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Solubility of Aqueous Mixtures of Alkaline Nitrates and Nitrites Determined by Differential Scanning Calorimetry

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The solubility of aqueous electrolyte solutions is a critical property for absorption refrigeration and heat pump working fluids. In this paper, we report a systematic study on the solubility of 21 alkaline nitrate and nitrite mixtures determined by a visual polythermal method. The solubility of the mixtures ($LiNO_3 + NaNO_3 + KNO_3$) + H_2O with salt mass ratios of 53:19:28 and 53:05:42 and ($LiNO_3 + KNO_3 + NaNO_2$) + H_2O with salt mass ratios of 53:35:12 and 60:36:04 was further determined accurately by differential scanning calorimetry. Saturation temperature data of these mixtures were correlated with the total salt mass fraction using empirical polynomial equations. The mixtures of $LiNO_3 + NaNO_3 + KNO_3$ (53:05:42) and $LiNO_3 + KNO_3 + NaNO_2$ (53:35:12) showed the highest solubility in water.

Introduction

Of the various absorption refrigeration technologies currently being investigated, the multiple effect types exploit the thermal potential of combustion fuel better than the double effect absorption systems and are therefore more energy efficient, being able to compete with the electrical systems. At present, triple effect systems are being developed but are still in the prototype stage. The greatest difficulty in this area has been found in the thermal stability of the working fluid and the components with which it is in contact, which must withstand working temperatures of above 430 K. The fluid that is most commonly used in direct-fired double effect absorption chillers is water/lithium bromide. It has serious drawbacks at temperatures above 415 K because of its corrosive effects and thermal decomposition.

In the mid-1980s, Erickson[1,2] patented the use of aqueous alkaline nitrate and nitrite solutions as working fluids for absorption heat pumps working at high temperatures (530 K). The main component was lithium nitrate because of its absorbent character. According to Erickson, the addition of alkaline nitrates and/or nitrites improved not only the solubility of the salt but also other characteristics of the mixture. Davidson and Erickson[3] suggested using an aqueous mixture of $LiNO_3 + KNO_3 + NaNO_3$ with a salt ratio in the mass fraction of 53:28:19. This composition led to optimal solubility and gave no problems of corrosion or thermal stability.

Ally[4,5] studied the vapor pressures and specific heats of this solution, and the absorption cycle of a heat transformer [(470 to 530) K], and found that it gave better efficiency, temperature lift, and absorption capacity than the water/lithium bromide mixture.

In the early 1990s, Howe and Erickson[6] termed the Davidson and Erickson[3] mixture "Alkitrates". They characterized the mixture by carrying out various tests on corrosivity and thermal stability in pilot plants and concluded that it was a suitable working fluid for absorption cycles at high temperature (530 K). Since then, several authors[7–11] have studied the thermophysical properties of the mixture and the absorption cycles when it is used as a working fluid.

Because there is little experimental information available on the solubility of the mixture proposed by Davidson and Erickson,[3] or on other possible mixtures with different ratios of alkaline nitrates and nitrites, we decided to study the solubility properties of these types of mixtures. Our objective was to identify, from the solubility point of view, which mixtures would be most useful in multieffect absorption cycles at high temperature. In the present study, we have determined the crystallization temperatures of 21 mixtures of alkaline nitrates and/or nitrates with different compositions as well as the one proposed by Davidson and Erickson[3] (which was used as a reference mixture). The crystallization temperature of each of the mixtures was roughly determined by means of a visual polythermal method. On the basis of the results obtained, the mixtures with a lower solubility than that of the reference mixture were discarded, and those with higher solubilities were selected for further investigation. The saturation temperatures of the thus selected mixtures were determined accurately using the differential scanning calorimetric technique. The present study is the first part of a wider and more systematic study on thermophysical properties of these mixtures.

Experimental Procedure and Data Processing

Materials. The mixtures were prepared using lithium nitrate (Aldrich, > 99.0 %), sodium nitrate (Merck, > 99.5 %), potassium nitrate (Aldrich, > 99.0 %), sodium nitrite (Aldrich, > 99.5 %), and deionized water. The salts were dried in a drying oven at 378 K for at least 24 h and then kept in a laboratory desiccator at ambient temperature until use.

