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High Pressure Phase Equilibria in the Systems Ammonia + Potassium Iodide, + Sodium Iodide, + Sodium Bromide, and + Sodium Thiocyanate: Solid–Liquid–Vapor and Liquid–Liquid–Vapor Equilibria[1]

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Solid salt–liquid–vapor equilibria and liquid–liquid–vapor equilibria were determined experimentally for the binary system $NH_3 + KI$ in the temperature range 333 to 673 K and at pressures up to 80 MPa. It is found that the system $NH_3 + KI$ belongs to Type V of fluid phase behavior according to the classification of van Konynenburg and Scott. The pressure of the three-phase curve solid salt–liquid–vapor is monotonically increasing in the temperature range investigated and reaches a value of 76 MPa at 670 K. The three-phase liquid–liquid–vapor curve starts in a lower critical end point at 407.3 K and 11.59 MPa and ends in an upper critical end point at 408.8 K and 11.92 MPa. For the systems $NH_3 + NaI$, $NH_3 + NaBr$, and $NH_3 + NaSCN$, Type V fluid phase behavior is also found. In the system $NH_3 + NaI$, the lower critical end point is found at 406.8 K and 11.52 MPa and the upper critical end point at 408.5 K and 11.86 MPa. For the system $NH_3 + NaBr$, these coordinates are 404.6 K, 11.03 MPa and 408.8 K, 11.90 MPa, respectively, and, for the system $NH_3 + NaSCN$, 409.2 K, 11.99 MPa and 409.6 K, 12.06 MPa.

KEY WORDS: ammonia; liquid–liquid–vapor equilibria; potassium iodide; sodium bromide; sodium iodide; sodium thiocyanate; solid–liquid–vapor equilibria; tricritical point.

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1. INTRODUCTION

The phase behavior of water–salt mixtures at superambient conditions has received much attention. Experimental methods, experimental results and types of phase behavior are discussed by Valyashko in three review articles [1–3]. Surprisingly, for systems of ammonia with salts there is hardly any information available on the phase behavior at superambient conditions. It can be expected that ammonia–salt systems show many of the interesting features that are also shown by water–salt systems. However, the critical temperature of ammonia is much lower than the critical temperature of water, so it is much easier to study the phase behavior of ammonia–salt systems close to the critical temperature of the solvent.

Valyashko [3] distinguishes between two main types of water–salt systems. The difference between these two types is the presence or absence of the intersection of the liquid–vapor critical curve ($L = V$) and the three-phase curve solid salt–liquid–vapor (SLV). Water–salt systems of both types can be complicated by immiscibility phenomena. According to Valyashko, immiscibility of Type II, III, IV, V, and VI in the classification of fluid phase behavior of van Konynenburg and Scott [4] can occur.

In this work experimental results for the systems $NH_3 + KI$, $NH_3 + NaI$, $NH_3 + NaBr$, and $NH_3 + NaSCN$ are presented for superambient conditions.

2. MEASUREMENTS

2.1. Specimens

The ammonia used (Matheson) had a purity of 99.99 mol%. GC analysis showed that the main impurities were traces of nitrogen (less than 0.07 mol%) and water (less than 0.0001 mol%). Potassium iodide, sodium bromide, sodium iodide, and sodium thiocyanate of pro analysis quality were obtained from Merck.

2.2. Procedure

The measurements were carried out in two types of high-pressure view cells. For measurements up to 15 MPa and 450 K a glass-tube apparatus, as described earlier by de Loos et al. [5], was used. For the measurements at higher pressures and temperatures an autoclave with sapphire windows was used, which can be used at pressures up to 100 MPa and temperatures up to 673 K. This autoclave is of the same type as described in Ref. 6.

