Vapor−Liquid Equilibrium of Ammonia + Lithium Nitrate + Water and Ammonia + Lithium Nitrate Solutions from (293.15 to 353.15) K

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The vapor pressure of ammonia + lithium nitrate + water and ammonia + lithium nitrate mixtures was measured by a static method from (293.15 to 353.15) K in ammonia mass fractions ranging from 0.2 to 0.6. The experimental vapor pressure data were correlated with the temperature and the liquid-phase composition using an analytical polynomial equation. The capability of the electrolyte nonrandom two liquid (E-NRTL) model to predict the vapor−liquid equilibrium (VLE) of the ternary mixture was evaluated by comparing predicted and experimental data of the ammonia + lithium nitrate + water solutions. The binary interaction parameters of ammonia + lithium nitrate needed for the prediction of ternary VLE were determined from binary experimental data.

Introduction

Nowadays, absorption refrigeration systems and heat pumps use water + lithium bromide and ammonia + water mixtures as working fluids. These working fluids have some drawbacks, such as crystallization and corrosion problems, low-pressure operation conditions for the lithium bromide + water mixtures, and the need of rectification of the refrigerant vapor at the desorber outlet for the ammonia + water mixtures. Alternative working fluids, such as ammonia + lithium nitrate,[1−5] have been studied, to avoid the need of rectification. Besides this advantage, the refrigeration cycle using this mixture operates at lower desorber temperatures than those required by ammonia + water. Nevertheless, the heat and mass transfer in the absorber are limited by the viscosity of the salt solutions. To overcome this drawback, Ehmke et al.[6] and Bokelmann[7] proposed the addition of water to the binary mixture to be used in absorption heat pumps. Later, Reiner and Zaltash[8,9] proposed the use of the ternary mixture for GAX systems as an alternative for the ammonia + water systems.

Ehmke[10] studied the effect of water on the solubility and viscosity of the ternary mixtures and suggested an optimal water mass fraction between 0.20 and 0.25 in the absorbent mixture ($LiNO_3$ + H_2O). This author also determined and correlated the density and vapor pressure of the solutions with a 0.25 water mass fraction of the absorbent mixture. Bokelmann[7] reported experimental research concerning the performances of an absorption heat pump. These data were reported by Manago[11] in a study on new mixtures for absorption heat pumps in the frame of the Heat Pump Program of The International Energy Agency. Reiner and Zaltash[8,9] measured the densities and viscosities of ternary mixtures with an ammonia mass fraction of 0.04 and a water mass fraction of 0.605, the typical composition for GAX systems. They also correlated these properties with the temperature using the least-squares method. In addition, the boiling point of this mixture was measured at atmospheric pressure.

In 1989, Bothe[12] presented a comparative study between the ammonia + water system and the ammonia + water + lithium nitrate ternary mixture. They obtained higher operation temperatures and important efficiency improvements for the ternary mixture compared with the binary, in refrigeration and heat pump applications. It was also remarked that rectification was a minor need, which increases the refrigeration capacity.

This work is part of a research project on absorption refrigeration cycles activated by low-temperature heat sources as waste heat, or solar thermal energy. Thermodynamic properties, especially vapor−liquid equilibria (VLE), are needed for the design of absorption systems. Ehmke[10] studied the VLE of the mixture for a water mass fraction in the absorbent mixture (lithium nitrate + water) of 0.25. The main objective of this work is to extend the database of vapor−liquid equilibrium data available for different water contents in the absorbent lithium nitrate + water mixture, in ammonia mass fraction and temperature ranges of interest for refrigeration absorption systems. Thus, the vapor−liquid equilibrium of the NH_3 + $LiNO_3$ + H_2O mixture was systematically studied in the temperature range (293.15 to 353.15) K, in 10 K steps, for ammonia total mass fractions from 0.20 to 0.55. The water total mass fraction in the absorbent solution was varied between 0.20 and 0.30.

