Electrical Conductivity and Phase Transitions of Calcium Nitrate + Ammonium Nitrate + Water Mixtures†

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ARTICLE

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Electrical Conductivity and Density of Ammonium Nitrate + Formamide Mixtures

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ABSTRACT: The electrical conductivity of ammonium nitrate + formamide mixtures was measured as a function of temperature for the ammonium nitrate concentration range (0 to 17) $mol \cdot kg^{-1}$. The report describes the application and validity of Casteel–Amis equation to fitting the experimental data as a function of salt content in the electrolyte in the temperature range (303.15 to 353.15) K. Also, the densities of the mixtures were determined pycnometrically at different temperatures and ammonium nitrate concentrations for all of the investigated melts.

INTRODUCTION

Salts characterized by low melting points, often below room temperature, have been developed and studied extensively during the past few years.[1,2] Liquid salts may serve as electrolytes in electrochemical devices, or may be used as a new phase change materials (PCM) suitable for thermal energy storage.[3] In a combination with some thermochromic substances, these PCMs containing eutectic mixture of two inorganic salts, or inorganic salt and one organic component, have been investigated earlier.[4−11] They have been proposed for simultaneous control of agricultural greenhouses from overheating, increasing the plant quality and decreasing the consumption of fossil fuels for heating. In our previous paper, we reported transport and thermal properties of calcium nitrate tetrahydrate–ammonium nitrate mixtures[12] giving a new assessment and experimental confirmation of quasi-crystal theory of molten salts using electrical conductivity measurements.

In this work, we systematically study and analyze the electrical conductivity of ammonium nitrate + formamide mixtures over a wide range of concentrations. Also, the density data are reported for all investigated mixtures. We applied and checked validity of the empirical Casteel–Amis equation[13] to fitting the experimental data as a function of salt content in the electrolyte in the investigated temperature range from (303.15 to 353.15) K. The background of Casteel-Amis equation and the attempts to extend the equation from a univariate to a multivariate function, was described elsewhere.[14]

EXPERIMENTAL SECTION

All used chemicals were pro analysi products. Ammonium nitrate (Merck) was dried at 353.15 K and stored in desiccator over phosphorus pentoxide. Formamide (J. T. Baker) was distilled and used without additional purification. The mixtures for the electrical conductivity measurements were prepared by melting together appropriate amounts of ammonium nitrate and formamide, dried by prolonged heating at 353.15 K. The electrical conductivity measurements were carried out in a Pyrex cell with platinum electrodes in the temperature range (303.15 to 353.15) K on a conductivity meter Jenco 3107. The total volume of the cell was 14 cm^3. The conductivity cell was thermostatted, and the temperature was kept constant to ± 0.1 K. Temperature and conductivity data acquisitions were made by a personal computer connected to a conductivity meter. The experimental cell was calibrated with standard 0.1000 $mol \cdot dm^{-3}$ KCl solution by the same experimental procedure. The resulting cell constant amounted to 0.8944 cm^{-1}, and it was checked from time to time to control any possible evolution. The estimated uncertainty for electrical conductivity was ± 0.5 %. Each experimental conductivity value used for further calculations is the average of three measurements.

The densities of the melt solutions, were determined pycnometrically at different temperatures and ammonium nitrate concentrations. They were determined using a pycnometer having a bulb volume of 10 cm^3. The volume of the pycnometer was calibrated as a function of temperature using distilled water at various temperatures. The pycnometer filled with liquid was kept in a thermostatically controlled and well-stirred water bath maintained at a constant temperature to within ± 0.1 K for (15 to 20) min to attain thermal equilibrium. The density measurements were carried out at temperatures from (308.15 to 348.15) K. Each experimental density value is the average of three measurements. Repeated experimental measurements showed reproducibility within 0.05 %, and an average value was used in further calculations.

Our experimental electrical conductivity and density data have been deposited at the editorial office and can be obtained upon request from the authors.