With both types of high-pressure cells, phase envelopes of mixtures of known composition and monovariant multi-phase equilibria could be visually determined. A sample of the mixture with known composition was present in a narrow glass tube, mounted in a thermostat (glass tube apparatus) or in the high-pressure autoclave. Mercury was used as a pressure intermediate between the sample and the oil in the pressure generating system. The temperature in the thermostat of the glass tube apparatus was kept constant within 0.02 K with circulating silicone oil. The temperature of the high-pressure autoclave was kept constant within 0.1 K using a PID controller and electric heating mantles. The temperature was measured with a 100 Ω platinum resistance thermometer, calibrated against a standard thermometer. The uncertainty in the measured temperature was approximately 0.02 K. The pressure was measured with Bourdon gauges calibrated against a dead-weight gauge with an uncertainty of approximately 0.1 %.

The mixtures are prepared by weighing the salt in the sealed end of the glass sample tube. After the sample tube with the salt is evacuated, the ammonia is added volumetrically using a mercury displacement method [7].

The vapor-pressure of saturated ammonia-potassium iodide solutions is determined by adjusting the volume of the mixture at constant temperature until solid salt, liquid, and vapor are observed visually. In this way the monovariant solid salt–liquid–vapor curve was determined.

For the measurement of the liquid–liquid–vapor equilibrium pressures, the volume of the sample is adjusted until two liquid phases and a vapor phase are observed simultaneously. This three-phase equilibrium can only be observed in a limited concentration range. The P, T- and T, x-projection of a binary Type V system is shown in Fig. 1. LV(A) and LV(B) are the vapor pressure curves of the light component (ammonia) and the low volatile component (salt), respectively. The three-phase L_2L_1V curve is found near the critical point of ammonia (C_A). It starts at a lower critical end point where the salt-rich liquid phase (L_2) and the ammonia-rich liquid phase (L_1) are critical in the presence of a vapor phase (V) (lower critical end point L: $L_2 = L_1 + V$) and ends in an upper critical endpoint where liquid L_1 and vapor are critical in the presence of liquid L_2 (upper critical end point K: $L_2 + L_1 = V$). The binary critical curve is divided into two branches: the $L_1 = V$ branch and the $L_2 = L_1/L_2 = V$ branch. In Fig. 2a–c the P, T-sections at compositions x_1, x_2, and x_3 are shown. The shape of the phase envelope and length of the L_2L_1V curve depend on concentration. At a $L_2 + L_1 = V$ critical end point, the three-phase curve ends in a point in which the top phase and the middle phase are critical and, at a $L_2 = L_1 + V$ critical endpoint, the liquid–liquid–vapor curve ends in a point where the bottom phase and the middle phase are critical. The uncertainty