Due to the complexity of the measurement of such mixtures, the capability of the electrolyte nonrandom two liquid (E-NRTL) model to predict the vapor−liquid equilibrium of ternary mixtures was verified by comparing calculated and experimental data. To predict the equilibrium of the studied ternary mixture, vapor−liquid equilibrium data of the binary NH_3 + $LiNO_3$ mixture were needed due to the absence of values for interaction parameters NH_3/Li^+NO^{3-}. Vapor−liquid equilibrium experimental data of the binary NH_3 + $LiNO_3$ mixture available in the literature are limited; therefore, it was also studied in the temperature range from (293.15 to 353.15) K, in 10 K steps, for ammonia total mass fractions from 0.35 to 0.65, because of the solubility problems for lower ammonia mass fraction.

The vapor pressures of the different compositions of binary (NH_3 + $LiNO_3$) and ternary (NH_3 + $LiNO_3$ + H_2O) mixtures were measured using a static method, and the vapor and liquid compositions were calculated from the total initial composition, the experimental pressure, and the temperature. Further, the

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equilibrium data were correlated using the polynomial equation proposed by Cacciola et al.,[13] and finally, experimental and calculated data were compared with those available in the literature.[10,14,15]

Experimental Section

Materials. Ammonia (Carburos Metálicos, 99.98 %), lithium nitrate (Fluka, ≥ 99 %), and Millipore water (resistivity lower than 18.2 MΩ) were used without further purification.

Equipment and Procedures. The vapor pressure of ammonia + lithium nitrate + water solutions was measured by a static method. The equipment and the measurement procedure were previously described by Herraiz et al.[16] and Salavera et al.[17] It consisted of an equilibrium cell, a differential pressure null transducer (DPT, Ruska model 2439-702), a differential pressure null indicator (Ruska model 2416-711), a precise pressure controller (Ruska model 3891-801), and a double walled thermostated bath of 0.40 m^3 capacity filled with water. The temperature in the bath was controlled using two Haake proportional temperature controllers with 0.1 K resolution, an N3 unit for heating, and an EK90 immersion cooler. For the measurement of the temperature, a digital precision thermometer (Anton Paar MKT100) was employed. The standard uncertainty of the temperature measured was ± 0.005 K, according to the respective calibration certificate. The equilibrium cell was made of stainless steel, with a volume of 166 cm^3. For the ammonia transport, an auxiliary high-pressure stainless steel vessel of 149 cm^3 capacity was used. The pressure was measured by two digital pressure gauges: the 6222 Ruska unit for pressures up to 130 kPa and up to 1 MPa and the 6222-750 Ruska for pressures up to 5 MPa. The pressure uncertainties were ± 0.05 kPa for pressures lower than 130 kPa, ± 0.3 kPa for pressures lower than 1 MPa, and ± 0.6 kPa for higher pressures. The components were weighted on a Mettler balance (Mettler Toledo PR2003DR) with a precision of $\pm\ 10^{-3}$ g, and the vacuum was provided using a high-vacuum pump (Vacuumbrand RZ2/HP40B) with its ultimate pressure in the 10^{-6} kPa range.

The first step in preparing the solutions of ammonia + lithium nitrate and ammonia + lithium nitrate + water was to load the equilibrium cell with lithium nitrate and then dry it in the oven for at least 24 h at 105 °C. Then, it was degassed by several cycles of heating at 105 °C and vacuum extraction. Next, the corresponding quantity of water was added, for the case of the ternary mixture, and the equilibrium cell was connected to the transducer. Three absorbent solutions ($LiNO_3 + H_2O$) were prepared with a water total mass fraction of 0.20, 0.25, and 0.30.

The equilibrium cell with the mixture $LiNO_3 + H_2O$ prepared was frozen with liquid nitrogen, and then the incondensable gases were extracted using the vacuum pump. Next, ammonia was introduced in the cell from the auxiliary stainless steel vessel. The exact quantity of ammonia introduced was determined weighting the auxiliary stainless steel vessel. The filling process was done slowly, heating the auxiliary vessel and maintaining the cell frozen. Finally, the cell was slowly heated, and the sample was stirred to achieve a complete mixing.

The sample composition was changed by adding ammonia successively to the cell. The ammonia total mass fraction varied from 0.35 to 0.65 for the binary and from 0.20 to 0.55 for the ternary mixture.

