Experimental Investigation of the Solubility of Ammonia in Methanol

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A high-pressure view-cell technique based on the synthetic method was used to determine the solubility of ammonia in liquid methanol (total pressure at a preset temperature and liquid-phase composition). The solubility pressure ranges up to about 4.2 MPa. The temperature amounts to (313.75, 354.35, and 395.0) K. The molality of ammonia in methanol (the mole fraction of ammonia in the liquid) ranges up to about 66.4 mol·kg^{-1} (about 0.68). Furthermore, a high-pressure cell technique based on the analytical method was used to investigate the vapor−liquid equilibrium of that same system (equilibrium pressure as well as liquid- and gas-phase compositions at a preset temperature). The solubility pressure ranges up to about 1.6 MPa. The temperature amounts to (353.1 and 393.1) K. The molality of ammonia in methanol (the mole fraction of ammonia in the liquid) ranges up to 13 mol·kg^{-1} (about 0.3). The experimental results are used to determine Henry's constant of ammonia in methanol. Furthermore, the experimental data are correlated by applying Pitzer's molality scale based equation for the Gibbs excess energy.

Introduction

The solubility of "weak electrolyte gases" in aqueous as well as nonaqueous mixed solvents must be known for the design of many separation processes in the chemical and oil-related industries. In particular, thermodynamic models are required to describe the vapor−liquid equilibrium encountered when a basic gas (such as ammonia) and sour gases (such as carbon dioxide or sulfur dioxide) are simultaneously dissolved in mixed solvents. Consistently describing such gas solubility is a striving toil mainly due to the influence of the solvent mixture composition on the relevant equilibrium constants (Henry's constants of the gases and chemical reaction equilibrium constants in the solvent mixtures). Furthermore, these chemical reactions result in the presence of a variety of ionic and nonionic species. In many applications, the liquid phase often contains strong electrolytes (e.g., salts) as well. To develop and test a thermodynamic model to describe such a phase equilibrium, one requires experimental data not only on the simultaneous solubility of any one of the interesting basic gases plus any one of the interesting sour gases in the mixed solvent systems (aqueous and/or organic phases, with as well as without salts) but also for the solubility of the single gases in those mixed solvent systems.

The solubility of ammonia in aqueous salt-free and salt-containing solutions was investigated in previous work.[1,2] That research shall be extended to salt-free and salt-containing aqueous/organic solvent systems, where methanol is arbitrarily chosen as the organic compound. The work presented here is restricted to one of the interesting subsystems; it deals with the solubility of ammonia in pure methanol.

Only few experimental data on the vapor−liquid equilibrium (VLE) of (ammonia + methanol) are found in the open literature.[3−8] However, most of these data are at relatively high ammonia concentrations in the liquid mixture. For example, only 4, 21, 4, 15, 12, and 4 data points by Inomata et al.,[3] Preuss,[4] Doering,[5] Kudo and Toriumi,[6] Xien et al.,[7] and Feng et al.,[8] respectively, are below 25 mol of ammonia per kilogram of methanol, which corresponds to mole fractions of ammonia below about 0.45. From those experimental points, in total only 34 are at temperatures beyond 313 K. The present work aims to contribute to filling that gap by mainly focusing on the low gas concentration region and on some higher temperatures.

A high-pressure view-cell technique based on the synthetic method was used to determine the solubility of ammonia in liquid methanol (total pressure at a preset temperature and liquid-phase composition). In these first series of experiments, the solubility pressure ranges up to about 4.2 MPa; the temperature amounts to (313.75, 354.35, and 395.0) K; and the molality of ammonia in methanol (the mole fraction of ammonia in the liquid) ranges up to about 66.4 mol·kg^{-1} (about 0.68). Furthermore, a high-pressure cell technique based on the analytical method was used to investigate the VLE of that same system (equilibrium pressure as well as liquid and gas-phase compositions at a preset temperature). In these second series of experiments, the solubility pressure ranges up to about 1.6 MPa; the temperature amounts to (353.1 and 393.1) K; and the molality of ammonia in methanol (the mole fraction of ammonia in the liquid) ranges up to 13 mol·kg^{-1} (about 0.3). The experimental results are used to determine Henry's constant of ammonia in methanol. Furthermore, the experimental data are correlated by applying Pitzer's molality scale based equation for the Gibbs excess energy.

Experimental Investigations

Method I: Gas Solubility Measurements. Details of the equipment used as well as of the experimental procedure applied have been reported before.[9,10] Therefore, only a few essentials are repeated here.

