Literature Cited

(1) Castellanos, M. A.; Caceres, M.; Nuñez, J. *J. Chem. Eng. Data* **1985**, *30*, 344.
(2) Linhard, M. *Z. Elektrochem*. **1944**, *50*, 224.
(3) Work, J. B. *Inorg. Synth*. **1946**, *2*, 221.
(4) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965.
(5) Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans: London, 1952.
(6) Pascal, P. *Nouveau Traite de Chemie Minerale*; Masson: Paris, 1959; Vol. XVIII.
(7) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1959.
(8) Clarke, E. C. W.; Glew, D. N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1911.

Received for review April 3, 1989. Accepted November 27, 1989.

Vapor-Liquid Equilibria for the System Ammonia + Water up to the Critical Region

C. L. Sassen, R. A. C. van Kwartel, H. J. van der Kooi,* and J. de Swaan Arons

Laboratory of Inorganic and Physical Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Bubble points, dew points, and critical points were measured in the system ammonia + water for several mixtures of constant overall composition by direct observation. Bubble points were determined for 6 different mixtures, varying in composition from 18.9 to 80.0 mol % ammonia over a temperature range of 389.4-613.5 K and a pressure range of 1.29-21.52 MPa. Dew points were measured for 15 compositions between 19.4 and 90.0 mol % ammonia over a temperature range of 373.2-453.2 K and a pressure range of 0.14-9.70 MPa. Results have been compared with those of Müller et al., Rizvi and Heidemann, and Gillespie et al. It is concluded that at lower temperatures and pressures the four sources of reference data present a unique and consistent picture of vapor-liquid equilibria in the system ammonia + water. At temperatures above 473 K, significant deviations exist.

Introduction

Ammonia and water participate in many industrial processes. One might think of the manufacturing of urea where ammonia and carbon dioxide react to an aqueous solution of urea. Thermodynamic modeling of such a process requires information on the phase equilibria of the relevant (sub)systems.

When this investigation was started, reliable data for the system ammonia + water were scarce if not absent. For example, Tsiklis (*1*) investigated the global phase behavior over a wide pressure and temperature range, but the accuracy of the data is insufficient for plant design. On the other hand, accurate data could be found in the literature but then the experimental range appeared to be very limited, see, for example, Guillevic et al. (*2*) and Pawlikowski et al. (*3*). More recently, Müller et al. (*4*), Rizvi and Heidemann (*5*), and Gillespie et al. (*6*) published data over a broad temperature and pressure range. Rizvi and Heidemann (*5*) and Gillespie et al. (*6*), in particular, present data almost up to the critical point of water. Gillespie et al. (*6*) in comparing their data with those of Rizvi report in some cases an average deviation of 24.0% in the relative volatility. In view of the great significance of reliable data for the system ammonia + water as a key industrial system, we have undertaken an independent study on the vapor-liquid equilibria of this system over the full concentration range.

In this paper, a description of the experimental procedure is given first, after which the bubble point and dew point measurements in the system ammonia + water are presented. Finally, the results are compared with those in the literature.

Experimental Procedure

***Equipment*.** The bubble point measurements were carried out in a stainless steel optical high-pressure cell for use with pressures up to 200 MPa and temperatures up to 673 K, which is described in detail by de Loos et al. (*7*). The cell is heated externally with two electric heating mantles, controlled by electronic regulators. The temperature was measured with a platinum resistance thermometer to an accuracy of +0.02 K; it was maintained constant better than ±0.1 K. A dead-weight pressure gauge was used to measure the pressure and to keep it constant. Bubble points could be measured within ±0.01 MPa.

The dew point measurements were performed in an apparatus for use with pressures up to 20 MPa and temperatures up to 473 K. This so called Cailletet apparatus is described earlier by de Loos et al. (*8*). The glass capillary tube that contains the mixture is kept at the desired temperature by a thermostat with circulating oil. The temperature was measured to an accuracy within ±0.01 K by using a platinum resistance thermometer; it was maintained constant better than ±0.05 K. The pressure was measured and kept constant with a dead-weight pressure gauge. Dew points could be measured within ±0.01 MPa.