The methodology adopted was previously validated for similar mixtures by Salavera et al.[17]

Results and Discussion

Experimental Results and Correlations. Vapor pressures of the $NH_3 + LiNO_3 + H_2O$ solutions were measured using a static method from 293.15 to 353.15 K, at 10 K intervals, varying the total ammonia mass fraction from 0.20 to 0.55, for three values of the total water mass fraction in $LiNO_3 + H_2O$: 0.20, 0.25, and 0.30. In addition, the vapor−liquid equilibrium data for ammonia + lithium nitrate were determined at the same temperatures for the ammonia mass fraction range 0.35 to 0.65.

The liquid-phase composition was determined using the Redlich−Kister equation (eq 1) to calculate the activity coefficient of the liquid phase (γ_i), as a polynomial difference between the amount-of-substance fractions (x_i)

$$\ln \gamma_i = \sum_{j=1}^{nc}\left[\sum_{n=1}^{5} x_j A_{n,ij}(x_i - x_j)^{n-2}(nx_i - x_j) - \frac{1}{2}\sum_{k=1}^{nc}\sum_{n=1}^{5} x_j x_k A_{n,jk}(x_j - x_k)^{n-2}[(2n-1)x_j - x_k]\right] \quad (1)$$

The adjustable parameters A_n of the Redlich−Kister equation depend lineally on the temperature and were regressed from the total initial composition, pressure, and temperature using the Deming algorithm,[18] to minimize the objective function Q defined as

$$Q = \sum\left(\frac{p_{e,i} - p_{m,i}}{\sigma_{P,i}}\right)^2 \quad (2)$$

where p_e and p_m are values of the estimated and measured pressure and $\sigma_{P,i}$ is the standard deviation. The vapor phase nonideality was modeled using the Redlich−Kwong equation-of-state. The calculations were carried out using the Aspen Properties software.[19]

The root-mean-square relative deviations were 0.002 % and 0.0003 % for the ternary and binary systems, respectively. The vapor pressure and liquid-phase composition at each temperature for the ternary and binary mixtures are shown in Tables 1 and 2, respectively.

The experimental values of pressure (p/kPa), temperature (T/K), and liquid-phase mass fraction (w_i) of the NH_3 (1) + $LiNO_3$ (2) mixture were correlated using a polynomial equation similar to that proposed by Cacciola et al.[13]

$$\ln(p/\text{kPa}) = \sum_{i=0}^{3} A_i w_1^i + \frac{\sum_{i=0}^{3} B_i w_1^i}{T/\text{K}} \quad (3)$$

The values of the adjustable parameters A_i and B_i are shown in Table 3, and the root-mean-square relative deviation is 0.8 %.

$p-T-w$ data for the ternary mixture NH_3 (1) + $LiNO_3$ (2) + H_2O (3) were fitted to the same equation, where A_i and B_i *are* polynomial functions of the water mass fraction as shown in eq 4.

$$A_i = \sum_{j=0}^{2} a_{ij} w_3^j \quad B_i = \sum_{j=0}^{2} b_{ij} w_3^j \quad \text{for } i = 0...3 \quad (4)$$

The values of the adjustable parameters a_{ij} and b_{ij} are shown in Table 4, with the root-mean-square relative deviation being 0.77 %.

Figures 1 and 2 show the comparison of the pressure values calculated using the Redlich−Kister equation (eq 1) and the

Table 1. Experimental Vapor Pressure *p* and Calculated Mass Fraction *w* for NH_3 (1) + $LiNO_3$ (2) + H_2O (3)