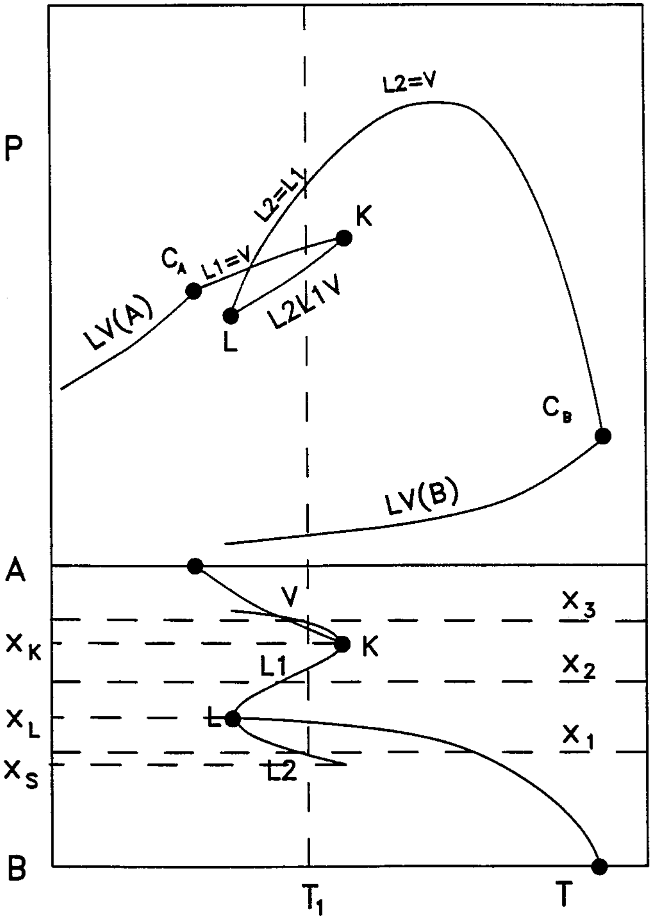

Fig. 1. P, T- and T, x-projection of monovariant equilibria of a binary system of a volatile (A) and a low volatile (B) component showing Type V phase behavior.

in the experimental determination of the critical end point temperature is 0.1 K. Points B in Fig. 2 provide information on the composition of the coexisting phases. These points represent points of intersection in the T, x-projection of Fig. 1 of a line at constant x with one of the three branches of the L_2L_1V equilibrium. Point B in Fig. 2a is a point of the V-branch, in Fig. 2b a point of the L_1-branch, and in Fig. 2c a point of the L_2-branch. So from the P, T-sections for mixtures of different overall composition, the composition of the three coexisting phases can be derived.

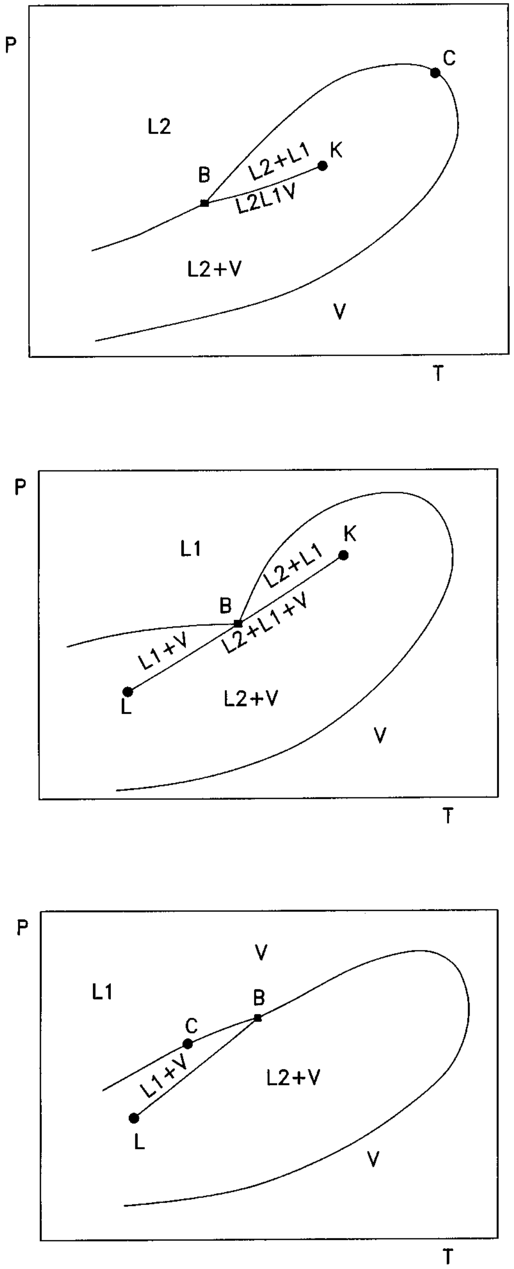

Fig. 2. P, T-sections for binary mixtures of constant composition: (a) x_1; (b) x_2; (c) x_3 (See Fig. 1.).

Table I. Vapor Pressure of Ammonia

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
342.32	3.262	382.15	7.449	403.97	11.10
352.31	4.064	392.05	8.935	404.99	11.30
362.22	5.035	401.96	10.70	405.09	11.31
372.22	6.155	402.98	10.91	405.38	11.36

3. RESULTS AND DISCUSSION

To check the purity of the ammonia used, the vapor pressure curve of ammonia was determined. The results are given in Table I and Fig. 3. The experimental data agree within the experimental uncertainty with literature data [8–12]. In Fig. 3, the three-phase curve solid KI–liquid–vapor is plotted. The corresponding data are presented in Table II. In the temperature range investigated this curve always shows a positive slope with a point of inflection at around 500 K. Also at the highest temperature no sign of critically is observed for this equilibrium, so it is uncertain whether this curve will show a pressure maximum or will intersect with the critical curve.