***Method*.** In the case of the bubble point measurements, mixtures were prepared by weighing a certain quantity of water in the top of a glass measuring vessel. The top of this measuring vessel is constructed of sapphire because water and ammonia corrode glass and even quartz at high temperatures and pressures. Besides the water, the measuring vessel also contained a nickel stirrer, which stirred the mixture during the experiments by means of a magnetic stirrer device of the high-pressure cell. The water was degassed by repeatedly melting and freezing the water in vacuum, after which a volumetrically determined amount of ammonia, at a well-known pressure and temperature, was pressed into the measuring vessel by mercury and condensed in the top of the vessel by means of liquid nitrogen. The mercury acted not only as a sealing liquid but also as a pressure-transmitting fluid between the mixture and the pressurizing fluid (silicon oil: Dow Corning 200 fluid 5CS) used in the high-pressure cell.

Then, the measuring vessel was placed between the windows of the high-pressure cell, after which the mixture was pressurized. At a constant temperature, variation of the pressure allowed one to determine visually that point at which

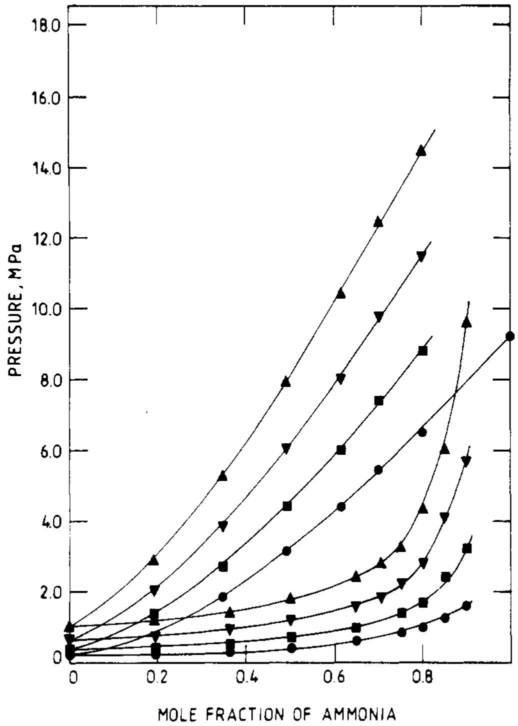

Figure 1. Vapor-liquid equilibria in the system ammonia + water: isothermal p,x,y diagram for several temperatures. Key: (●) 393.0 K; (■) 413.0 K; (▼) 433.0 K; (▲) 453.0 K.

Table I. Ammonia + Water Equilibrium Data: Bubble Point Pressures p as a Function of Temperature T for a Given Mole Fraction x of Ammonia

