JOURNAL OF CHEMICAL & ENGINEERING DATA

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pubs.acs.org/jced

Experimental Investigation of the Simultaneous Solubility of Chemically Reacting Gases NH_3 and CO_2 in Liquid Mixtures of (H_2O + CH_3OH)

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ABSTRACT: A high-pressure-cell technique based on the analytical method was used to investigate the simultaneous solubility of the chemically reacting gases ammonia and carbon dioxide in solvent mixtures of (water + methanol). Seven (gas-free) solvent compositions were considered (methanol mole fractions of about 0, 0.05, 0.25, 0.5, 0.75, 0.95, and 1). The temperatures were approximately (313, 353, and 393) K. In the isothermal experimental series, carbon dioxide was added stepwise to a cell containing a mixture of (water + methanol + ammonia). The stoichiometric molality of ammonia in the solvent mixture of (water + methanol) was approximately (6 and 12) mol·(kg of solvent mixture)$^{-1}$. The carbon dioxide loading (i.e., the ratio of the stoichiometric molalities of carbon dioxide and ammonia) ranged up to 1.07. The total pressure ranged up to 5.5 MPa. Vapor−liquid equilibrium data, including partial pressures of all components, are reported.

INTRODUCTION

The solubility of "weak electrolyte gases" in aqueous mixed solvents must be known for the design of a wide variety of separation processes in the chemical and petrochemical industries. In particular, thermodynamic models are required in order to describe the vapor−liquid equilibrium (VLE) encountered when a basic gas (such as ammonia) and an acidic gas (such as carbon dioxide or sulfur dioxide) are simultaneously dissolved in such mixed solvents. It is difficult to consistently describe such a phase equilibrium over the whole solvent composition range (i.e., from one pure solvent to the other one). This is mainly due to the influence of the solvent mixture composition on the relevant equilibrium constants (Henry's constants of the gases, chemical reaction equilibrium constants, and salt solubility products in the solvent mixtures). Furthermore, these chemical reactions, which are mainly dissociation reactions, result in the presence of numerous ionic species, and in many applications, the liquid phase may contain strong electrolytes (e.g., salts) as well.

This paper reports experimental results for the simultaneous solubility of the chemically reacting gases ammonia and carbon dioxide in liquid mixtures of (water + methanol) when low to moderate amounts of the gases are dissolved in the solvent mixture. To the best of our knowledge, no experimental data on the VLE of this system is available in the open literature.

The present work is a continuation of experimental research on (a) the solubilities of the single gases ammonia and carbon dioxide in pure water, in a purely organic solvent (methanol), and in liquid mixtures of water and that organic solvent without or with a single salt and (b) on the simultaneous solubility of those gases in water without or with a single salt.[1−19] It will be extended in an upcoming contribution to the influence of some single salts on the simultaneous solubility of ammonia and carbon dioxide in liquid mixtures of (water + methanol).

APPARATUS, METHOD, AND MATERIALS

A high-pressure-cell technique based on the analytical method was used. The experimental arrangement has been employed in previous investigations, such as studies of the simultaneous solubility of ammonia and carbon dioxide in aqueous solutions (without or with additional salts)[14−17] and of the solubility of ammonia in liquid mixtures of (water + methanol) without or with additional salts.[11,12] Therefore, we provide here only a short description of both the apparatus and the method.

An evacuated thermostatted cell (with a volume of about 1.6 dm^3) was charged with a known amount (about 1 kg) of the solvent mixture of (water + methanol). The composition of that solvent mixture was known from its gravimetric preparation. Next, ammonia was added to achieve the desired stoichiometric molality of that gas. The amount of ammonia was exactly known, as it was taken from a small tank that was weighed before and after the filling procedure. Afterward, in an isothermal experimental series, carbon dioxide was added in a similar way from a second tank in several steps. After each addition, the phases were equilibrated, and then the temperature, pressure, and vapor-phase volume were measured and small vapor-phase samples were taken and analyzed by online gas chromatography. To avoid condensation, the temperature in the sampling system (volume ≈ 3 cm^3) was kept at about 10 K above the temperature of the cell. The results were used together with the virial equation of state for the vapor phase (truncated after the second virial coefficient) to determine the amounts of ammonia, carbon dioxide, water, and methanol in that vapor phase. Details concerning the calculation of the second virial coefficients