T/K	w_1	w_2	p/kPa	T/K	w_1	w_2	p/kPa	T/K	w_1	w_2	p/kPa
293.12	0.1994	0.6383	10.71	313.11	0.2005	0.5954	32.96	333.10	0.5959	0.3027	1678.5
303.17	0.1995	0.6381	17.75	323.10	0.1997	0.5962	49.88	341.95	0.5965	0.3021	2090.0
313.07	0.1996	0.6379	28.13	333.09	0.1993	0.5966	73.57	293.11	0.1993	0.5547	14.49
323.13	0.1988	0.6389	42.88	343.11	0.1991	0.5966	106.01	303.26	0.1997	0.5541	24.07
333.08	0.1983	0.6393	63.39	353.13	0.1991	0.5963	149.0	313.10	0.1987	0.5553	37.11
343.09	0.1980	0.6395	91.45	293.11	0.3021	0.5224	42.35	323.13	0.1987	0.5551	56.78
353.16	0.1979	0.6394	129.08	303.27	0.3024	0.5219	67.75	333.13	0.1985	0.5552	83.81
293.06	0.2990	0.5590	36.35	313.13	0.3017	0.5226	102.06	343.10	0.1987	0.5547	120.95
303.30	0.2993	0.5586	58.74	323.09	0.3012	0.5229	150.3	353.08	0.1986	0.5545	169.4
313.08	0.2990	0.5589	89.06	333.13	0.3004	0.5236	215.1	293.10	0.3006	0.4838	47.20
323.09	0.2981	0.5597	131.43	343.17	0.2997	0.5240	300.4	303.11	0.3001	0.4843	74.02
333.09	0.2978	0.5599	189.6	353.12	0.2988	0.5247	407.4	313.11	0.2991	0.4851	111.70
343.12	0.2974	0.5601	266.5	293.14	0.3975	0.4514	121.85	323.11	0.2981	0.4861	163.3
353.09	0.2970	0.5603	364.8	303.22	0.3975	0.4513	184.0	333.11	0.2970	0.4870	232.3
293.08	0.3982	0.4799	113.52	313.19	0.3974	0.4513	268.0	343.10	0.2962	0.4877	322.8
303.16	0.3972	0.4808	170.2	323.14	0.3970	0.4516	378.4	353.16	0.2952	0.4884	438.6
313.07	0.3971	0.4808	248.1	333.13	0.3961	0.4522	520.3	293.08	0.3981	0.4169	131.22
323.09	0.3967	0.4810	352.5	343.14	0.3951	0.4529	698.7	303.15	0.3986	0.4164	198.6
333.11	0.3965	0.4811	488.9	353.14	0.3939	0.4538	917.5	313.18	0.3983	0.4166	288.7
343.11	0.3959	0.4815	660.2	293.11	0.4452	0.4140	192.9	323.10	0.3976	0.4171	405.8
353.15	0.3948	0.4824	869.9	303.18	0.4460	0.4131	286.0	333.10	0.3966	0.4179	556.5
293.08	0.4475	0.4406	184.9	313.12	0.4456	0.4133	405.9	343.10	0.3954	0.4188	745.6
303.16	0.4476	0.4405	273.3	323.14	0.4449	0.4139	561.3	353.07	0.3942	0.4197	977.8
313.12	0.4479	0.4401	391.5	333.10	0.4440	0.4145	756.5	293.13	0.4491	0.3814	210.6
323.08	0.4471	0.4407	541.4	343.09	0.4429	0.4153	998.4	303.18	0.4493	0.3811	309.2
333.09	0.4466	0.4411	734.3	353.11	0.4416	0.4163	1291.5	313.07	0.4485	0.3818	435.1
343.14	0.4458	0.4417	974.0	293.11	0.5003	0.3740	300.4	323.10	0.4474	0.3825	599.5
353.11	0.4448	0.4425	1262.0	303.14	0.5000	0.3743	429.3	333.08	0.4464	0.3833	806.1
293.09	0.4995	0.3989	286.8	313.17	0.4991	0.3750	595.6	343.07	0.4451	0.3843	1060.7
303.08	0.4996	0.3987	412.9	323.17	0.4981	0.3757	806.0	353.13	0.4436	0.3854	1370.6
313.08	0.4987	0.3994	574.9	333.13	0.4971	0.3765	1066.6	293.09	0.5023	0.3441	317.8
323.08	0.4977	0.4003	780.9	343.12	0.4958	0.3775	1383.7	303.15	0.4994	0.3465	445.2
333.09	0.4967	0.4011	1038.7	353.16	0.4948	0.3782	1768.3	313.13	0.4986	0.3470	616.0
343.07	0.4955	0.4021	1351.9	293.10	0.5492	0.3358	412.4	323.10	0.4978	0.3477	831.8
353.17	0.4943	0.4031	1734.3	303.15	0.5486	0.3362	578.4	333.08	0.4970	0.3482	1101.3
293.07	0.5508	0.3578	406.5	313.11	0.5478	0.3368	788.1	343.19	0.4960	0.3490	1432.7
303.14	0.5498	0.3587	572.1	323.12	0.5471	0.3374	1052.6	353.13	0.4952	0.3495	1826.2
313.13	0.5483	0.3600	781.5	333.16	0.5463	0.3380	1379.0	293.08	0.5478	0.3132	420.5
323.13	0.5469	0.3612	1045.9	343.10	0.5455	0.3385	1769.8	303.19	0.5483	0.3127	592.3
333.14	0.5455	0.3624	1371.7	293.07	0.5968	0.3022	521.5	313.13	0.5484	0.3127	807.2
343.12	0.5439	0.3637	1764.3	303.30	0.5972	0.3018	728.9	323.10	0.5479	0.3130	1074.6
293.07	0.2005	0.5955	12.65	313.16	0.5968	0.3021	980.0	333.11	0.5480	0.3128	1408.1
303.15	0.2007	0.5953	20.91	323.09	0.5961	0.3026	1292.4	343.09	0.5483	0.3126	1809.6