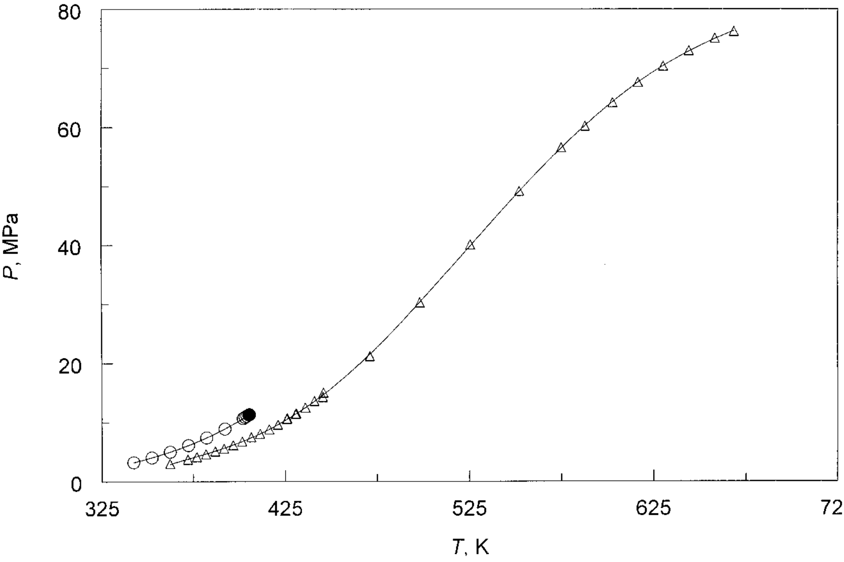

Fig. 3. P, T-projection of the vapor-pressure curve of ammonia (○) and the three-phase curve $S_{KI}LV$ of the system $NH_3 + KI$ (△). ●: critical point of ammonia.

Table II. $NH_3 + KI$ System: $S_{KI}LV$ Equilibria

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
342.47	1.904	411.20	8.131	498.40	30.26
352.31	2.422	416.13	8.896	525.68	40.06
362.07	3.037	420.89	9.661	552.25	49.14
371.92	3.757	425.74	10.62	575.02	56.54
376.83	4.183	426.10	10.70	587.85	60.19
381.75	4.640	430.56	11.43	602.90	64.14
386.74	5.135	430.95	11.52	616.75	67.58
391.60	5.615	435.88	12.55	630.31	70.32
396.54	6.214	440.76	13.64	644.18	72.95
401.41	6.807	445.35	14.32	658.30	75.08
406.34	7.521	445.68	15.06	668.57	76.20
411.20	8.140	471.05	21.19		

Table III. P, T-Projection of L_2L_1V Equilibria in $NH_3 + \text{Salt}$ Systems

$NH_3 + KI$		$NH_3 + NaI$		$NH_3 + NaBr$		$NH_3 + NaSCN$	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
407.28	11.59	406.85	11.52	404.58	11.03	409.21	11.99
407.31	11.60	406.98	11.54	405.53	11.24	409.28	12.00
407.41	11.62	407.09	11.56	405.77	11.28	409.39	12.01
407.56	11.64	407.20	11.59	406.23	11.35	409.52	12.04
407.67	11.66	407.33	11.63	406.46	11.40	409.60	12.06
407.80	11.70	407.45	11.65	406.82	11.46		
407.93	11.73	407.57	11.67	407.10	11.53		
408.05	11.76	407.68	11.70	407.40	11.58		
408.20	11.79	407.80	11.70	407.77	11.67		
408.34	11.82	407.93	11.75	408.15	11.75		
408.47	11.84	408.09	11.78	408.49	11.82		
408.63	11.87	408.20	11.81	408.63	11.85		
408.73	11.89	408.30	11.82	408.73	11.88		
408.79	11.92	408.42	11.85	408.79	11.90		
		408.49	11.86				