The central part of the equipment is a thermostated cylindrical high-pressure view-cell made of stainless steel with sapphire

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windows on both ends. The inner volume of that cell is about 30 cm^3.

In an experiment, the cell is at first carefully evacuated and then partially filled with a known amount of methanol. Afterward, a likewise known amount of ammonia is added to the cell from a small condenser, before more solvent is stepwise added by a high-pressure spindle press until the gas is completely dissolved in the liquid phase. The amount of solvent charged to the cell is always only slightly above the minimum amount needed to dissolve the gas completely. After equilibration, the pressure is decreased in small steps by withdrawing very small amounts of the liquid mixture from the cell back into the spindle press until the first small and stable bubbles appear. The pressure then attained is the equilibrium pressure to dissolve the charged amount of ammonia in the remaining amount of methanol at the particular fixed temperature. Because the liquid mixture is almost incompressible, the mass that was withdrawn from the cell to decrease the pressure is negligible. The mass of ammonia filled into the cell ranges from about (0.4 to 10.75) g. It is determined gravimetrically by weighing the condenser before and after the charging process on a high-precision balance. The uncertainty of that amount of ammonia is below 0.008 g. The mass of methanol filled into the cell (from about (9.5 to 22.6) g) is calculated from the volume displacement in the calibrated spindle press and the solvent density with a relative uncertainty of 0.2 % at a maximum. The density of liquid methanol is known from the literature (e.g., from ref 21), and it was also determined from separate measurements with a vibrating tube densimeter (Anton Paar GmbH, Graz, Austria). The resulting uncertainty in the molality of ammonia ranges from about 0.2 % (at the highest gas concentration) to about 2 % (at the lowest gas concentration).

One pressure transducer (WIKA GmbH, Klingenberg, Germany) for pressures up to 6 MPa was used to determine the solubility pressure. A second pressure transducer (for pressures up to 10 MPa) was used to verify the results. Before and after each series of measurements, the transducers were calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). The maximum systematic uncertainty in the solubility pressure measurement is estimated to 0.016 MPa. It results from the uncertainty of the pressure transducer (0.1 % of the transducer's full scale) and an additional contribution of about 0.01 MPa caused by a small temperature drift in the isolated tubes filled with the solvent, which connect the cell with the pressure transducers. That temperature drift contribution was determined in test runs. The temperature was determined with two calibrated platinum-resistance thermometers placed in the heating jacket of the cell with an uncertainty below 0.1 K.

Method II: VLE Measurements. The experimental arrangement resembles the one used in previous investigations on the simultaneous solubility of ammonia and carbon dioxide in aqueous solutions.[11−15] Therefore, only the main characteristics of the experimental investigation are given here.

A high-pressure thermostated cell (with a volume of about 1.6 dm^3 and about 20 cm in inner height) is at first carefully evacuated and then partially filled with about 1 kg of liquid methanol. Then, ammonia is added in several steps. The charged amounts of methanol and ammonia are known as they are taken from a stock tank and from a small condenser, respectively, which are weighed before and after the filling procedures. After each addition of ammonia, the coexisting phases are equilibrated before the temperature, the pressure, and the vapor-phase volume are measured, and small samples are taken from the vapor phase for an analysis by gas chromatography. To avoid condensation, the temperature in the sampling system (sample valves, sample volume, and feed line to the gas chromatograph) is kept at about 10 K higher than in the cell. The amounts of ammonia and methanol in the gaseous phase are calculated from the mentioned direct experimental data by applying the virial equation of state (details are given below). Finally, from a mass balance, and after applying corrections for the small amounts of the volatile components previously withdrawn from the cell for analysis, the composition of the liquid phase is calculated.

Two pressure transducers (WIKA GmbH, Klingenberg, Germany), placed at the top of the cell and suitable for pressures up to (1 and 10) MPa, respectively, were used to determine the equilibrium pressure. They were calibrated before and after each series of measurements (cf. previous section). The maximum uncertainty in the experimental results for the total pressure is 0.5 kPa (1 kPa) for pressures below (above) 1 MPa. The temperature was determined with a calibrated platinum-resistance thermometer placed inside the cell and in contact with the liquid phase. The overall accuracy of the temperature measurement is about 0.1 K. The vapor-phase volume is determined as follows: From the top, a rod is led into the equilibrium cell. The rod and the cell are electrically isolated from each other, and a small voltage is applied between them. The rod is then slowly moved down until it contacts the surface of the liquid, which results in an electric current, which is detected by an amperemeter. The position of the rod is then read from a dial meter. The relation between the rod position and the vapor-phase volume is determined from (isothermal) calibration measurements. To accomplish that, at first, the total cell volume is accurately determined by means of a high-precision displacement pump (type M118 from Leukert Instruments, Adendorf, Germany). Then, known amounts of liquid water (with tiny amounts of sodium chloride to increase its electrical conductivity) are stepwise added to the equilibrium cell. The density of saturated liquid water is known from the literature.[16] The experimental uncertainty of the vapor-phase volume is estimated not to surmount about 5 cm^3. The resulting overall experimental uncertainty for the molality of ammonia in the liquid phase is estimated to 0.5 % at the upmost.