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
$x = 0.189$					
410.8	1.29	501.1	6.18	592.9	18.49
419.2	1.54	508.6	6.91	598.4	19.47
428.6	1.85	519.5	7.98	603.0	20.27
438.0	2.25	529.2	9.03	604.2	20.46
447.1	2.62	540.9	10.44	607.6	21.00
457.3	3.15	550.6	11.72	610.9	21.36
467.1	3.70	559.8	13.03	612.7	21.49
480.2	4.54	575.1	15.45	613.5	21.52
490.8	5.34	583.9	16.92		
$x = 0.346$					
391.1	1.78	460.3	5.90	541.2	15.60
401.1	2.17	467.9	6.56	550.6	17.12
410.0	2.57	483.4	8.03	551.1	17.15
419.0	3.04	491.8	8.97	558.8	18.44
427.2	3.51	501.5	10.12	567.4	19.67
437.2	4.14	512.8	11.57	576.4	20.71
446.9	4.83	522.8	12.90	578.7	20.77
453.0	5.30	532.2	14.25	580.1	20.83
$x = 0.491$					
392.1	3.10	455.9	8.30	521.4	16.84
402.0	3.69	465.0	9.29	532.5	18.43
411.0	4.29	474.3	10.36	539.8	19.34
420.2	4.99	483.9	11.55	547.3	19.97
429.1	5.71	495.1	13.05	549.8	20.08
438.6	6.53	504.3	14.33	551.1	20.13
447.6	7.39	511.7	15.45		
$x = 0.613$					
389.7	4.14	457.9	11.11	515.7	18.79
400.0	4.94	467.4	12.41	518.3	19.09
420.5	6.72	486.3	15.07	522.3	19.34
439.4	8.71	497.2	16.50	527.3	19.49
449.8	10.17	505.7	17.73		
$x = 0.699$					
391.4	5.34	438.6	10.52	483.9	16.86
401.3	6.24	448.5	11.85	488.4	17.39
410.1	7.13	459.5	13.43	492.7	17.78
418.6	8.05	468.3	14.73	495.2	17.99
430.5	9.48	478.4	16.15	498.1	18.13
$x = 0.800$					
389.3	6.13	424.1	10.24	454.5	14.72
397.1	6.94	424.8	10.33	461.4	15.68
410.3	8.49	439.1	12.42	465.3	16.14
419.8	9.70	446.4	13.53	470.0	16.57

the last gas bubble is about to (dis)appear, the so-called bubble point.

Mixtures for measuring bubble points could be prepared with a maximum error in the mole fraction of 0.004.

In the high-pressure cell, it was also possible to measure critical points. At a critical point, the meniscus should disappear, for thermodynamic reasons, in the midst of the measuring vessel and the observed phase behavior changes from bubble point to dew point behavior. So, when the descent or ascent of the meniscus at constant temperature was observed upon varying the pressure and when this procedure was followed at different temperatures, it was possible to locate the critical point for each mixture. The errors in the critical temperature and critical pressure are estimated to be ±0.5 K and ±0.02 MPa, respectively.

Mixtures for measuring dew points were prepared almost in the same way as with the bubble point experiments. Now, in view of the very small amounts of water to be used, a volumetrically determined amount of water as a vapor was brought in the measuring vessel at a well-known pressure and temperature. Furthermore, because of the milder conditions with respect to temperature and pressure, the measuring vessel was a borosilicate glass tube. After the water was condensed in the tube, ammonia was introduced in the same way as described before.

Then, the measuring vessel was placed in the autoclave of the Cailletet apparatus, and by varying the pressure at constant temperature, one could determine visually that pressure at which the last droplet of liquid is about to (dis)appear, the so-called dew point.

In the case of dew point measurements, the mixtures were prepared with a maximum error of about 0.01 in the mole fraction for mixtures that were poor in ammonia. The error reduced to 0.005 for mole fractions of ammonia larger than 0.700.

Materials. The water used was demineralized and double-distilled and had a conductivity of less than 10^{-6} S cm^{-1}. The ammonia had a purity of 99.995 wt % and was supplied by Aga Gas. The purity of the ammonia used was checked by measuring the critical point. The experimental critical point (p_c = 11.34 MPa, T_c = 405.4 K) agreed within the experimental uncertainty with that in the literature (*9*, *10*).

Results

The results of the bubble point and dew point measurements are presented in Tables I and II, respectively. Table III gives the measured critical points. The bubble point pressures as well as the critical pressures at higher temperatures (above 500 K) are corrected for the vapor pressure of mercury and the so-called Poynting factor, with data given in ref 11. From plots of these p,T isopleths, isothermal p,x,y sections can be obtained by interpolation. For several temperatures, p,x,y sections are presented in Figure 1. Figure 2 shows p,x sections for different temperatures above 473 K. In this figure, a projection of the critical line is also given; it runs smoothly from the critical point of ammonia to that of water.