RESULTS AND DISCUSSION

Density. The best linear fit of our experimental density (d) data

$$d/g \cdot cm^{-3} = A - B \cdot (T/K) \quad (1)$$

yielded the coefficients A and B given in Table 1 for the dependence of the melt density on temperature (T) over the

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Table 1. Coefficients of the Equation $d/g \cdot cm^{-3} = A + B \cdot T(K)$ of Ammonium Nitrate + Formamide Mixtures in the Temperature Range (308.15 to 348.15) K for Different Formamide/Ammonium Nitrate Mole Ratios (R)

$m(NH_4NO_3)$	R	A	$B \cdot 10^4$	correlation	$SD \cdot 10^3$
17.08	1.3	1.566	7.546	0.9978	0.7851
14.80	1.5	1.532	6.999	0.9993	0.4612
13.06	1.7	1.525	7.141	0.9990	0.5855
11.10	2.0	1.517	7.436	0.9986	0.7255
8.881	2.5	1.495	7.417	0.9976	0.9368
7.401	3.0	1.477	7.379	0.9992	0.5457
5.551	4.0	1.467	7.759	0.9991	0.5905
4.441	5.0	1.435	7.304	0.9993	0.4805
3.700	6.0	1.446	8.000	0.9980	0.9137
3.172	7.0	1.430	7.858	0.9993	0.5164
2.775	8.0	1.443	8.410	0.9998	0.2781
2.467	9.0	1.424	8.037	0.9989	0.6850
2.220	10	1.412	7.828	0.9978	0.9598
2.018	11	1.407	7.840	0.9993	0.5312
1.850	12	1.408	7.961	0.9986	0.7672
1.708	13	1.410	8.088	0.9990	0.6650
1.586	14	1.412	8.296	0.9980	0.9563
1.480	15	1.398	7.910	0.9996	0.3868
1.388	16	1.411	8.372	0.9992	0.6221
1.306	17	1.403	8.181	0.9984	0.8425
1.234	18	1.405	8.264	0.9999	0.2656
1.169	19	1.384	7.712	0.9991	0.5985
1.110	20	1.394	8.042	0.9993	0.5551
0.8881	25	1.398	8.313	0.9981	0.9323
0.7401	30	1.403	8.587	0.9991	0.6553
0.6344	35	1.390	8.260	0.9985	0.8271
0.5551	40	1.397	8.527	0.9990	0.6859
0.4934	45	1.392	8.398	0.9997	0.4051
0.4440	50	1.399	8.676	0.9981	0.9637
0.2775	80	1.388	8.458	0.9994	0.5419
0.2220	100	1.378	8.222	0.9994	0.4994
0.1480	150	1.379	8.300	0.9998	0.3236
0.1110	200	1.381	8.410	0.9986	0.8071
0.04440	500	1.373	8.264	0.9994	0.5039
0		1.373	8.300	0.9999	0.07504

range (308.15 to 348.15) K and for ammonium nitrate molality (m) up to 17 $mol \cdot kg^{-1}$. The uncertainties in the ammonium nitrate molality and the temperature were less than ± 0.0001 $mol \cdot kg^{-1}$ and ± 0.05 K, respectively.

In Figure 1, the experimental densities at five different temperatures were plotted against ammonium nitrate molality (m). Density increases with the increase of ammonium nitrate molality, with significantly larger changes in the region with less ammonium nitrate.

Electrical Conductivity. The electrical conductivity was determined at different temperatures for the ammonium nitrate + formamide mixtures with different $HCONH_2/NH_4NO_3$ mole ratios (R). Conductivity measurements of these liquid mixtures were performed for the first time. The conductivity of the mixtures was measured in the composition range of ammonium nitrate molality (m) 0.04 < $m/mol \cdot kg^{-1}$ < 17.1 or $HCONH_2/NH_4NO_3$ mole ratio 1.3 < R < 500.

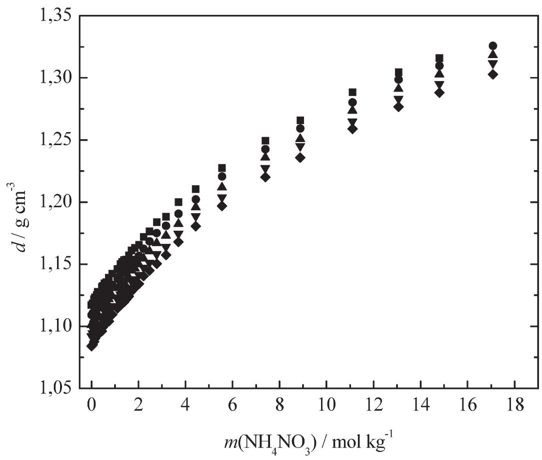

Figure 1. Variation of experimental density values vs ammonium nitrate molality at different temperatures (in Kelvin): ■, 308.15; ●, 318.15; ▲, 328.15; ▼, 338.15; ♦, 348.15.