Equipment and Experimental Procedure. All the samples were prepared using a Mettler balance (AE260 DeltaRang) with an accuracy of ± 0.1 mg. The initial assays to identify

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Table 1. Components and Compositions of the 21 Aqueous Solutions of Alkaline Nitrates and Nitrites Measured in the Present Study

sample	components	salt mass fraction ratio
A1	$(LiNO_3 + NaNO_3 + KNO_3) + H_2O$	53:19:28
A2	“	53:28:19
A3	“	53:23:24
A4	“	53:20:27
A5	“	53:11:36
A6	“	53:05:42
A7	“	60:04:36
A8	“	55:05:40
B1	$(LiNO_3 + NaNO_3 + NaNO_2) + H_2O$	53:30:17
B2	“	53:40:07
B3	“	53:17:30
B4	“	51:11:38
C1	$(LiNO_3 + KNO_3 + NaNO_2) + H_2O$	53:28:19
C2	“	53:35:12
C3	“	53:42:05
C4	“	53:20:27
C5	“	53:10:37
C6	“	55:33:12
C7	“	60:30:10
C8	“	55:40:05
C9	“	60:36:04

the mixtures with relatively high solubilities were carried out in test tubes, and the temperature was kept constant by using a Haake C35 temperarature controller with 0.1 K resolution. The aqueous solution of $LiNO_3 + NaNO_3 + KNO_3$ prepared with a salt mass ratio of 53:19:28, respectively, and a total salt mass fraction of 0.75 was taken as the reference mixture (A1). Twenty more mixtures were prepared with different salt compositions but keeping the total mass fraction of salt in water constant at 0.75. Table 1 lists the composition of each mixture studied.

The approximate crystallization temperature of mixture A1 (reference) was determined by placing the test tube with the sample in the thermal bath at 353.15 K for 30 min with constant manual stirring to ensure that all the salts were completely dissolved. The mixture was then cooled at intervals of 5 K, with stirring for at least 15 min at each interval. The crystallization temperature for this sample was observed to be between (338.15 and 343.15) K. The crystallization temperatures for the remaining mixtures were also determined by the same procedure. Three mixtures whose crystallization temperatures were found to be lower than that of the reference sample were used for further investigation.

The precise saturation temperatures of different concentrations in aqueous solution of these three mixtures were determined by a calorimetric technique. The method used a DSC Setaram C80 calorimeter, which included a system for constant agitation by inversion during the measurements. Each sample was held in a Reversal Mixing Cell provided by Setaram. The proper formation of the salt solution was assured by increasing the temperature of the calorimeter to at least 10 K above the estimated saturation temperature, at a heating rate of 1 $K \cdot min^{-1}$ and maintaining this temperature for 2 h. Subsequently, the sample was cooled to 303.15 K at a cooling rate of 1 $K \cdot min^{-1}$ and kept at this temperature for 2 h.

The heating rate selected for each measurement was 0.1 $K \cdot min^{-1}$, and the temperature range was extended from (303.15 to 10) K above the estimated saturation temperature. Finally, a cooling ramp was programmed with a cooling rate of 1 $K \cdot min^{-1}$ until the initial temperature of 303.15 K was reached.

Table 2. Saturation Temperatures of Aqueous Sodium Nitrate Solutions, for Different Total Salt Mass Fractions (w_{salts}), Heating Rates ($r/K \cdot min^{-1}$), and Standard Deviations (sd_T) of the Measurements

$r/K \cdot min^{-1}$	$100\ w_{salts}$	T/K	sd_T
0.010	53.60	325.29	0.01
0.050	53.86	325.26	0.01
0.075	53.86	325.24	0.01
0.100	53.60	325.23	0.02
0.150	53.60	324.65	0.03
0.200	53.60	325.18	0.05
0.250	53.04	322.91	0.02
0.500	53.04	322.55	0.03
0.750	53.04	322.78	0.05
1.000	53.04	322.90	0.02

Data Processing. To determine the saturation temperature with the calorimeter, we considered the extrapolated initial baseline from the heat flow rate signal (Φ/W) as the saturation temperature. Data processing was carried out using a MatLab program, since the calorimeter's software did not permit this treatment. For each experiment, the process was as follows: from the heat flow rate and the temperature (T/K) values, a Gaussian-type fit was obtained (eq 1)

$$\Phi = a_1 \cdot \exp(-((T - b_1)/c_1)^2) + a_2 \cdot \exp(-((T - b_2)/c_2)^2) \tag{1}$$

where a_i, b_i, and c_i are the adjustable parameters of the equation. The initial extrapolated baseline is obtained by the cutting point of the baseline with the tangent in the inflection point on the heat flow rate curve. Since the coordinates of the inflection point depend on the fit and this in turn depends on the upper and lower limits selected for obtaining this fit, at least six calculations were carried out with different limits of the fit. Finally, a mean value of the extrapolated initial baseline is calculated with its corresponding standard deviation, and this is considered to be the saturation temperature.