Table 2. Experimental Vapor Pressure *p* and Calculated Mass Fraction *w* for NH_3 (1) + $LiNO_3$ (2)

T/K	w_1	p/kPa	T/K	w_1	p/kPa
293.15	0.3492	43.01	303.12	0.4966	347.6
303.13	0.3487	68.32	313.15	0.4959	491.3
313.14	0.3478	104.25	323.15	0.4949	675.3
323.09	0.3467	153.5	333.08	0.4935	903.5
333.10	0.3452	218.9	343.15	0.4917	1186.5
343.08	0.3438	304.0	353.08	0.4897	1522.5
353.06	0.3420	409.4	293.09	0.5466	362.8
293.14	0.3981	80.67	303.15	0.5451	511.6
303.14	0.3986	126.30	313.10	0.5432	700.3
313.09	0.3978	188.5	323.14	0.5407	936.4
323.11	0.3968	273.1	333.13	0.5378	1223.7
333.09	0.3953	383.2	343.15	0.5345	1567.6
343.08	0.3934	523.9	293.12	0.5986	502.4
353.10	0.3913	699.3	303.10	0.5971	695.1
293.09	0.4460	140.4	313.10	0.5947	936.4
303.11	0.4465	213.1	323.11	0.5921	1235.0
313.12	0.4462	311.0	333.13	0.5893	1598.2
323.16	0.4434	431.9	293.08	0.6475	618.0
333.16	0.4408	586.6	303.15	0.6471	851.6
343.13	0.4378	777.5	313.10	0.6457	1139.5
353.15	0.4341	1007.2	323.11	0.6442	1496.8
293.07	0.4975	239.5	333.17	0.6426	1932.6

empirical correlation (eq 3) as a function of the temperature, for different ammonia compositions.

In Figure 3, the vapor pressure data calculated with the correlation are compared with those reported by Ehmke[10] for the ternary mixture with a water mass fraction of 0.25 in the lithium nitrate + water mixture. The maximum deviation obtained was 7.1 % and the rmsd was 2.3 %.

Table 3. Coefficients of Equation 3 for the NH_3 (1) + $LiNO_3$ (2) System

coefficient	value	coefficient	value
A_0/kPa	4.99×10^0	B_0/kPa·K	-1.79×10^3
A_1/kPa	8.85×10^1	B_1/kPa·K	-2.23×10^4
A_2/kPa	-1.98×10^2	B_2/kPa·K	6.13×10^4
A_3/kPa	1.35×10^2	B_3/kPa·K	-4.52×10^4