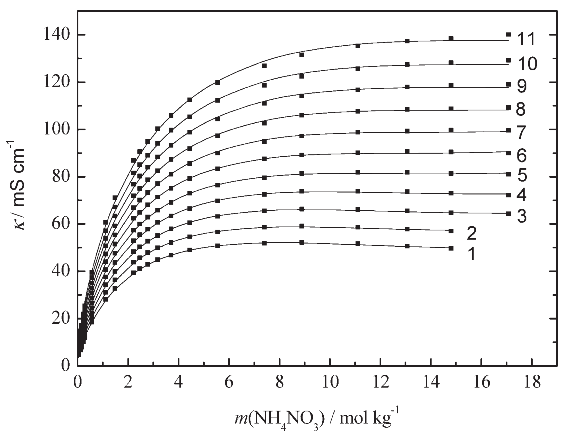

Figure 2. Electrical conductivity isotherms of ammonium nitrate + formamide mixtures at different temperatures (in Kelvin): **1**, 303.15; **2**, 308.15; **3**, 313.15; **4**, 318.15; **5**, 323.15; **6**, 328.15; **7**, 333.15; **8**, 338.15; **9**, 343.15; **10**, 348.15; **11**, 353,15.

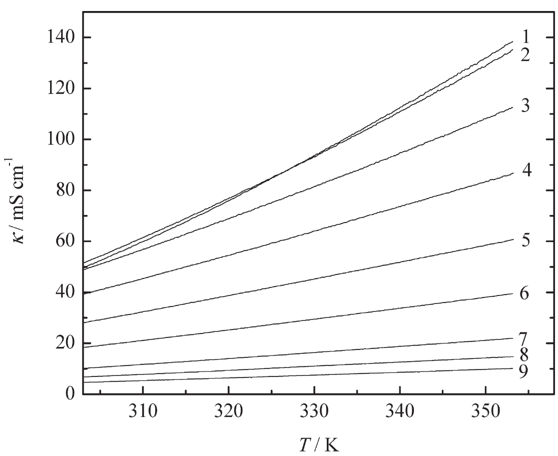

Figure 3. Electrical conductivity of ammonium nitrate + formamide mixtures vs temperature at different $HCONH_2/NH_4NO_3$ mole ratio R: **1**, 1.5; **2**, 2.0; **3**, 5.0; **4**, 10; **5**, 20; **6**, 40; 7, 100; **8**, 200; **9**, 500.

In Figure 2 the experimental conductivity isotherms at eleven different temperatures were plotted against ammonium nitrate molality. As it can be seen from Figure 2, the electrical conductivity increases with the increase of temperature and ammonium nitrate molality. In the region of low ammonium nitrate concentration, the electrical conductivity is low, due to a strong solvation effect and small mobility of solvated ions. Addition of ammonium nitrate caused desolvation process and strong ion−ion interactions, which will be reflected in the conductivity increase. These changes are significant in the formamide-rich region.

Electrical conductivity of several selected ammonium nitrate + formamide mixtures which cover all the composition range is presented in Figure 3 as a function of temperature. From Figure 3 it can be seen that specific conductivity increase with increase of ammonium nitrate content in the mixture (lower $HCONH_2/NH_4NO_3$ mole ratio) at constant temperature. These values are significantly lower than the corresponding conductivity data obtained for aqueous ammonium nitrate solutions.[15]

The experimental conductivity, κ, was well-represented by the following equation:

$$\kappa/\mathrm{mS \cdot cm^{-1}} = \mathrm{A} + \mathrm{B} \cdot (T/\mathrm{K}) + \mathrm{C} \cdot (T/\mathrm{K})^2 \qquad (2)$$

where κ is specific conductivity, T is the absolute temperature, and A, B, and C are coefficients determined by the least-squares method. All coefficients are listed in Table 2.

After large number of trials to fit our measured conductivity data with different widely used equations, we applied the so-called Casteel−Amis equation in the following form for the fitting:

$$\kappa = \kappa_{\max}(m/\mu)^a \exp[b(m-\mu)^2 - a(m-\mu)/\mu] \qquad (3)$$

where κ is the specific conductivity, $\kappa_{\max}$ is the parameter corresponding to a maximum conductivity at μ molality, and m is the salt molality. The parameters a and b are the constants. The obtained a, b, $\kappa_{\max}$,and μ values of the eq 3 are reported in Table 3.