Special Issue: John M. Prausnitz Festschrift

Received: October 18, 2010
Accepted: December 21, 2010
Published: January 31, 2011

Table 1. Experimental Results for the Vapor−Liquid Equilibrium of Ammonia (1) + Carbon Dioxide (2) + Water (3) + Methanol (4) (ΔT = 0.1 K)[a]

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	kPa	kPa	kPa	kPa	kPa
313.10	0.0496 ± 0.0001	6.031 ± 0.004	0	24.1 ± 4.1	0	7.1 ± 1.1	2.3 ± 0.4	33.5 ± 5.0
313.10	0.0496 ± 0.0001	6.034 ± 0.004	0.614 ± 0.001	20.7 ± 3.8	0.5 ± 0.1	6.6 ± 1.1	2.3 ± 0.4	30.1 ± 5.0
313.10	0.0496 ± 0.0001	6.038 ± 0.004	1.418 ± 0.001	15.1 ± 3.2	0.5 ± 0.1	6.9 ± 1.4	2.8 ± 0.6	25.3 ± 5.0
313.10	0.0496 ± 0.0001	6.043 ± 0.004	2.236 ± 0.001	9.2 ± 2.3	1.5 ± 0.4	7.0 ± 1.7	3.5 ± 0.8	21.1 ± 5.0
313.10	0.0496 ± 0.0001	6.047 ± 0.004	3.002 ± 0.001	4.6 ± 1.1	6.5 ± 1.5	7.1 ± 1.6	3.5 ± 0.8	21.9 ± 5.0
313.10	0.0496 ± 0.0001	6.050 ± 0.004	4.076 ± 0.002	0.6 ± 0.1	47.1 ± 4.6	7.1 ± 0.6	3.5 ± 0.3	58.3 ± 5.0
313.10	0.0496 ± 0.0001	6.050 ± 0.004	4.638 ± 0.004	0.2 ± 0.04	95.1 ± 6.4	6.6 ± 0.3	3.4 ± 0.2	105.8 ± 5.0
313.10	0.0496 ± 0.0001	6.050 ± 0.004	5.140 ± 0.006	0	144.1 ± 8.4	6.6 ± 0.3	3.3 ± 0.2	154.2 ± 5.0
313.15	0.0496 ± 0.0001	6.050 ± 0.004	5.833 ± 0.023	0	477 ± 29	6.8 ± 0.2	3.2 ± 0.2	487.1 ± 5.0
313.10	0.0496 ± 0.0001	6.050 ± 0.004	5.929 ± 0.035	0	631 ± 44	6.5 ± 0.2	3.2 ± 0.2	641.1 ± 5.0
313.10	0.0496 ± 0.0001	6.050 ± 0.004	5.963 ± 0.039	0	692 ± 50	6.9 ± 0.2	3.1 ± 0.2	702.9 ± 5.0
313.15	0.0490 ± 0.0001	12.030 ± 0.005	0	57.0 ± 6.6	0	6.7 ± 0.6	2.0 ± 0.2	65.7 ± 5.0
313.15	0.0490 ± 0.0001	12.040 ± 0.005	1.920 ± 0.001	43.3 ± 5.6	1.2 ± 0.1	4.7 ± 0.5	2.3 ± 0.3	51.5 ± 5.0
313.15	0.0490 ± 0.0001	12.054 ± 0.004	4.032 ± 0.001	24.8 ± 4.1	0.8 ± 0.1	6.3 ± 0.9	3.3 ± 0.5	35.2 ± 5.0
313.10	0.0490 ± 0.0001	12.063 ± 0.004	5.530 ± 0.001	12.4 ± 2.4	6.7 ± 1.2	5.9 ± 1.0	3.5 ± 0.6	28.6 ± 5.0
313.10	0.0490 ± 0.0001	12.070 ± 0.004	6.870 ± 0.001	4.0 ± 0.7	20.1 ± 3.0	6.3 ± 0.9	4.3 ± 0.6	34.6 ± 5.0
313.10	0.0490 ± 0.0001	12.070 ± 0.004	7.581 ± 0.001	3.4 ± 0.5	23.0 ± 3.3	6.4 ± 0.9	4.1 ± 0.6	36.9 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	8.970 ± 0.001	1.3 ± 0.2	34.3 ± 4.0	6.5 ± 0.7	4.1 ± 0.5	46.3 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	10.394 ± 0.003	0.1 ± 0.02	73.2 ± 5.6	6.3 ± 0.4	3.9 ± 0.3	83.7 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	10.839 ± 0.005	0	145.2 ± 8.5	6.2 ± 0.2	3.8 ± 0.2	164.2 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	11.279 ± 0.015	0	364 ± 21	6.3 ± 0.2	3.7 ± 0.2	376.0 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	11.379 ± 0.030	0	589 ± 41	6.2 ± 0.2	3.6 ± 0.2	600.3 ± 5.0