Table 4. Coefficients of Equation 4 for the NH_3 (1) + $LiNO_3$ (2) + H_2O (3) System

coefficient	value	coefficient	value
a_{00}/kPa	1.19×10^1	b_{00}/kPa·K	-4.02×10^3
a_{10}/kPa	2.77×10^1	b_{10}/kPa·K	-2.43×10^3
a_{20}/kPa	-8.13×10^1	b_{20}/kPa·K	8.45×10^3
a_{30}/kPa	4.66×10^1	b_{30}/kPa·K	-7.46×10^3
a_{01}/kPa	-2.34×10^2	b_{01}/kPa·K	2.48×10^4
a_{11}/kPa	6.93×10^2	b_{11}/kPa·K	-5.09×10^4
a_{21}/kPa	-1.17×10^2	b_{21}/kPa·K	2.92×10^4
a_{31}/kPa	5.48×10^2	b_{31}/kPa·K	-2.65×10^4
a_{02}/kPa	-1.64×10^3	b_{02}/kPa·K	-1.35×10^1
a_{12}/kPa	9.39×10^1	b_{12}/kPa·K	-2.48×10^4
a_{22}/kPa	-5.13×10^2	b_{22}/kPa·K	1.82×10^4
a_{32}/kPa	1.58×10^3	b_{32}/kPa·K	-1.54×10^2

The results for the binary ammonia + lithium nitrate mixture were compared to the experimental data reported by Aggarwal.[14] The rmsd obtained was 6.9 %, with a maximum deviation of 18 %. The existence of a good agreement for low temperatures can be pointed out, but the deviation increases with the temperature.

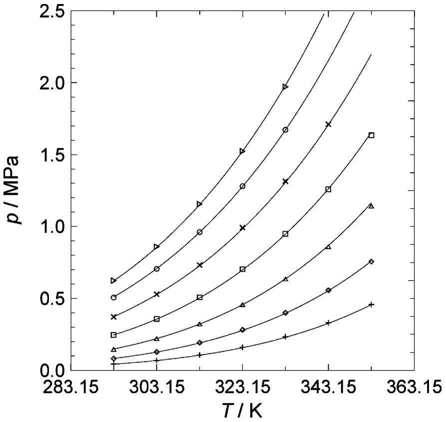

Figure 1. Comparison of calculated pressure using the Redlich−Kister method and the polynomial equation of the NH_3 (1) + $LiNO_3$ (2) system: +, $w_1 = 0.35$; ◇, $w_1 = 0.40$; △, $w_1 = 0.45$; □, $w_1 = 0.50$; ×, $w_1 = 0.55$; ○, $w_1 = 0.60$; |>, $w_1 = 0.65$; −, calculated pressure using eq 3.

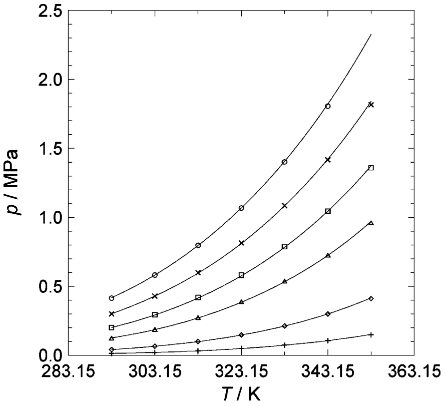

Figure 2. Comparison of calculated pressure using the Redlich−Kister method and the polynomial equation of the NH_3 (1) + $LiNO_3$ (2) + H_2O (3) system with $w_2/w_3 = 3{:}1$: +, $w_1 = 0.20$; ◇, $w_1 = 0.30$; △, $w_1 = 0.4$; □, $w_1 = 0.45$; ×, $w_1 = 0.55$; ○, $w_1 = 0.55$; −, calculated pressure using eq 4.

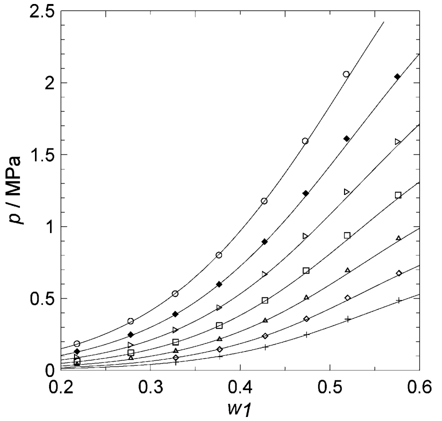

Figure 3. Total pressure of NH_3 (1) + $LiNO_3$ (2) + H_2O (3) at different temperatures for $w_2/w_3 = 3{:}1$. Experimental data presented by Ehmke:[10] +, 293.15 K; ◇, 303.15 K; △, 313.15 K; □, 323.15 K; |>, 333.15 K; ◆, 343.15 K; ○, 353.15 K; −, calculated pressure from eq 4.