Validation of the Method

The calorimetric method was validated measuring the saturation temperature of aqueous solutions of sodium nitrate with salt mass fractions between 0.5331 and 0.5387, at heating rate values between 0.01 $K \cdot min^{-1}$ and 1.00 $K \cdot min^{-1}$. The composition uncertainty was determined by the following method: first, the composition of each sample was calculated, taking into account that the initial sodium nitrate was (99.5 ± 0.5) % pure. To calculate the combined uncertainty, we considered a rectangular distribution for the uncertainty associated with the purity ($u\{\text{purity}\} = 0.005/\sqrt{3}$), and the uncertainty of the weighing based on technical information given by the manufacturer. The results yielded a combined uncertainty of ± 0.0015 for all the samples prepared.

Table 2 shows the results obtained for the different measurements at different heating rate values. The results compared with the values proposed by Archer[12] showed relative deviations lower than 0.15 % and also that there was no significant variation in this relative deviation as a function of the heating rate. So, the heating rate value can be selected as a useful compromise between the duration of the measurement (the slower it is, the longer the measurement lasts) and the quality of the signal (the faster it is, the more likely it is that the signal is not stable when the solubility value is obtained). These criteria and the results obtained were used to choose a heating rate of 0.10 $K \cdot min^{-1}$ in this study.

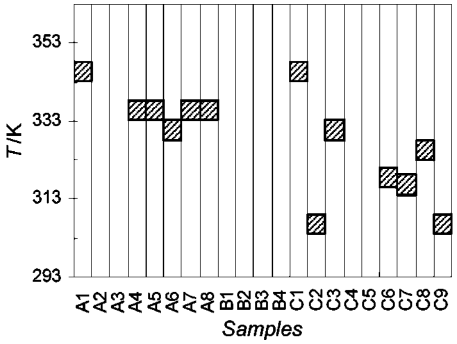

Figure 1. Crystallization temperatures determined for 21 salt-mixture samples by a visual polythermal method.

Table 3. Saturation Temperatures of Mixture A1 ($LiNO_3$ + $NaNO_3$ + KNO_3) + H_2O with a Salt Mass Ratio of 53:19:28 for Different Total Salt Mass Fractions (w_{salts}) and Standard Deviations (sd_T) of the Measurements

100 w_{salts}	T/K	sd_T
68.47	319.36	0.01
70.37	324.05	0.04
72.19	330.97	0.01
75.11	342.31	0.05
76.73	344.39	0.02
79.95	353.65	0.10
82.62	352.56	0.01
84.95	367.58	0.01
87.70	392.79	0.06
89.83	408.07	0.03
93.29	425.56	0.05

Table 4. Saturation Temperatures of Mixture A6 ($LiNO_3$ + $NaNO_3$ + KNO_3) + H_2O with a Salt Mass Ratio of 53:5:42 for Different Total Salt Mass Fractions (w_{salts}) and Standard Deviations (sd_T) of the Measurements

100 w_{salts}	T/K	sd_T
68.62	327.80	0.08
71.93	328.05	0.02
74.07	329.15	0.10
75.07	329.21	0.03
77.34	331.49	0.01
78.04	330.08	0.02
79.37	335.24	0.01
82.41	341.23	0.02
84.81	358.20	0.11
87.31	382.02	0.02
89.54	397.77	0.04
93.33	415.65	0.01

Table 5. Saturation Temperatures of Mixture C2 ($LiNO_3$ + KNO_3 + $NaNO_2$) + H_2O with a Salt Mass Ratio of 53:35:12 for Different Total Salt Mass Fractions (w_{salts}) and Standard Deviations (sd_T) of the Measurements

100 w_{salts}	T/K	sd_T
72.48	314.71	0.01
75.01	318.20	0.05
77.50	327.44	0.03
80.00	333.30	0.03
81.23	337.44	0.01
83.06	341.90	0.02
84.92	346.09	0.01
86.26	358.75	0.04
88.50	372.38	0.08
88.80	379.23	0.02
90.01	387.50	0.10
90.56	390.45	0.08
91.44	398.69	0.06
92.34	406.11	0.01
94.04	416.38	0.02

Table 6. Saturation Temperature of Mixture C9 ($LiNO_3$ + KNO_3 + $NaNO_2$) + H_2O with a Salt Mass Ratio of 60:36:04 for Different Total Salt Mass Fractions (w_{salts}) and Standard Deviations (sd_T) of the Measurements

100 w_{salts}	T/K	sd_T
69.98	315.93	0.01
72.49	315.33	0.01
74.92	314.24	0.01
77.37	314.77	0.16
78.96	332.91	0.01
80.68	344.15	0.02
81.50	349.52	0.11
83.05	366.12	0.11
83.67	369.93	0.01
85.80	388.12	0.06
87.02	396.26	0.01
88.45	409.10	0.01
90.01	418.67	0.00