313.10	0.0490 ± 0.0001	12.072 ± 0.004	11.454 ± 0.033	0	626 ± 44	6.5 ± 0.2	3.6 ± 0.2	637.6 ± 5.0
313.10	0.2483 ± 0.0006	6.056 ± 0.004	0	29.2 ± 4.0	0	5.9 ± 0.7	10.0 ± 1.2	45.0 ± 5.0
313.10	0.2483 ± 0.0006	6.060 ± 0.004	0.640 ± 0.001	24.0 ± 3.6	0.2 ± 0.04	5.7 ± 0.7	10.7 ± 1.4	40.6 ± 5.0
313.15	0.2482 ± 0.0006	6.067 ± 0.004	1.665 ± 0.001	15.3 ± 2.5	1.6 ± 0.2	5.8 ± 0.8	11.9 ± 1.8	34.6 ± 5.0
313.10	0.2482 ± 0.0006	6.073 ± 0.004	2.453 ± 0.001	9.0 ± 1.5	5.5 ± 0.9	5.5 ± 0.8	13.1 ± 2.1	33.0 ± 5.0
313.20	0.2482 ± 0.0006	6.077 ± 0.004	3.421 ± 0.001	3.6 ± 0.5	23.8 ± 2.8	5.1 ± 0.6	13.1 ± 1.6	45.7 ± 5.0
313.10	0.2482 ± 0.0006	6.078 ± 0.004	4.041 ± 0.002	2.2 ± 0.3	36.6 ± 3.6	5.4 ± 0.5	13.0 ± 1.3	57.3 ± 5.0
313.10	0.2482 ± 0.0006	6.080 ± 0.004	4.808 ± 0.002	0.8 ± 0.1	55.9 ± 4.5	5.3 ± 0.4	13.1 ± 1.1	75.1 ± 5.0
313.15	0.2482 ± 0.0006	6.080 ± 0.004	5.357 ± 0.004	0.1 ± 0.02	95.4 ± 6.2	4.9 ± 0.2	12.7 ± 0.9	113.2 ± 5.0
313.10	0.2482 ± 0.0006	6.080 ± 0.004	5.957 ± 0.017	0	344 ± 21	4.9 ± 0.1	12.3 ± 0.7	361.5 ± 5.0
313.10	0.2482 ± 0.0006	6.080 ± 0.004	6.093 ± 0.038	0	556 ± 46	4.5 ± 0.2	12.2 ± 0.7	573.7 ± 5.0
313.10	0.2482 ± 0.0006	6.080 ± 0.004	6.146 ± 0.055	0	683 ± 64	4.4 ± 0.2	12.0 ± 0.8	700.3 ± 5.0
313.15	0.2450 ± 0.0006	11.961 ± 0.006	0	71.8 ± 7.4	0	5.7 ± 0.4	8.4 ± 0.7	86.0 ± 5.0
313.15	0.2450 ± 0.0006	11.989 ± 0.005	3.162 ± 0.001	36.8 ± 4.6	0.8 ± 0.1	5.5 ± 0.5	11.0 ± 1.2	54.2 ± 5.0
313.10	0.2450 ± 0.0006	11.999 ± 0.004	4.300 ± 0.001	25.5 ± 3.5	2.2 ± 0.3	5.6 ± 0.6	12.0 ± 1.5	45.3 ± 5.0
313.20	0.2450 ± 0.0006	12.010 ± 0.004	5.990 ± 0.001	11.3 ± 1.6	12.1 ± 1.5	5.4 ± 0.6	13.9 ± 1.8	42.7 ± 5.0
313.15	0.2450 ± 0.0006	12.011 ± 0.004	6.888 ± 0.001	9.8 ± 1.4	14.1 ± 1.7	5.8 ± 0.7	13.5 ± 1.7	43.1 ± 5.0
313.15	0.2450 ± 0.0006	12.013 ± 0.004	7.592 ± 0.001	7.9 ± 1.1	16.0 ± 2.0	5.7 ± 0.7	14.1 ± 1.8	43.7 ± 5.0
313.10	0.2450 ± 0.0006	12.014 ± 0.004	8.461 ± 0.001	6.8 ± 0.9	18.5 ± 2.2	5.9 ± 0.7	13.8 ± 1.7	45.0 ± 5.0
313.15	0.2450 ± 0.0006	12.016 ± 0.004	9.655 ± 0.001	4.0 ± 0.5	27.4 ± 2.9	6.2 ± 0.6	14.2 ± 1.5	51.8 ± 5.0
313.25	0.2450 ± 0.0006	12.019 ± 0.004	10.325 ± 0.003	0.5 ± 0.1	87.3 ± 5.8	5.5 ± 0.3	13.9 ± 1.0	107.8 ± 5.0
313.10	0.2450 ± 0.0006	12.019 ± 0.004	10.660 ± 0.014	0	323 ± 18	6.0 ± 0.2	14.0 ± 0.7	343.7 ± 5.0
313.15	0.2449 ± 0.0006	12.019 ± 0.004	10.733 ± 0.035	0	592 ± 44	5.4 ± 0.2	13.8 ± 0.8	613.3 ± 5.0
313.10	0.2449 ± 0.0006	12.019 ± 0.004	10.810 ± 0.041	0	607 ± 51	4.6 ± 0.2	13.7 ± 0.9	626.6 ± 5.0
313.75	0.4984 ± 0.0014	6.050 ± 0.005	0	38.3 ± 4.5	0	5.7 ± 0.5	16.1 ± 1.6	60.2 ± 5.0
313.00	0.4983 ± 0.0014	6.062 ± 0.005	1.051 ± 0.001	25.6 ± 3.4	1.4 ± 0.2	5.1 ± 0.5	16.6 ± 1.9	48.8 ± 5.0