A gas chromatograph {Agilent (type 6890), equipped with a capillary column (Alltech, type Heliflex AT-Q 30 m, 0.32 mm i.d.) and a thermal conductivity detector} was used to determine the composition of the vapor phase. The primary data collected in the chromatographic measurements are the peak areas of ammonia and methanol. The following well-known relation holds between the peak areas A_i and the mole fractions y_i of those components

$$\frac{y_i}{y_j} = \frac{y_i}{(1 - y_i)} = \alpha_{ij}\frac{A_i}{A_j} \tag{1}$$

Before, during, and after the series of VLE experiments, the proportionality factor α_{ij} was determined from calibration measurements, where gaseous mixtures of ammonia and methanol of known composition were expanded into the feed line of the gas chromatograph. In the different calibration series, α_{ij} was reproduced within 5 % at a maximum. The overall experimental uncertainty of the vapor-phase composition (mole fraction y_i) depends on the experimental conditions. For most of the experimental data points, the following numbers are reasonable estimates: 0.02 and 0.03 at 353.1 K and 393.1 K, respectively (cf. also Figure 2).

Substances and Sample Pretreatment. Ammonia (mole fraction ≥ 0.99999) was purchased from Messer-Griesheim,

Table 1. Solubility of Ammonia (1) in Methanol (2)[a]

m_1 / mol·kg^{-1}	p_{exptl} / MPa	p_{calcd} / MPa	m_1 / mol·kg^{-1}	p_{exptl} / MPa	p_{calcd} / MPa
		$T = 313.75$ K			
7.087	0.123	0.118	26.64	0.461	0.471
10.66	0.161	0.171	35.34	0.596	0.638
13.08	0.211	0.210	43.66	0.699	0.763
15.18	0.260	0.247	48.32	0.760	0.808
19.14	0.308	0.321	60.00	0.875	0.825
23.63	0.410	0.410	66.35	0.913	0.780
		$T = 354.35$ K			
1.506	0.248	0.232	13.12	0.695	0.680
4.313	0.336	0.322	15.35	0.795	0.782
5.676	0.382	0.371	20.23	1.019	1.005
7.908	0.472	0.457	23.75	1.165	1.156
10.97	0.598	0.585	30.36	1.422	1.389
12.68	0.673	0.660	41.18	1.801	1.538
		$T = 395.0$ K			
2.182	0.835	0.822	15.94	2.027	2.074
3.548	0.939	0.925	24.93	2.791	2.811
7.634	1.266	1.271	34.54	3.509	3.095
11.49	1.617	1.638	46.63	4.226	2.691
12.27	1.696	1.714			

[a] Experimental results from method I and correlation/prediction results (using the second set of parameters, eqs 14 to 17).

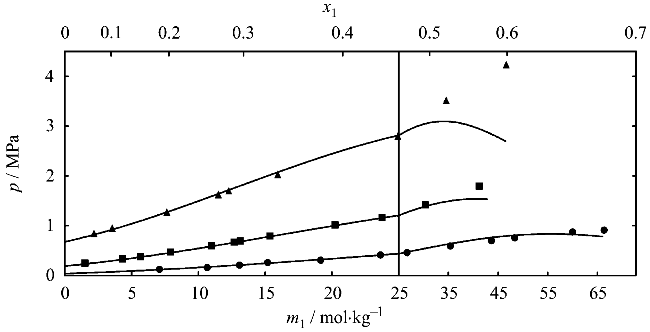

Figure 1. Total pressure p above liquid mixtures of {ammonia (1) + methanol (2)} plotted against the molality m_1 (the mole fraction x_1) of ammonia in the liquid: (●, $T = 313.75$ K; ■, $T = 354.35$ K; ▲, $T = 395.0$ K), experimental results from method I (gas solubility measurements); —, correlation results using the second set of parameters (eqs 14 to 17).

Ludwigshafen, Germany, and used without further purification. For the gas solubility measurements, methanol (mole fraction ≥ 0.998) was purchased from Honeywell Specialty Chemicals, Seelze, Germany. For the VLE measurements, methanol (mass fraction ≥ 0.998) was purchased from Merck KGaA, Darmstadt, Germany.