Table IV. $[(1-x)NH_3 + xKI]$ System: T, x-Projection of the L_2L_1V Curve (x is the mole fraction KI)

T (K)	$x(V) \times 10^2$	$x(L_1) \times 10^2$	$x(L_2) \times 10^2$
135.39	0.073		
135.64	0.103		
135.64	0.198	0.198	
135.54		0.299	
135.19		0.407	
135.34		0.463	
134.94		0.598	
134.59		0.625	
134.65		0.638	
134.64		0.654	
134.49		0.805	
134.43		0.819	
134.32		0.946	
134.15		1.165	
134.12		1.419	
134.12			1.617
134.11			1.720
134.15			1.865
134.28			2.122
134.62			2.649
135.33			3.056
135.45			3.319

Table V. $[(1-x)NH_3 + xKI]$ System: $L_1 = V$ Critical Curve (x is the mole fraction KI)

$x_{KI} \times 10^2$	T (K)	P (MPa)
0	405.38	11.36
0.038	406.22	11.46
0.073	407.14	11.59
0.103	407.72	11.73
0.198	408.79	11.92

In the system $NH_3 + KI$ a liquid–liquid–vapor equilibrium of Type V is also found at temperatures a few K above the critical temperature of ammonia. The data are presented in Tables III and IV. This equilibrium exists only in a temperature interval of 1.5 K. See Fig. 4, in which the P, T-projection of the three-phase equilibrium is shown together with the vapor-pressure curve of ammonia and the critical curve $L_1 = V$ (Table V). Figure 5 shows the T, x-projection of the $L_1 = V$ curve and the L_2L_1V equilibria in the system $NH_3 + KI$. As can be seen from these figures the L-point is found at $T = 407.3$ K, $P = 11.59$ MPa and $x_{KI} \approx 15 \times 10^{-3}$ and the K-point at $T = 408.8$ K, $P = 11.92$ MPa, and $x_{KI} \approx 2 \times 10^{-3}$.

Also, in the systems $NH_3 + NaI$, $NH_3 + NaBr$, and $NH_3 + NaSCN$ fluid phase equilibria of Type V were found. The data are given in Table III. In the system $NH_3 + NaI$ the lower critical end point is found at 406.8 K and 11.52 MPa and the upper critical end point at 408.5 K and 11.86 MPa. The lower critical endpoint in the system $NH_3 + NaBr$ is located at a temperature lower than the critical temperature of ammonia. This point is found at 404.6 K and 11.03 MPa, the upper critical end point at 408.8 K and 11.90 MPa. For the system $NH_3 + NaSCN$ theses coordinates are 409.2 K, 11.99 MPa and 409.6 K, 12.06 MPa, respectively. In the later system the three-phase curve is only 0.4 K long.