Table 1. Continued

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	kPa	kPa	kPa
313.00	0.4983 ± 0.0014	6.073 ± 0.004	2.019 ± 0.001	14.1 ± 2.0	5.3 ± 0.7	4.1 ± 0.5	21.8 ± 4.5	45.2 ± 5.0
313.05	0.4983 ± 0.0014	6.078 ± 0.004	2.974 ± 0.001	8.2 ± 1.0	21.4 ± 2.2	4.7 ± 0.4	19.2 ± 2.1	53.6 ± 5.0
313.10	0.4983 ± 0.0014	6.080 ± 0.004	3.984 ± 0.001	5.6 ± 0.7	26.3 ± 2.6	4.7 ± 0.4	19.6 ± 2.1	56.3 ± 5.0
313.10	0.4983 ± 0.0014	6.083 ± 0.004	4.901 ± 0.002	2.0 ± 0.2	47.2 ± 3.9	3.9 ± 0.3	20.2 ± 2.0	73.3 ± 5.0
313.10	0.4983 ± 0.0014	6.085 ± 0.004	5.496 ± 0.005	0.1 ± 0.02	114.2 ± 7.0	3.4 ± 0.1	19.8 ± 1.6	138.0 ± 5.0
313.10	0.4983 ± 0.0014	6.085 ± 0.004	5.836 ± 0.017	0	285 ± 19	3.4 ± 0.1	19.3 ± 1.5	308.2 ± 5.0
313.00	0.4983 ± 0.0014	6.085 ± 0.004	6.068 ± 0.044	0	497 ± 49	3.1 ± 0.1	19.1 ± 1.7	519.8 ± 5.0
313.15	0.4983 ± 0.0014	6.085 ± 0.004	6.199 ± 0.076	0	650 ± 83	3.0 ± 0.2	19.1 ± 1.8	673.2 ± 5.0
313.10	0.4966 ± 0.0014	11.916 ± 0.009	0	95 ± 10	0	4.8 ± 0.3	14.3 ± 1.1	113.6 ± 5.0
313.10	0.4966 ± 0.0014	11.955 ± 0.005	2.969 ± 0.001	48.8 ± 5.3	1.4 ± 0.1	4.2 ± 0.3	16.7 ± 1.6	71.2 ± 5.0
313.05	0.4966 ± 0.0014	11.969 ± 0.005	4.249 ± 0.001	32.7 ± 3.9	3.9 ± 0.4	3.7 ± 0.3	18.6 ± 2.0	59.0 ± 5.0
313.05	0.4966 ± 0.0014	11.980 ± 0.004	5.658 ± 0.001	19.2 ± 2.4	8.5 ± 0.9	3.8 ± 0.4	20.0 ± 2.4	51.5 ± 5.0
313.10	0.4965 ± 0.0014	11.988 ± 0.004	6.737 ± 0.001	10.1 ± 1.2	19 ± 2	4.1 ± 0.4	21.0 ± 2.4	54.2 ± 5.0
313.10	0.4965 ± 0.0014	11.987 ± 0.004	7.596 ± 0.001	12.2 ± 1.5	17 ± 2	4.5 ± 0.4	21.2 ± 2.4	54.4 ± 5.0
313.10	0.4965 ± 0.0014	11.989 ± 0.004	8.662 ± 0.001	10.9 ± 1.3	21 ± 2	4.4 ± 0.4	23.8 ± 2.6	59.8 ± 5.0
313.15	0.7354 ± 0.0024	6.015 ± 0.019	0	45 ± 22	0	0.6 ± 0.1	28 ± 12	73.9 ± 5.0