Experimental Results

Method I: Gas Solubility Measurements. The solubility of ammonia (1) in liquid methanol (2) was measured at temperatures $T = (313.75, 354.35, \text{and } 395.0)$ K and total pressures p up to about (0.9, 1.8, and 4.2) MPa, resulting in a maximum molality of ammonia m_1 of about (66.4, 41.2, and 46.6) mol·kg^{-1} of methanol {a maximum mole fraction of ammonia in the liquid x_1 of (0.68, 0.57, and 0.60)}, respectively. The experimental results from these first series of experiments are given in Table 1. The experimental results for the total pressure are plotted against the molality of ammonia at a preset temperature in Figure 1.

Method II: VLE Measurements. The solubility of ammonia in liquid methanol was measured at temperatures of (353.1 and 393.1) K and total pressures up to about (0.65 and 1.6) MPa, resulting in a maximum molality of ammonia of about 13 mol·kg^{-1} of methanol (a maximum mole fraction of ammonia in the liquid of about 0.29). The experimental results from these second series of experiments are reported in Table 2, where y_1 denotes the mole fraction of ammonia in the vapor. The experimental results for the total pressure and for the partial pressures of both components are plotted against the molality of ammonia at a preset temperature in Figure 2.

Table 2. Solubility of Ammonia (1) in Methanol (2)[a]

m_1 / mol·kg^{-1}	p_{exptl} / MPa	p_{calcd} / MPa	$y_{1,\mathrm{exptl}}$	$y_{1,\mathrm{calcd}}$
		$T = 353.1$ K		
0	0.181	0.181	0	0
1.334	0.215	0.218	0.15	0.20
2.726	0.254	0.259	0.31	0.35
3.782	0.288	0.293	0.40	0.44
5.546	0.349	0.353	0.53	0.56
6.292[b]	0.374	0.380	0.57	0.60
7.280	0.414	0.417	0.62	0.65
8.695	0.470	0.472	0.68	0.70
11.17	0.573	0.574	0.75	0.78
13.00	0.653	0.653	0.79	0.81
		$T = 393.1$ K		
0[c]	0.635	0.640	0	0
1.533	0.740	0.738	–	–
3.039	0.846	0.843	0.35	0.29
4.547	0.963	0.958	0.43	0.40
5.748[c]	1.062	1.052	0.49	0.47
7.211	1.190	1.179	0.56	0.55
9.243	1.369	1.360	0.61	0.63
11.30	1.549	1.552	–	–
11.99[c]	1.606	1.613	–	–

[a] Experimental results from method II and correlation/prediction results (using the second set of parameters, eqs 14 to 17). [b] Here: $T = 353.0$ K. [c] Here: $T = 393.0$ K.

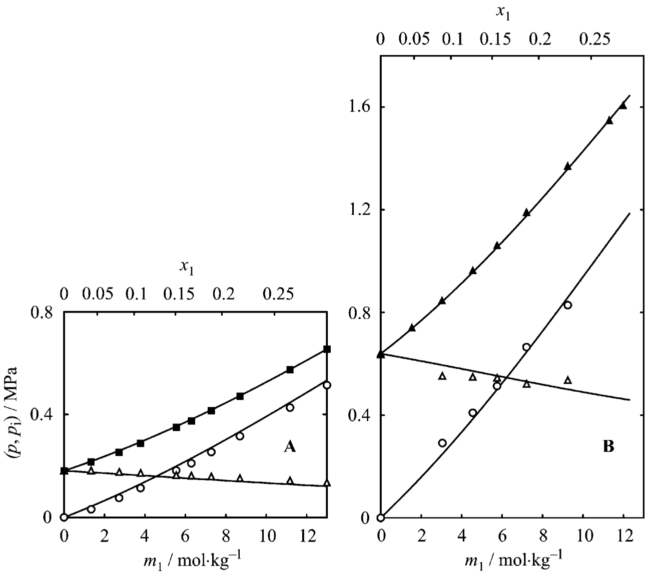

Figure 2. Total and partial pressures (p, p_i) above liquid mixtures of {ammonia (1) + methanol (2)} plotted against the molality m_1 (the mole fraction x_1) of ammonia in the liquid {(A) $T = 353.1$ K, (B) $T = 393.05$ K}: {■, ▲, p; ○, p_1; △, p_2}, experimental results from method II (VLE measurements); —, correlation results using the second set of parameters (eqs 14 to 17).