Comparison with Literature Data

In Figures 3–6, several measured isothermal p,x,y or p,x sections of Müller et al. (*4*), Rizvi and Heidemann (*5*), and

Table II. Ammonia + Water Equilibrium Data: Dew Point Pressures p as a Function of Temperature T for a Given Mole Fraction y of Ammonia

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
y = 0.194					
383.3	0.18	413.2	0.42	443.1	0.93
393.1	0.23	423.1	0.55	453.1	1.18
403.2	0.32	433.2	0.72		
y = 0.237					
383.2	0.20	413.1	0.47	443.2	1.00
393.3	0.24	423.2	0.60	453.1	1.24
403.2	0.33	433.1	0.77		
y = 0.304					
373.2	0.14	403.3	0.38	433.1	0.87
383.2	0.21	413.2	0.51	443.2	1.06
393.1	0.27	423.2	0.65	453.2	1.30
y = 0.363					
373.2	0.16	403.2	0.38	433.2	0.90
383.2	0.24	413.2	0.54	443.3	1.13
393.1	0.29	423.3	0.68	453.1	1.41
y = 0.414					
373.2	0.19	403.1	0.47	433.1	1.00
383.2	0.28	413.3	0.65	443.2	1.28
393.2	0.35	423.2	0.76	453.3	1.53
y = 0.451					
373.2	0.21	403.1	0.50	433.1	1.05
383.3	0.29	413.3	0.70	443.2	1.32
393.2	0.37	423.2	0.81	453.3	1.62
y = 0.500					
373.2	0.24	403.2	0.55	433.2	1.19
383.2	0.34	413.1	0.74	443.2	1.45
393.2	0.43	423.2	0.90	453.2	1.81
y = 0.570					
373.2	0.25	403.1	0.64	433.2	1.33
383.2	0.38	413.1	0.86	443.1	1.64
393.2	0.50	423.2	1.06	453.2	2.00
y = 0.602					
373.2	0.27	403.3	0.67	433.1	1.40
383.3	0.41	413.2	0.92	443.2	1.79
393.2	0.54	423.2	1.13	453.1	2.21
y = 0.647					
373.2	0.29	403.2	0.77	433.2	1.57
383.2	0.46	413.1	1.02	443.1	2.00
393.3	0.61	423.2	1.28	453.2	2.43
y = 0.706					
373.2	0.34	403.2	0.91	433.2	1.79
383.2	0.53	413.2	1.23	443.1	2.28
393.1	0.70	423.1	1.48	453.2	2.81
y = 0.749					
373.3	0.38	403.2	1.09	433.2	2.20
383.2	0.61	413.1	1.43	443.1	2.78
393.2	0.82	423.2	1.78	453.4	3.29
y = 0.800					
373.2	0.45	403.1	1.29	433.2	2.77
383.1	0.72	413.2	1.76	443.4	3.47
393.2	0.98	423.3	2.26	453.1	4.38
y = 0.850					
373.2	0.54	403.1	1.76	433.2	4.10
383.3	0.85	413.2	2.42	443.3	5.03
393.1	1.25	423.3	3.28	453.1	6.08
y = 0.900					
373.2	0.77	403.3	2.35	433.2	5.70
383.3	1.16	413.1	3.25	443.3	7.43
393.2	1.58	423.2	4.42	453.2	9.70

Gillespie et al. (*6*) are compared with our data. For this comparison, it was necessary to interpolate our data to the temperatures at which the other authors had measured. The lines in these figures are those fitted to our interpolated data. For

Table III. Ammonia + Water Critical Points

$x\mathrm{NH_3}$	T/K	p/MPa	$x\mathrm{NH_3}$	T/K	p/MPa
0.189	613.5	21.52	0.699	498.1	18.13
0.346	580.1	20.83	0.800	470.0	16.57
0.491	551.1	20.13	1.000	405.4	11.34
0.613	527.3	19.49			