313.15	0.7354 ± 0.0024	6.042 ± 0.004	1.973 ± 0.001	13.9 ± 2.1	9.7 ± 1.0	3.8 ± 0.3	30.1 ± 3.4	57.6 ± 5.0
313.15	0.7354 ± 0.0024	6.049 ± 0.004	3.236 ± 0.002	4.9 ± 0.7	29.6 ± 2.8	2.9 ± 0.2	28.8 ± 3.2	66.2 ± 5.0
313.10	0.7354 ± 0.0024	6.051 ± 0.004	3.917 ± 0.003	2.5 ± 0.3	66.3 ± 5.1	3.0 ± 0.2	28.1 ± 2.7	100.1 ± 5.0
313.10	0.7354 ± 0.0024	6.050 ± 0.004	4.447 ± 0.003	3.2 ± 0.4	47.9 ± 4.0	2.7 ± 0.2	29.3 ± 3.1	83.2 ± 5.0
313.10	0.7354 ± 0.0024	6.052 ± 0.004	5.228 ± 0.004	1.9 ± 0.2	87.0 ± 6.3	2.7 ± 0.1	30.6 ± 3.1	122.3 ± 5.0
313.10	0.7354 ± 0.0024	6.053 ± 0.004	5.803 ± 0.012	0	211 ± 15	3.2 ± 0.1	27.9 ± 2.5	242.1 ± 5.0
313.10	0.7354 ± 0.0024	6.055 ± 0.004	6.265 ± 0.028	0	439 ± 34	4.2 ± 0.1	38.3 ± 3.2	482.2 ± 5.0
313.05	0.7354 ± 0.0024	6.055 ± 0.004	6.418 ± 0.033	0	532 ± 41	5.4 ± 0.2	39.9 ± 3.0	577.9 ± 5.0
313.05	0.7353 ± 0.0024	6.055 ± 0.004	6.482 ± 0.039	0	580 ± 47	4.9 ± 0.2	41.3 ± 3.3	626.3 ± 5.0
353.05	0.0495 ± 0.0001	5.502 ± 0.010	0	92 ± 14	0	39.2 ± 1.6	14.6 ± 0.8	146.2 ± 5.0
353.00	0.0494 ± 0.0001	5.512 ± 0.009	0.575 ± 0.001	78 ± 12	1.9 ± 0.1	39.6 ± 2.2	15.9 ± 1.1	135.3 ± 5.0
353.05	0.0494 ± 0.0001	5.519 ± 0.008	0.971 ± 0.001	68 ± 10	5.5 ± 0.4	40.9 ± 2.2	17.4 ± 1.1	131.9 ± 5.0
353.05	0.0494 ± 0.0001	5.527 ± 0.007	1.452 ± 0.001	57.0 ± 8.5	13.7 ± 1.0	41.0 ± 2.0	18.4 ± 1.2	130.3 ± 5.0
353.05	0.0494 ± 0.0001	5.535 ± 0.006	1.863 ± 0.001	46.3 ± 6.9	26.9 ± 1.9	41.8 ± 1.9	19.5 ± 1.2	134.5 ± 5.0
353.05	0.0494 ± 0.0001	5.546 ± 0.005	2.422 ± 0.003	31.8 ± 4.6	65.3 ± 4.2	43.9 ± 1.6	21.6 ± 1.1	162.4 ± 5.0
353.05	0.0494 ± 0.0001	5.552 ± 0.005	2.793 ± 0.005	23.9 ± 3.5	115.8 ± 7.3	42.6 ± 1.3	21.7 ± 1.1	204.1 ± 5.0
353.10	0.0493 ± 0.0001	5.557 ± 0.004	3.107 ± 0.009	17.3 ± 2.5	201 ± 13	43.0 ± 1.2	23.1 ± 1.1	284.9 ± 5.0