As shown in those two figures, a purely physical gas solubility behavior is observed. For "small amounts" of the gas in the liquid, and according to Henry's law, the solubility pressure almost linearly increases with augmenting amount of dissolved gas. For "higher amounts" of the gas in the liquid, that linearity turns into a more or less pronounced curvature which may be mainly due to the physical interactions between the gas molecules in the liquid phase. And because the pressure is not very high, its influence on Henry's law constant (of ammonia in methanol) may not be relevant here.

Correlation

The vapor–liquid equilibrium condition results in the extended Raoult's law for the solvent methanol (component 2)

$$p_2^{s}\phi_2^{s}\exp\left[\frac{v_2(p-p_2^{s})}{RT}\right]a_2 = y_2 p\phi_2 \tag{2}$$

and in the extended Henry's law for the solute gas ammonia (component 1)

$$k_{H,1,2}a_1 = y_1 p\phi_1 \tag{3}$$

p_2^{s}, ϕ_2^{s}, and v_2 are the vapor pressure, the fugacity coefficient of the saturated vapor, and the molar liquid volume of methanol, respectively. R is the universal gas constant. a_i is the activity of component i ($i = 1, 2$) in the liquid phase. y_i and ϕ_i are the mole fraction and the fugacity coefficient of component i in the vapor phase. The (molality scale based) Henry's constant of ammonia in methanol $k_{H,1,2}$ is expressed as

$$k_{H,1,2}(T,p) = k_{H,1,2}^{(0)}(T)\exp\left[\frac{v_{1,2}^{\infty}(T)\cdot(p-p_2^{s})}{RT}\right] \tag{4}$$

$k_{H,1,2}^{(0)}(T)$ is the (molality scale based) Henry's constant of ammonia in methanol at the vapor pressure of pure methanol, that is, at a vanishing amount of the gas in the solvent. $v_{1,2}^{\infty}(T)$ is the partial molar volume of ammonia infinitely diluted in liquid methanol. The exponential term in eq 4 (the so-called Krichevsky–Kasarnovski term) accounts for the influence of pressure on Henry's constant.

The activity a_i is calculated by applying the molality scale based Gibbs excess energy model of Pitzer.[17,18] Following that model, and because—at least within the investigated ranges—chemical reactions can be neglected in liquid mixtures of (ammonia + methanol), for the gaseous solute ammonia, the activity is expressed as

$$a_1(T,m_1) = \left(\frac{m_1}{m^{\circ}}\right)\gamma_1(T,m_1) \tag{5}$$

$$\ln\gamma_1(T,m_1) = 2\left(\frac{m_1}{m^{\circ}}\right)\beta_{1,1}^{(0)}(T) + 3\left(\frac{m_1}{m^{\circ}}\right)^2\mu_{1,1,1}(T) \tag{6}$$

m° is the reference molality ($m^{\circ} = 1\ \mathrm{mol\cdot kg^{-1}}$), and $\beta_{1,1}^{(0)}(T)$ and $\mu_{1,1,1}(T)$ are a binary and a ternary parameter for interactions between ammonia molecules in liquid methanol.

For the solvent methanol, Pitzer's model results in

$$\ln a_2(T,m_1) = -M_2^{*}\left[\left(\frac{m_1}{m^{\circ}}\right) + \left(\frac{m_1}{m^{\circ}}\right)^2\beta_{1,1}^{(0)}(T) + 2\left(\frac{m_1}{m^{\circ}}\right)^3\mu_{1,1,1}(T)\right] \tag{7}$$

M_2^{*} is the relative molar mass of methanol divided by 1000 ($M_2^{*} = 0.03204216$).

Like in previous work,[19] the vapor pressure and the molar volume of liquid methanol are taken from Reid et al.[20] and Hales and Ellender,[21] respectively. The virial equation of state is used to calculate the fugacity coefficients in the vapor phase. That equation is truncated after the second virial coefficient. Pure component second virial coefficients $\{B_{11}(T), B_{22}(T)\}$ are calculated from the correlation equations reported in refs 1 and 19. These equations are based on the experimental data compiled by Dymond and Smith,[22] as recommended by Hayden and O'Connell.[23] The mixed second virial coefficient $B_{12}(T)$ is estimated as proposed by the latter authors. Details are given in the Appendix.