The most important parameters of the eq 3 are $\kappa_{\max}$ and μ. These parameters determine the position of the maximal electrical conductivity value on the isotherm and may be used for the validity check of the eq 3 at different salt compositions and

Table 2. Coefficients of the Equation $\kappa/\mathrm{mS \cdot cm^{-1}} = \mathrm{A} + \mathrm{B}(T/\mathrm{K}) + \mathrm{C}(T/\mathrm{K})^2$ of Ammonium Nitrate + Formamide Mixtures in the Temperature Range (303.15 to 353.15) K

$m(NH_4NO_3)$	R	A	B	$C \cdot 10^3$	correlation	SD
17.08	1.3	120.6	−2.026	5.890	0.9999	0.2010
14.80	1.5	160.7	−2.211	6.080	0.9999	0.2002
13.06	1.7	123.0	−1.936	5.600	1.0000	0.1936
11.10	2.0	89.95	−1.670	5.090	1.0000	0.1509
8.881	2.5	−5.022	−1.012	3.960	1.0000	0.1519
7.401	3.0	−28.02	−0.8059	3.530	1.0000	0.1501
5.551	4.0	−41.98	−0.6134	3.030	1.0000	0.1282
4.441	5.0	−60.07	−0.4232	2.580	1.0000	0.1207
3.700	6.0	−120.8	0.01085	1.790	1.0000	0.1226
3.172	7.0	−106.7	−0.01986	1.710	1.0000	0.1110
2.775	8.0	−146.5	0.2712	1.170	1.0000	0.1085
2.467	9.0	−143.2	0.2811	1.080	0.9999	0.1100
2.220	10	−127.0	0.2073	1.130	0.9999	0.1053
2.018	15	−125.0	0.3028	0.7159	0.9999	0.09633
1.850	20	−106.7	0.2678	0.5835	1.0000	0.07161
1.708	40	−62.82	0.1353	0.4372	1.0000	0.04667
1.586	80	−39.33	0.07850	0.2966	0.9999	0.03325
1.480	100	−39.96	0.1047	0.2000	0.9999	0.03739
1.388	150	−41.62	0.1432	0.06648	0.9998	0.03544
1.306	200	−33.09	0.1062	0.08321	0.9998	0.03851
1.234	500	−10.81	9.912×10^{-4}	0.1653	0.9998	0.02229

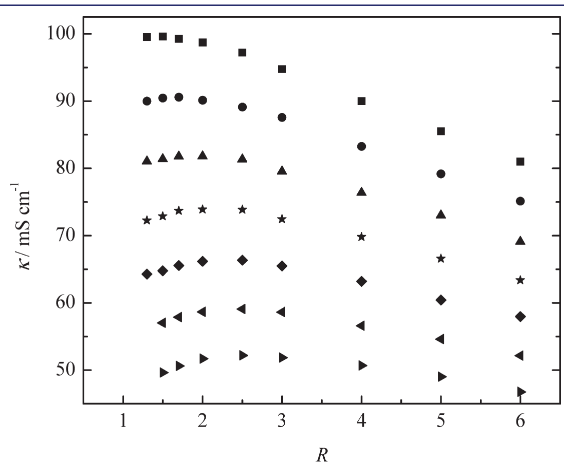

Figure 4. Electrical conductivity vs $HCONH_2/NH_4NO_3$ mole ratio R at different temperatures: right pointing triangle, 303.15 K; left pointing triangle, 308.15 K; ♦, 313.15 K; ★, 318.15 K; ▲, 323.15 K; ●, 328.15 K; ■, 333.15 K.