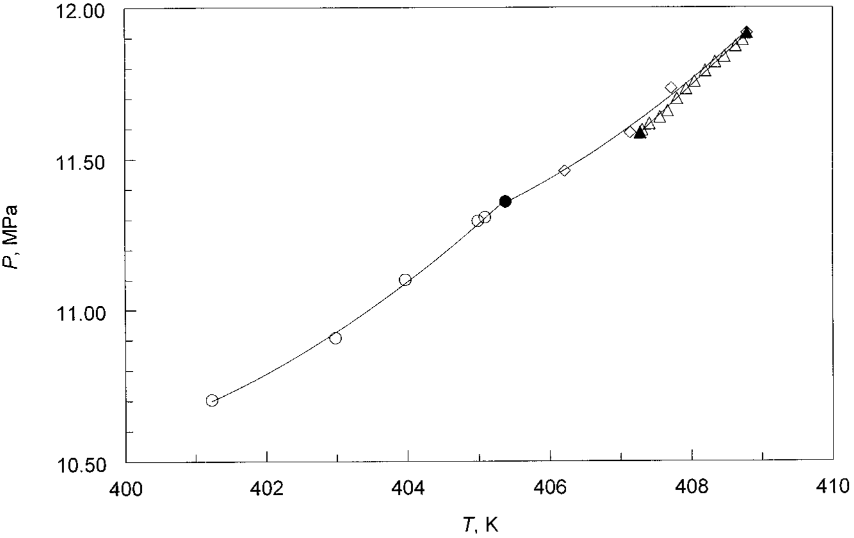

Fig. 4. P, T-projection of the vapor-pressure curve of ammonia (○) and the critical curve $L_1 = V$ (◇) and the three-phase curve L_2L_1V of the system $NH_3 + KI$ (△). ●: critical point of ammonia; ▲: critical end points.

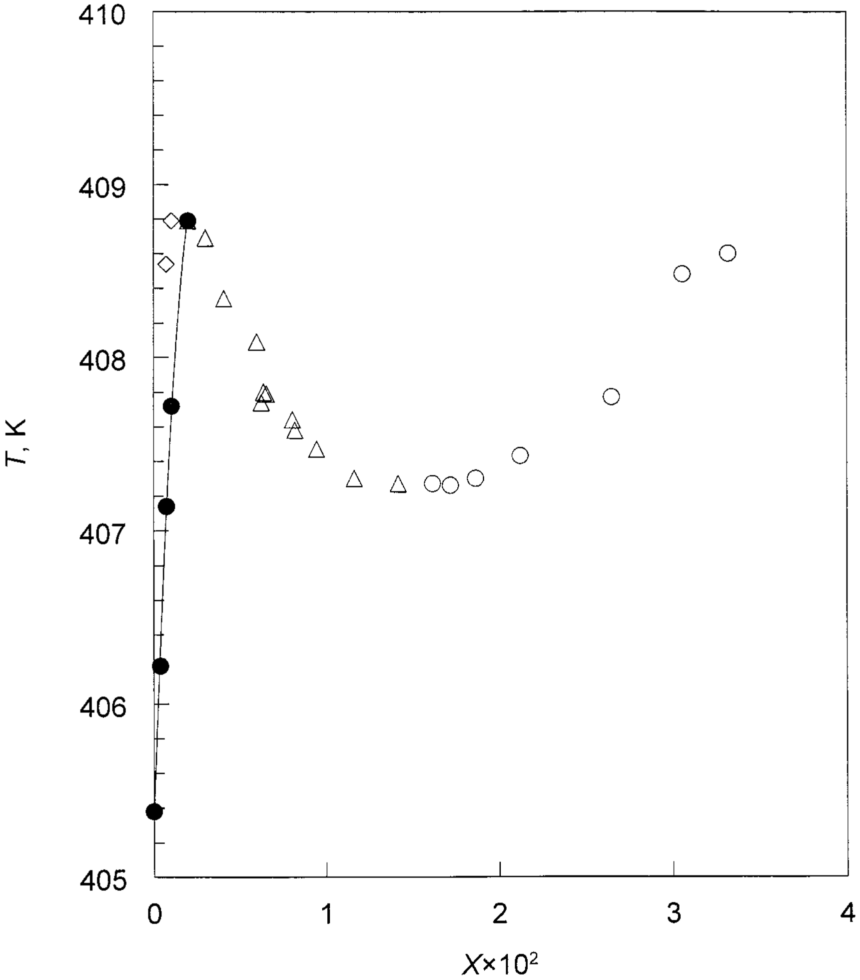

Fig. 5. T, x-projection of the $L_1 = V$ (●) and the three-phase curve L_2L_1V of the system $NH_3 + KI$. ○: $x(L_2)$; △: $x(L_1)$; ◇: $x(V)$.

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