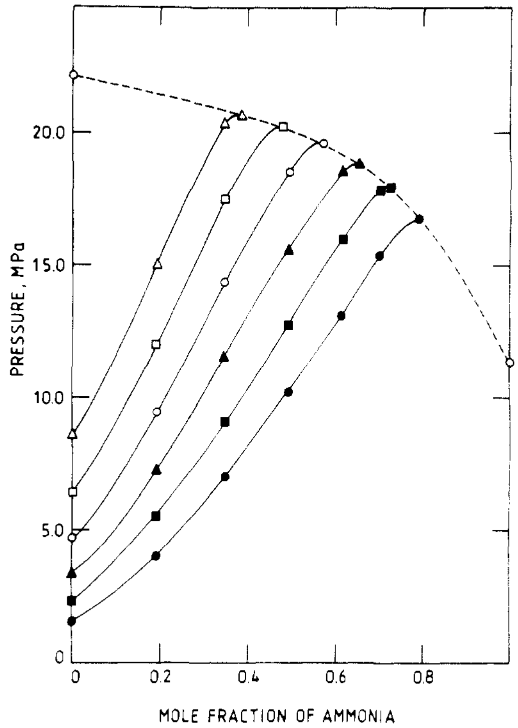

Figure 2. Bubble points and critical points in the system ammonia + water: isothermal p,x diagram for several temperatures. Key: (●) 473.0 K; (■) 493.0 K; (▲) 513.0 K; (○) 533.0 K; (□) 553.0 K; (△) 573.0 K; (- -) critical curve.

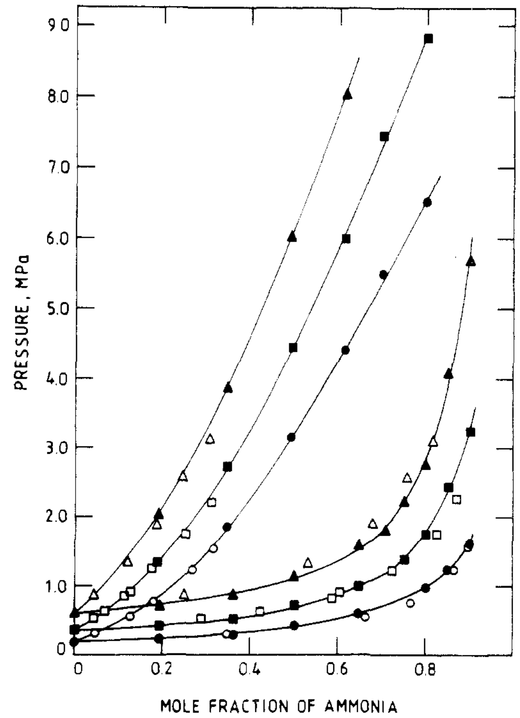

Figure 3. Vapor–liquid equilibria in the system ammonia + water: comparison with the work of Müller et al. (*4*). Key: (●, ○) 393.15 K; (■, □) 413.15 K; (▲, △) 433.15 K; (closed symbols) this work.

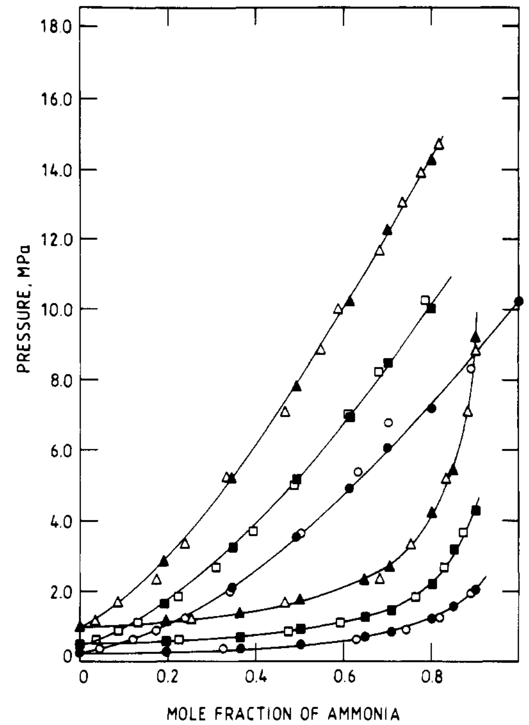

Figure 4. Vapor–liquid equilibria in the system ammonia + water: comparison with the work of Rizvi and Heidemann (*5*). Key: (●, ○) 399.1 K; (■, □) 422.5 K; (▲, △) 451.5 K; (closed symbols) this work.