Table 3. Coefficients of the eq 3 Obtained by Fitting the Experimental Data

T/K	$\kappa_{\max}/\mathrm{mS \cdot cm^{-1}}$	error $\kappa_{\max}$	a	error $a \cdot 10^3$	$b \cdot 10^3$	error $b \cdot 10^3$	$\mu/\mathrm{mol \cdot kg^{-1}}$	error μ	corr.	SD
303.15	52.21	0.198	0.6753	9.86	2.583	0.220	7.86	0.115	0.9998	0.3785
308.15	58.91	0.228	0.6731	9.93	2.554	0.220	8.39	0.139	0.9998	0.4249
313.15	66.23	0.229	0.6644	8.93	2.271	0.151	8.91	0.140	0.9997	0.4607
318.15	73.75	0.278	0.6611	9.68	2.169	0.162	9.54	0.185	0.9998	0.5487
323.15	81.45	0.294	0.6597	9.31	2.162	0.154	10.48	0.318	0.9996	0.5747
328.15	89.90	0.301	0.6557	9.32	2.067	0.153	12.58	13.9	0.9998	0.6260
333.15	98.77	0.368	0.6468	10.7	1.803	0.175	13.35	162	0.9998	0.7785
338.15	108.1	0.439	0.6379	11.6	1.559	0.188	14.40	126	0.9997	0.9080
343.15	117.7	0.587	0.6312	12.6	1.380	0.203	15.23	110	0.9994	1.064
348.15	127.4	0.742	0.6255	13.4	1.241	0.215	16.08	386	0.9993	1.207
353.15	137.6	1.04	0.6216	15.0	1.129	0.239	17.01	110	0.9992	1.438

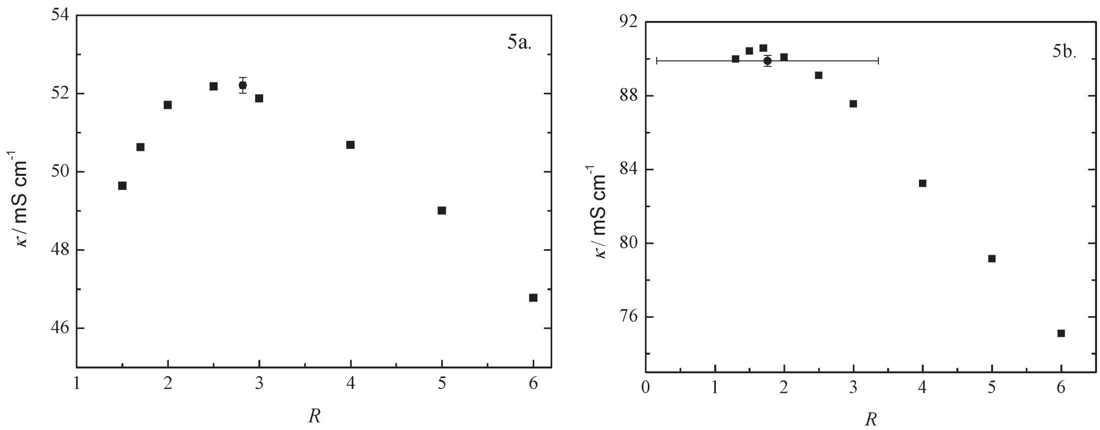

Figure 5. Comparison of the experimental obtained and calculated κ_{max} value at μ molality of ammonium nitrate (molality is recalculated and expressed as mole ratio R) at 303.15 K (a) and 328.15 K (b): ■, experimental values; ●, calculated values.

temperatures. In Figure 4 several electrical conductivity isotherms are presented vs $HCONH_2/NH_4NO_3$ mole ratio R using the coefficients from Table 3. The mole ratio scale was used instead of ammonium nitrate molality to mark maximal conductivity values more visible. Looking at the position of this value in Figure 3 and obtained values of κ_{max} and μ in Table 3, one can be concluded that these parameters have their significant meaning only up to 323.15 K. Above that temperature, the eq 3 can be used to fit obtained experimental data, since the correlation parameters of the equation are very high. However, parameters κ_{max} and μ in that case will not represent the value of conductivity maximum and its position, since the substantial errors (also presented in Table 3) are too large.

As it can be seen from Figure 5, the experimental value of electrical conductivity maximum and its position are in a good agreement with calculated one using the Casteel-Amis equation (Figure 5a). After this temperature, equation satisfactory fits the experimental results, but the calculated position of the maximal electrical conductivity and ammonium nitrate molality are not in agreement with experimental value (Figure 5b).

■ CONCLUSION

In this paper the electrical conductivity and density of several ammonium nitrate + formamide binary mixtures were determined. The application and validity of the Casteel−Amis equation to fit the experimental conductivity data as a function of the ammonium nitrate content in the temperature range (303.15 to 353.15) K was checked. The equation was used in the entire temperature range to fit our data, but the parameter of the equation κ_{max} successfully determines the position of the electrical conductivity maximum at ammonium nitrate molality μ only up to 323.15 K. Also, the density of ammonium nitrate formamide mixtures were determined and reported for the first time.

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