Table 5. Parameters of Equation 5 for the NH_3 (1) + $LiNO_3$ (2) System

parameter	value
C_{13}	-2.143×10^1
C_{31}	-6.675×10^0
$D_{13}/(T/K)$	1.458×10^4
$D_{31}/(T/K)$	-9.219×10^2
E_{13}	3.679×10^2
E_{31}	1.194×10^1

Vapor−Liquid Equilibrium Prediction. Thermodynamic Model. The E-NRTL model was used to predict the vapor−liquid equilibrium of the ammonia + lithium nitrate + water ternary mixture. This activity coefficient model was proposed by Chen et al.[20,21] for electrolyte systems. The model is based on two fundamental assumptions: (a) the like-ion repulsion assumption which states that the local composition of cations around cations is zero and (b) the local electroneutrality assumption which states that the distribution of cations and anions around a central molecular species is such that the net local ionic charge is zero. On the basis of these assumptions, the model expresses the excess Gibbs energy as a sum of two contributions: one contribution due to the long-range ion−ion interactions (calculated using the Pitzer−Debye−Hückel model[22]) and the other, the short-range contribution, related to the local interactions between all the species (calculated using the NRTL model[23]).

The different equations that shape the E-NRTL model have been studied in different works;[20,21,24,25] therefore, in this paper, the parameters needed for the studied mixture NH_3 (1) + H_2O (2) + $LiNO_3$ (3) are presented. These are short-range binary interaction parameters (τ_{12}, τ_{21}, τ_{13}, τ_{31}, τ_{23}, and τ_{32}), representing the interaction energy between the liquid species, and the nonrandomness factors (α_{12}, α_{13}, and α_{23}).

An advantage of the local composition models is that the interaction parameters between two species in a binary mixture are the same in a multiple component mixture. This means that the vapor−liquid equilibrium of multiple component mixtures can be determined using the interaction parameters between the different species of the mixture, which can be obtained from the vapor−liquid equilibrium experimental data of the binary mixtures.

The complete thermodynamic treatment has been carried out using the Aspen Properties software, which has integrated an extensive database with properties and parameters of mixtures and pure components. For the thermodynamic treatment of the experimental data, the equilibrium reaction of ammonia + water and the total dissociation of lithium nitrate were taken into account. No other reactions, for LiOH formation, were considered. Thus, the interaction parameters of ammonia/water (τ_{12}, τ_{21}, and α_{12}) and water/lithium nitrate (τ_{23}, τ_{32}, and α_{23}) were found in the Aspen database but not those of ammonia/lithium nitrate (τ_{13}, τ_{31}, and α_{13}) that were obtained from our experimental VLE data.

Data Regression. Interaction parameters between ammonia and lithium nitrate were calculated from the binary experimental data (pressure, temperature, and total composition). Following the suggestion of Moch et al.[26] for electrolytes with nonaqueous solvent, we fixed the value of the nonrandomness factor α_{13} as 0.1. The binary interaction parameters τ_{13} and τ_{31} depend on the temperature as follows:

$$\tau_{ca,B} = C_{ca,B} + \frac{D_{ca,B}}{T} + E_{ca,B}\left[\frac{(T^{ref} - T)}{T}\right] + \ln\left(\frac{T}{T_{ref}}\right) \qquad (5)$$

where the subscript ca refers to electrolyte $Li^+NO_3^-$ and B refers to the NH_3 molecule. C, D, and E are adjustable coefficients, and the temperature is expressed in Kelvin. The value of the reference temperature (T^{ref}) is 293.15 K. Therefore, for our regression, the adjustable coefficients are C_{13}, C_{31}, D_{13}, D_{31}, E_{13}, and E_{31}. For the minimization of the objective function, carried out by the maximum likelihood, the Deming algorithm[18] was used. The parameters obtained by regression are shown in Table 5, and the corresponding rmsd value was 0.8 %.