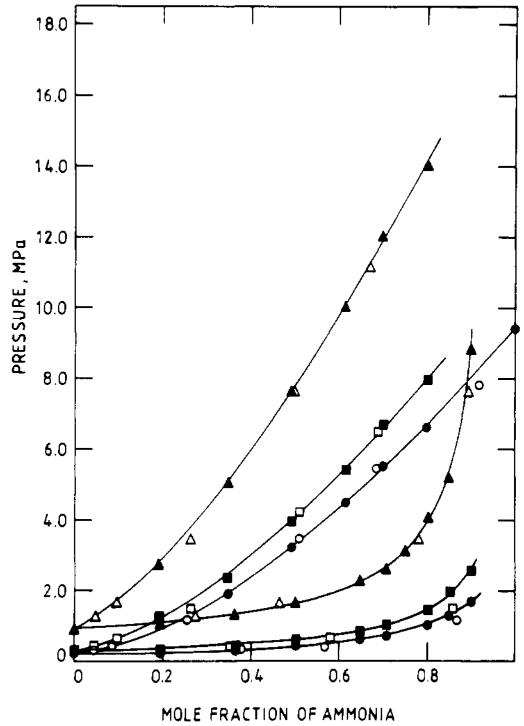

Figure 5. Vapor–liquid equilibria in the system ammonia + water: comparison with the work of Gillespie et al. (*6*). Key: (●, ○) 394.25 K; (■, □) 405.95 K; (▲, △) 449.85 K; (closed symbols) this work.

some isotherms, a quantitative comparison has been made by calculating a relative deviation, which is defined as

$$\text{relative deviation} = \frac{\sum_{i=1}^{n}(p - p')/p}{n} \times 100\% \qquad (1)$$

with p, the interpolated pressure at composition x; p', the pressure of the other author at composition x; and n, the total number of data considered.

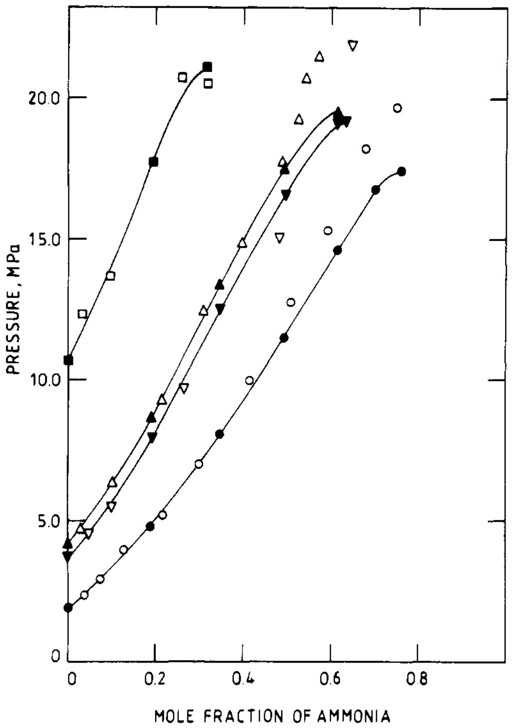

Figure 6. Bubble points in the system ammonia + water: comparison with the work of Rizvi and Heidemann (*5*) and Gillespie et al. (*6*). Key: (●, ○) 483.3 K; (▲, △) 526.2 K; (●, ▲) this work; (○, △) Rizvi and Heidemann; (▼, ▽) 519.25 K; (■, □) 588.75 K; (▼, ■) this work; (▽, □) Gillespie et al.