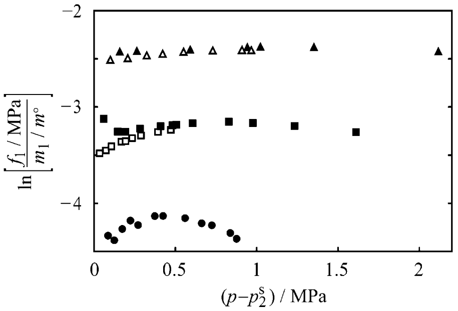

Figure 3. Influence of $p - p_2^{s}$ (p = total pressure above liquid mixtures of {ammonia (1) + methanol (2)}, p_2^{s} = vapor pressure of methanol) on the ratio of the fugacity of ammonia (in the vapor) to the molality of ammonia (in the liquid). (●, T = 313.75 K; ■, T = 354.35 K; ▲, T = 395.0 K), results from method I (gas solubility measurements); (□, T = 354.35 K; △, T = 395.0 K) results from method II (VLE measurements).

The model requires the physical properties $k_{H,1,2}^{(0)}(T)$ and $v_{1,2}^{\infty}(T)$ as well as the model parameters $\beta_{1,1}^{(0)}(T)$ and $\mu_{1,1,1}(T)$. Because those data were not found in the open literature, all properties/parameters were determined from the gas solubility data presented here. At first, $k_{H,1,2}^{(0)}(T)$ was determined by means of the well-known extrapolation procedure (at constant temperature)

$$\ln k_{H,1,2}^{(0)}(T) = \lim_{p\to p_2^{s}}\ln\left[\frac{f_1(T,p,y_1)}{(m_1/m^{\circ})}\right] \tag{8}$$

In eq 8

$$f_1(T,p,y_1) = y_1 p\phi_1(T,p,y_1) \tag{9}$$

is the fugacity of ammonia in the vapor-phase at equilibrium temperature, pressure, and vapor-phase composition. That vapor-phase composition is not experimentally known from the first set of experimental data (Table 1). However, it can be estimated in an iteration process[19] from eqs 2 and 7. In that estimation, both interaction parameters $\{\beta_{1,1}^{(0)}(T)$ and $\mu_{1,1,1}(T)\}$ are set to zero. Furthermore, for the second set of experimental data (Table 2), and in particular for the series of measurements at T = 393.1 K, a large scattering is observed in the mole fractions of the components in the vapor (see Figure 2), which results in a large scattering in the calculated values for $\ln[f_1/(m_1/m^{\circ})]$. Therefore, for the extrapolation to determine $k_{H,1,2}^{(0)}(T)$, the vapor-phase composition was also estimated from the iteration process mentioned above. In Figure 3, the calculated values for $\ln[f_1/(m_1/m^{\circ})]$ are plotted against the difference between the total pressure above the binary mixture (ammonia + methanol) and the vapor pressure of pure methanol. However, a correct extrapolation is difficult to perform as the calculated values for $\ln[f_1/(m_1/m^{\circ})]$ scatter due to experimental uncertainties. That scattering gets still worse when the literature data[3−8] are included in the evaluation. Therefore, the extrapolation results are not presented here, as they were only used as starting guesses in the following correlations for all adjustable properties and parameters $\{k_{H,1,2}^{(0)}(T), v_{1,2}^{\infty}(T), \beta_{1,1}^{(0)}(T)$, and $\mu_{1,1,1}(T)\}$.

Table 3. Comparison of Experimental Data with Correlation/Prediction Results (Using the Second Set of Parameters, Equations 14 to 17)

reference	N^a (M^b)	T/K	m_1/mol·kg^{-1}	x_1	$100\cdot\lvert\Delta p/p_{\mathrm{exptl}}\rvert^c$	$\lvert\Delta y_i\rvert^c$
Correlation						
this work, exptl method I	12 (6)	313.75	< 66.4	< 0.68	3.2	
	12 (10)	354.35	< 41.2	< 0.57	2.7	
	9 (7)	395.0	< 46.7	< 0.60	1.3	
this work, exptl method II	9 (9)	353.1	< 13	< 0.29	1.0	0.033
	8 (8)	393.1	< 12	< 0.28	0.5	0.026
Prediction						
Inomata et al.[3]	14 (4)	313−333	6.2−456	0.166−0.936	5.7	0.02
Preuss[4]	51 (21)	323−393	0−∞	0−1	3.2	
Doering[5]	13 (4)	253	0−∞	0−1	70	
Kudo and Toriumi[6]	40 (15)	273−293	6.8−424	0.179−0.931	18	
Xien et al.[7]	41 (12)	303−363	0−∞	0−1	29	
Feng et al.[8]	18 (4)	283−293	9.6−90	0.24−0.74	14	0.01

[a] N = number of reported data points. [b] M = number of data points considered in the comparison. Only data at $m_1 < 25$ mol·kg^{-1} ($x_1 < 0.45$) are taken into account. [c] $|\Delta p/p_{\mathrm{exptl}}| = (1/M)\cdot\sum_{i=1}^{M}|p_{i,\mathrm{exptl}} - p_{i,\mathrm{calcd}}|/p_{i,\mathrm{exptl}}$; $|\Delta y_i| = (1/M)\cdot\sum_{j=1}^{M}|y_{i,j,\mathrm{exptl}} - y_{i,j,\mathrm{calcd}}|$.

