.1748	7.4288	6.6426
50.0	19.095	14.654	14.200	13.098	10.915	8.8371	7.8279
55.0	22.854	17.661	16.870	15.724	13.296	10.365	9.1410
60.0	26.813	20.823	19.906	18.495	15.441	11.964	10.477
65.0	31.101	24.263	22.955	21.533	18.018	13.707	11.950
70.0	35.692	28.080	26.388	24.794	20.695	15.576	13.520
75.0	40.424	32.183	29.930	28.313	23.446	17.469	15.120
80.0	45.419	36.370	33.906	31.948	26.352	19.470	16.776
85.0	50.725	40.929	37.869	35.827	29.380	21.504	18.490
90.0	56.088	45.406	41.628	39.646	32.441	23.602	20.250
95.0	61.495	53.539	45.973	43.729	35.397	25.795	22.102
100.0	67.295	58.614	49.748	47.949	38.904	28.038	23.932

Vogel-Tammann-Fulcher (VTF) equation of the form

$$\lambda/(\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}) = A \exp\{(B/K)/(T - T_0)\} \quad (2)$$

The least-squares-fitted values of the three constants A , B , and T_0 are listed in Table 4. The ideal glass transition temperature, T_0 , of the molten mixture decreases with the addition of acetamide. The variation of κ/κ_0 , where κ_0 is the specific conductivity of the hydrate melt, with x is shown in Figure 1b. A similar plot has also been drawn in Figure 1b for the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{KNO}_3$ melt on the basis of its reported specific conductivity data (12). These

Table 4. Values of the Parameters of Eq 2 for $(1 - x)$ $\text{Ca}(\text{NO}_3)_2 \cdot 4.26\text{H}_2\text{O} + x \text{CH}_3\text{CONH}_2$ Melts and Standard Deviation σ of $\ln \lambda$

x	$\ln A$	B	T_0/K	$\sigma(\ln \lambda)$
0.0	-4.0597	470.50	210.4	0.0028
0.111	-4.0993	509.42	209.0	0.0195
0.300	-4.4690	489.49	208.2	0.0058
0.401	-4.4384	524.08	205.1	0.0028
0.597	-4.7963	535.89	201.6	0.0071
0.801	-5.5399	501.79	200.6	0.0029
0.900	-5.8014	513.37	196.7	0.0025

plots indicate that κ of a hydrate melt decreases with the addition of a solute, whether the solute is an inorganic or organic salt.

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