Figure 3 shows the comparison with the work of Müller et al. (*4*) who present data between 373.2 and 473.2 K, for three isotherms. One can see that the agreement is fairly reasonable. At 413.2 K, the relative deviations for the bubble point and dew point curves are 12.3% and 6.3%, respectively.

In Figure 4, the results of Rizvi and Heidemann (*5*) are being compared with our data for three temperatures. The agreement is very good. The relative deviations for the bubble point and dew point curves at 422.5 K are 3.0% and 7.0%, respectively.

Figure 5 gives the comparison with *pTxy* measurements of Gillespie et al. (*6*) for three isotherms. The agreement is fair although at constant pressure the dew points of Gillespie seem to be shifted to the ammonia side. At 406.0 K, the relative deviations for the bubble point and dew point curves are 11.3% and 12.4%, respectively. These values are somewhat higher than the values obtained in the comparison with Rizvi and Heidemann.

Figure 6 compares two isotherms of Rizvi and Heidemann (*5*) and two isotherms of Gillespie et al. (*6*) at higher temperatures with this work. For each isotherm, strong deviations occur near the critical point, in line with the fact that Rizvi and Heidemann (*5*) report a critical curve with a maximum critical pressure ($dp_c/dx_c = 0$) of 22.5 MPa at a mole fraction of ammonia of 0.244. According to this work, the critical curve rises monotonically from the critical point of ammonia to that of water. This agrees with the earlier work of Tsiklis (*1*). There is no obvious explanation for this discrepancy.

Conclusions

It is concluded that at lower temperatures and pressures there is a good correspondence between this work and the data of Müller et al. (*4*), Rizvi and Heidemann (*5*), and Gillespie et al. (*6*). At temperatures above 473 K, significant deviations have been observed especially in the critical region.

Registry No. Ammonia, 7664-41-7.

Literature Cited

(1) Tsiklis, D. S.; Linshits, L. R.; Goryunova, N. P. *Russ. J. Phys. Chem.* **1965**, *39*, 1590.
(2) Guillevic, J.-L.; Richon, D.; Renon, H. *J. Chem. Eng. Data* **1985**, *30*, 332.
(3) Pawlikowski, E. M.; Newman, J.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 764.
(4) Müller, G.; Bender, E.; Maurer, G. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 148.
(5) Rizvi, S. S. H.; Heidemann, R. A. *J. Chem. Eng. Data* **1987**, *32*, 183.
(6) Gillespie, P. C.; Wilding, W. V.; Wilson, G. M. *AIChE Symp. Ser.* **1987**, *83*, 97.
(7) Loos, Th. W. de; Wijen, A. J. M.; Diepen, G. A. M. *J. Chem. Thermodyn.* **1980**, *12*, 193.
(8) Loos, Th. W. de; Kooi, H. J. van der; Ott, P. L. *J. Chem. Eng. Data* **1986**, *31*, 166.
(9) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(10) Brunner, E. *J. Chem. Thermodyn.* **1988**, *20*, 1397.
(11) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 56th ed.; CRC: Cleveland, 1975.

Received for review April 10, 1989. Accepted October 2, 1989.

Thermodynamics of Electrolyte Solutions: Activity and Osmotic Coefficients of the Ternary System KCl–$BaCl_2$–H_2O at 25, 35, and 45 °C

D. Chinnappa Reddy and J. Ananthaswamy*
Department of Chemistry, Osmania University, Hyderabad 500 007, India

The activity coefficients of KCl in the aqueous mixtures of KCl–$BaCl_2$ were determined by electromotive force measurements at 25, 35, and 45 °C and the total ionic strengths of 0.5, 1.0, 2.0, and 3.0 *m*. The Harned coefficients and Pitzer binary and ternary interaction parameters ($^s\Theta$ and Ψ) were evaluated. Osmotic coefficients, excess free energies of mixing, and the activity coefficient of $BaCl_2$ were calculated at all the ionic strengths and temperatures studied.