Several correlation attempts were performed. The following first set of parameters resulted on the basis of the experimental data (total pressures only) given in Tables 1 and 2

$$\ln(k_{\mathrm{H},1,2}^{(0)}/\mathrm{MPa}) = 5.5689 - \frac{3162.61}{T/\mathrm{K}} \tag{10}$$

$$\beta_{1,1}^{(0)} = 0.01193 \tag{11}$$

$$\mu_{1,1,1} = -0.00007475 \tag{12}$$

$$v_{1,2}^{\infty}/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}) = -2954.53 + 5.8875(T/\mathrm{K}) \tag{13}$$

With this set of parameters, the model describes almost all experimental data (total and partial pressures) of the present work up to the highest ammonia concentrations (66.35 mol·kg^{-1} at a maximum) nearly within the estimated experimental uncertainty. However, the numerical values for the partial molar volume of ammonia in pure methanol $v_{1,2}^{\infty}(T)$ resulting from eq 13 are negative and their absolute values are large (for example, at $T = 353$ K, $v_{1,2}^{\infty} = -876.2$ cm^3·mol^{-1}). By way of comparison, the partial molar volume of ammonia in pure water as estimated from the method of Brelvi and O'Connell[24] is about 32 cm^3·mol^{-1} {at that same temperature and with characteristic parameters according to Edwards et al.[25] ($v_{\mathrm{NH}_3}^{+} = 65.2$ cm^3·mol^{-1}, $v_{\mathrm{H_2O}}^{+} = 46.4$ cm^3·mol^{-1})}. Therefore, it may be assumed that the set of parameters given by eqs 10 to 13 is not "thermodynamically correct" but mainly just the result of a fitting procedure. The good agreement up to the very high ammonia concentrations is obviously being paid for by presumably unrealistic values for some model parameters.

Therefore, a second correlation attempt was started where the partial molar volume of ammonia at infinite dilution in methanol was set to zero and where only the other properties/model parameters {$k_{\mathrm{H},1,2}^{(0)}(T)$, $\beta_{1,1}^{(0)}(T)$, and $\mu_{1,1,1}(T)$} were simultaneously fit to the experimental data from Tables 1 and 2 (again total pressures only). Various iterations finally revealed that this method gives only a good representation of the experimental data as long as the molality of ammonia is below about 25 mol·kg^{-1} (corresponding to a mole fraction of ammonia of about 0.45). The following second set of parameters resulted from that new correlation

$$\ln(k_{\mathrm{H},1,2}^{(0)}/\mathrm{MPa}) = 5.36125 - \frac{3113.48}{T/\mathrm{K}} \tag{14}$$

$$\beta_{1,1}^{(0)} = 0.002229 + \frac{3.7229}{T/\mathrm{K}} \tag{15}$$

$$\mu_{1,1,1} = -0.00071762 + \frac{0.1817}{T/\mathrm{K}} \tag{16}$$

$$v_{1,2}^{\infty} = 0 \tag{17}$$

Henry's constants calculated for $T = 300$ K and 400 K from eq 14 are only about 4 % and 8 %, respectively, smaller than those calculated from eq 10.

Along with the experimental data, the calculation results (at a preset temperature and liquid-phase composition) resulting from the model by using this second set of parameters are plotted in Figures 1 and 2 against the molality of ammonia. As can be seen from those figures, the calculated results for p (and p_i) match the experimental data very well as long as the molality of ammonia does not exceed 25 mol·kg^{-1}. Beyond that limit, the shape of the pressure curves is only an artifact of the model. This set of parameters shall therefore only be applied up to that maximum molality. A detailed comparison between the experimental results and the correlation results for p and y_1 (by applying the second set of parameters) is given in Table 3.

At this point, it might be worthy to recall the final aim of the ongoing research: It is to develop and test a model to describe the *simultaneous solubility of basic and sour gases in aqueous/organic solvent mixtures* in the presence of strong electrolytes.[19] In this context, the molality of molecular ammonia dissolved in the liquid will by far never reach 25 mol·kg^{-1}. Therefore, in that model, the second set of parameters will be adopted.