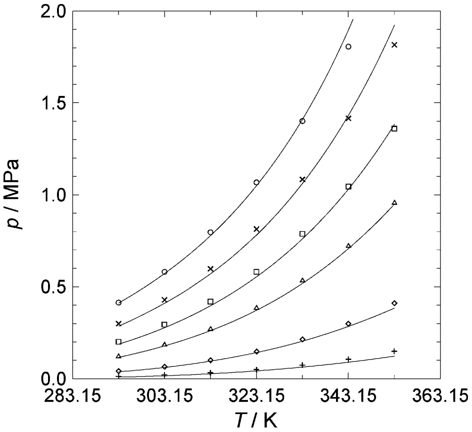

Figure 4. Comparison of calculated pressure using the Redlich−Kister method and predicted pressure using the E-NRTL model of the NH_3 (1) + $LiNO_3$ (2) + H_2O (3) system for w_2/w_3 = 3:1: +, $w_1 = 0.20$; ◇, $w_1 = 0.30$; △, $w_1 = 0.40$; □, $w_1 = 0.45$; ×, $w_1 = 0.55$; ○, $w_1 = 0.55$; −, predicted pressure using the E-NRTL model.

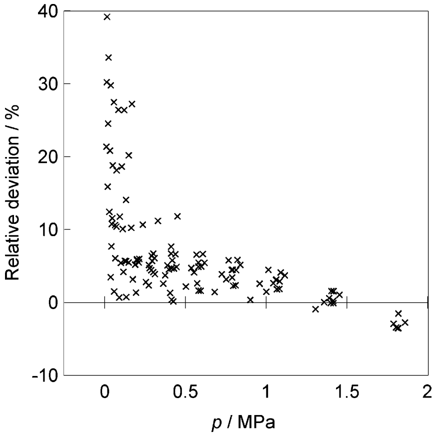

Figure 5. Relative deviation between the calculated pressure using the Redlich−Kister method and the predicted pressure using the electrolyte-NTRL model.

Vapor−Liquid Equilibrium Prediction. Using the regressed parameters from the experimental data for the ammonia + lithium nitrate mixture and those included in the Aspen Properties database for the other binary mixtures, the vapor pressures of the ammonia + lithium nitrate + water mixture for the compositions experimentally measured have been determined in the same temperature range from 293.15 K to 353.15 K. The rmsd value between the calculated data using the Redlich−Kister equation and predicted data using the E-NRTL model was 10.4 %.

The predicted and calculated vapor pressure values are graphically represented in Figure 4, for a mixture with 0.25 water total mass fraction in the absorbent solution ($LiNO_3$ + H_2O). Figure 5 shows relative deviations between experimental and predicted pressures for the whole range of compositions; high relative deviations can be observed for low pressure when the ammonia mass fraction is 0.2, but deviations reduce to less than 10 % when the ammonia composition is higher. This behavior is probably due to the parameters of binary interaction of the E-NRTL model that were calculated for a ammonia composition range from 0.35 to 0.65.

Conclusions

The vapor pressure of NH_3 + $LiNO_3$ + H_2O mixtures was measured from 293.15 K to 353.15 K, at 10 K intervals, varying the refrigerant (ammonia) total mass fraction from 0.20 to 0.55 for three absorbent compositions ($LiNO_3$ + H_2O), with the water total mass fractions of 0.20, 0.25, and 0.30. In addition, the vapor pressure of ammonia + lithium nitrate was determined from 293.15 K to 353.15 K, at 10 K intervals, for an ammonia total mass fraction from 0.35 to 0.65. The equilibrium liquid and vapor compositions were determined using the Redlich−Kister equation for activity coefficients of the liquid phase and the Redlich−Kwong equation of state for modeling the vapor phase nonideality. Vapor pressure, temperature, and liquid-phase composition were correlated using an empirical equation. Calculated and measured data showed a good agreement.

The E-NRTL model was used to predict the vapor−liquid equilibrium of the ammonia + lithium nitrate + water solution using interaction parameters of the binary ammonia + lithium nitrate, lithium nitrate + water, and ammonia + water mixtures. The interaction parameters of the binary ammonia + lithium nitrate were regressed from the experimental data of the binary mixture. The comparison of the results with the experimental data shows that E-NRTL is suitable to predict the vapor−liquid equilibrium of this mixture in the range of temperatures studied and in the range of ammonia compositions from 0.25 to 0.55.

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