Table 7. Parameters of Equation 2 for Different Mixtures

sample	composition range	a_0/K	a_1/K	a_2/K	rmsd[a]
A1	68.41 to 82.62	−594.653	22.241	−0.130	0.46
"	82.62 to 93.29	−1628.292	38.911	−0.181	0.52
A6	68.62 to 82.41	882.606	−15.562	0.109	0.29
"	82.41 to 93.33	−2089.92	49.318	−0.241	0.50
C2	72.48 to 84.92	160.058	1.668	0.006	0.30
"	84.92 to 94.04	−797.374	18.626	−0.061	0.36
C9	69.98 to 77.34	576.076	−6.909	0.046	0.08
"	77.34 to 90.01	−794.599	19.632	−0.068	0.42

[a] Root mean standard deviation.

Results and Discussion

Figure 1 shows the results obtained from the measurements of the crystallization temperature for the 21 mixtures studied using the visual polythermal method. The crystallization temperatures of mixtures A2, A3, B1, B2, B3, B4, C4, and C5 are higher than that of the reference mixture (A1). For this reason, they have not been represented in Figure 1.

The systematic study of saturation temperature was made by differential scanning calorimetry for mixtures A1, A6, C2, and C9, with salt mass fractions of between 0.68 and 0.94. Mixture A6 was chosen, despite not being one of the most soluble, so as not to limit the study to mixtures with the same components in different compositions.

Tables 3 to 6 show the experimental results obtained for each of the selected mixtures.

The experimental values of the saturation temperature for each mixture were correlated with the total salt mass fraction using second-order polynomial functions (eq 2) in two ranges. The parameters obtained, as well as the resulting deviations, are given in Table 7.

$$T/\mathrm{K} = a_0 + a_1(100\cdot w) + a_2(100\cdot w)^2 \qquad (2)$$

Figure 2 shows the saturation temperature in relation to the total salt mass fraction of the four mixtures and includes both the experimental and calculated results.

As shown in Figure 2, the solubilities of mixtures A6 and C2 are higher than that of the reference A1 throughout the range of compositions studied.

It can also be observed that mixture C9, with the highest content of $LiNO_3$ (mass fraction of 0.6), is less soluble than the reference mixture for compositions with total salt mass fractions higher than 0.81 and more soluble below it.

Conclusions

To find useful working fluids for heat absorption cycles, a systematic study was made of the solubility of different ternary

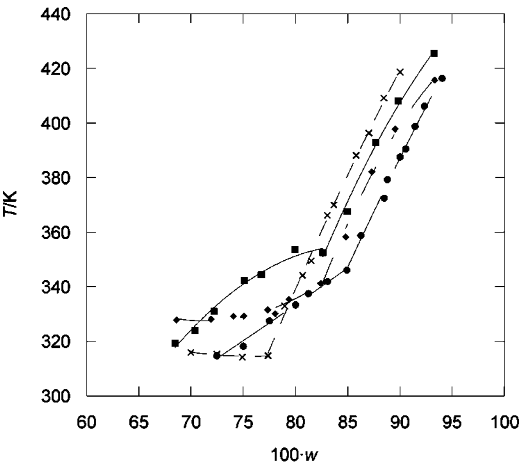

Figure 2. Experimental and calculated values of the saturation temperature as a function of the total salt mass fraction for the mixtures studied. Calculated values obtained using eq 2. Experimental values: ■, A1; ♦, A6; ●, C2; **x**, C9.

mixtures of alkaline nitrates and nitrites in water. Initially, the crystallization temperatures of 21 mixtures of alkaline nitrates and nitrites were roughly determined by a visual polythermal technique to select some mixtures for precise determination of their saturation temperatures.

The precise saturation temperatures of aqueous solutions of $LiNO_3 + NaNO_3 + KNO_3$ with salt mass ratio values of 53:05:42 and 53:19:28 and of $LiNO_3 + KNO_3 + NaNO_2$ with salt mass ratio values of 53:35:12 and 60:36:04 were determined by using a calorimetric technique. The total salt mass fractions of the solutions ranged between 0.68 and 0.95. The experimental results were correlated with the total salt mass fraction for each mixture.

The mixtures of $LiNO_3 + NaNO_3 + KNO_3$ (53:05:42) and $LiNO_3 + KNO_3 + NaNO_2$ (53:35:12) showed better solubility in water than the mixture proposed by Davidson and Erickson.[3] So, these mixtures are potential working fluids for high-temperature absorption chillers.

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