Comparison with Literature Data

Table 3 lists all sources of VLE data (solubility data) found in the open literature as well as the pertaining number of experimental points and the investigated ranges for the temperature and the liquid-phase composition. From all those data, only some results by Inomata et al.,[3] Preuss,[4] and Xien et al.[7] are within the ranges of the correlation (eqs 14 to 17, 313 K ≤ T ≤ 395 K, $m_1 \leq 25$ mol·kg^{-1}, see Table 3). For the four data points from Inomata et al.,[3] the average relative deviation between the experimental results and the calculation results for the total pressure (at a preset temperature and liquid-phase composition) is about 5.7 % (with a maximum absolute deviation of 0.039 MPa). The absolute deviation in the composition of the vapor (mole fraction of any component) is 0.02. The 21 (10) data points from Preuss[4] (Xien et al.[7]) are

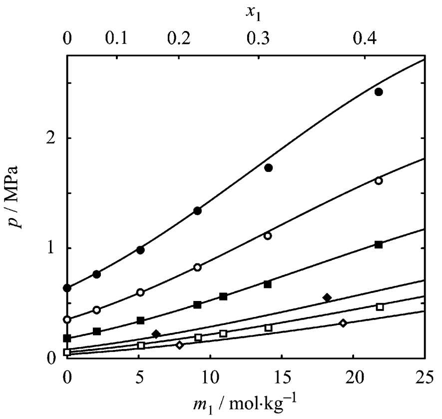

Figure 4. Total pressure (p) above liquid mixtures of {ammonia (1) + methanol (2)} plotted against the molality m_1 (the mole fraction x_1) of ammonia in the liquid: symbols represent experimental data from Inomata et al.[3] (◊, T = 313.05 K; ♦, T = 332.15 K) and from Preuss[4] (□, T = 323.15 K; ■, T = 353.15 K; ○, T = 373.15 K; ●, T = 393.15 K). Curves represent prediction results from the present model using the second set of parameters (eqs 14 to 17).

described (when temperature and liquid-phase composition are used to calculate the pressure) with a relative deviation of 3.4 % (25 %) and a maximum absolute deviation of 0.088 MPa (0.062 MPa). In Figure 4 and by way of comparison, those experimental results from Inomata et al.[3] and Preuss[4] and the prediction results for the total pressure are plotted against the molality of ammonia at a preset temperature.

Conclusions

The solubility of ammonia in liquid methanol was experimentally investigated. The measurements cover temperatures between about 313 K and 395 K and total pressures up to about 4.2 MPa. The new data were used to determine Henry's constant of ammonia in methanol as well as to parametrize a thermodynamic model (based on Pitzer's molality scale based equation for the Gibbs excess energy) for the solubility of ammonia in methanol. The set of interaction parameters reported here is required to allow for a description of the simultaneous solubility of ammonia and carbon dioxide in mixtures of water and methanol as well as of the influence of salts on that gas solubility, which will be investigated in forthcoming publications.

Appendix

Second Virial Coefficients. The following equation (with given parameters) for the pure component second virial coefficients (B_{11}, B_{22}) are adopted from refs 1 and 19

$$\frac{B_{ii}}{\text{cm}^3\cdot\text{mol}^{-1}} = a_i + b_i\left[\frac{c_i}{T/\text{K}}\right]^{d_i} \qquad \text{(A1)}$$

i	a_i	b_i	c_i	d_i	T/K
NH_3 (1)	4.059	−117.713	405.6	2.5	323−598
CH_3OH (2)	−59.649	−103.781	513.2	5.7	335−573

The mixed second virial coefficient B_{12} is calculated as proposed by Hayden and O'Connell.[23] Critical temperatures and pressures ($T_{c,i}$, $p_{c,i}$), molecular dipole moments (μ_i), and mean radii of gyration ($R_{D,i}$) of the pure components, as well as association parameters (η_{ij}), are taken from that reference as well:

i	$T_{c,i}$ / K	$p_{c,i}$ / MPa	μ_i / 10^{-30} Cm	$R_{D,i}$ / 10^{-10} m
NH_3 (1)	405.6	11.28	4.90	0.8533
CH_3OH (2)	513.2	7.95	5.54	1.536

η_{ij}	NH_3	CH_3OH
NH_3	0	0
CH_3OH	0	1.63

The following numerical values result for B_{12} (at several temperatures):

T/K	B_{12}/cm^3·mol^{-1}
313.75	−272.9
354.35	−202.2
395.0	−155.4

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