Introduction

A wide variety of industrial geological and biochemical processes involve aqueous multicomponent electrolyte solutions. Christenson and Gieskes (*1*) determined the mean activity coefficients of aqueous KCl in KCl–$BaCl_2$–H_2O at 25 °C and a total ionic strength of 1 *m* using a potassium-selective glass and Ag–AgCl electrodes. Robinson and Bower (*2*) measured the vapor pressures of this system isopiestically at 25 °C over an ionic strength range of 1.0–4.0 *m*. They have also calculated the activity coefficients of each salt and excess free energies of mixing in the mixture. Thus, the activity and osmotic coefficients of the system are not yet determined as a function of temperature. We are now reporting the activity coefficients of KCl and $BaCl_2$ in the mixture KCl–$BaCl_2$–H_2O at 25, 35, and 45 °C over an ionic strength range of 0.5–3.0 *m*.

Experimental Section

The cell arrangement consisted of a potassium ion-selective electrode (Elico, India) and Ag–AgCl electrode immersed in a mixture of KCl and $BaCl_2$ aqueous solutions placed in a double-walled glass vessel whose temperature was maintained constant (±0.01 °C) by circulating thermostated water.

K ion-selective glass electrode	KCl (m_A) + $BaCl_2$ (m_B) + H_2O	AgCl, Ag electrode

The silver–silver chloride electrodes were prepared according to the thermal method (*3*). The electrodes were connected to a high-impedance ($\simeq 10^{12}$ Ω) unit gain amplifier. The output of this amplifier was measured by an electrometer (Keithley, Model DMM 191). The accuracy of the emf measurements was ±0.1 mV or better.

Analytical-grade potassium chloride (GR, S. Merk) and barium chloride (GR, Sarabhai) were used without further purification. The stock solutions were standardized volumetrically by a potentiometric titration against $AgNO_3$ solution with an accuracy of ±0.01%. All solutions were taken by weight. Also, all titrations and dilutions were made with weight burets.

At every ionic strength, the potassium ion-selective electrode was first calibrated with the aqueous KCl solutions of various molalities. Next, its selectivity toward Ba^{2+} ions was estimated by measuring the cell emf values with pure $BaCl_2$ solutions at several molalities. The third set consisted of the emf measurements in KCl–$BaCl_2$–H_2O mixtures. For this set, the potentials were first measured by starting with pure KCl solution and adding aliquots of pure $BaCl_2$ solutions. Next, starting with pure $BaCl_2$ solution, aliquots of KCl solutions of the same ionic strength were successively added. The overlapping portion between these two experiments was used to test the reproducibility and accuracy of the measurements. All sets were repeated at least twice to get consistent and reproducible results.

Calculations and Discussion

The emf values of the potassium ion-selective electrode vs the Ag–AgCl electrode in the ternary system KCl–$BaCl_2$–H_2O are given by the relation

$$E_{KCl\text{-}BaCl_2} = E_0 + k \log (a_K a_{Cl} + K' a_{Ba}{}^{1/2} a_{Cl}) \qquad (1)$$

where K' is the selectivity coefficient of potassium ion-selective electrode for Ba^{2+} ions and $k = 2.303RT/nF$, which is the Nernst slope. In pure KCl solutions, $a_{Ba} = 0$, and, therefore, eq 1 reduces to

$$E_{KCl} = E_0 + k \log (a_K a_{Cl}) \qquad (2)$$

Similarly in pure $BaCl_2$ solutions, $a_K = 0$, and, therefore, eq 1 could be rearranged as

$$K' = (1/a_{BaCl_2}{}^{3/2}) 10^{(E_{BaCl2} - E_0)/k} \qquad (3)$$

At each ionic strength, the emf data obtained in the calibration run was fitted to eq 2 by a least-squares procedure to find the E_0 and k values. The activity coefficients for pure aqueous KCl were calculated with the ion interaction parameters (β^0, β^1, and

0021-9568/90/1735-0144$02.50/0 © 1990 American Chemical Society