353.10	0.0494 ± 0.0001	5.559 ± 0.004	3.355 ± 0.013	13.9 ± 2.0	289 ± 19	41.4 ± 1.1	22.2 ± 1.1	366.5 ± 5.0
353.05	0.0494 ± 0.0001	5.561 ± 0.004	3.606 ± 0.021	10.5 ± 1.5	415 ± 29	40.6 ± 1.2	21.7 ± 1.1	488.4 ± 5.0
353.10	0.0494 ± 0.0001	5.564 ± 0.004	3.853 ± 0.036	6.6 ± 1.0	600 ± 49	40.0 ± 1.4	21.2 ± 1.1	668.3 ± 5.0
353.10	0.0494 ± 0.0001	10.998 ± 0.021	0	201 ± 30	0	36.5 ± 1.4	12.4 ± 0.7	249.7 ± 5.0
353.10	0.0494 ± 0.0001	11.014 ± 0.019	0.969 ± 0.001	176 ± 27	1.4 ± 0.1	36.8 ± 2.2	13.6 ± 1.0	227.3 ± 5.0
353.10	0.0493 ± 0.0001	11.031 ± 0.016	1.867 ± 0.001	151 ± 23	4.8 ± 0.4	36.8 ± 2.1	14.7 ± 1.0	207.6 ± 5.0
353.10	0.0493 ± 0.0001	11.049 ± 0.013	2.868 ± 0.001	125 ± 19	11.1 ± 0.8	37.6 ± 2.0	17.6 ± 1.2	191.1 ± 5.0
353.10	0.0493 ± 0.0001	11.068 ± 0.011	3.821 ± 0.001	98 ± 15	26.7 ± 1.9	39.7 ± 1.9	19.9 ± 1.2	183.9 ± 5.0
353.10	0.0492 ± 0.0001	11.077 ± 0.010	4.610 ± 0.003	88 ± 13	75.2 ± 4.9	48.9 ± 1.7	26.2 ± 1.4	238.4 ± 5.0
353.10	0.0492 ± 0.0001	11.095 ± 0.007	5.378 ± 0.006	61.7 ± 8.9	148 ± 9	48.3 ± 1.3	27.0 ± 1.3	285.0 ± 5.0
353.10	0.0492 ± 0.0001	11.111 ± 0.005	6.191 ± 0.013	37.0 ± 5.3	314 ± 20	46.5 ± 1.2	25.8 ± 1.2	423.2 ± 5.0
353.10	0.0492 ± 0.0001	11.117 ± 0.005	6.592 ± 0.022	28.1 ± 4.1	457 ± 32	44.8 ± 1.3	25.3 ± 1.2	555.7 ± 5.0
353.05	0.0492 ± 0.0001	11.118 ± 0.005	6.808 ± 0.028	26.4 ± 3.8	553 ± 41	46.0 ± 1.4	24.8 ± 1.2	651.3 ± 5.0
353.05	0.2478 ± 0.0006	5.799 ± 0.013	0	108 ± 17	0	33.9 ± 1.9	54.4 ± 4.1	196.6 ± 5.0
353.05	0.2477 ± 0.0006	5.826 ± 0.010	1.118 ± 0.001	75 ± 11	19.3 ± 1.3	33.8 ± 1.3	61.6 ± 4.1	190.1 ± 5.0

Table 1. Continued

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	kPa	kPa	kPa
353.05	0.2476 ± 0.0006	5.845 ± 0.007	1.980 ± 0.003	51.5 ± 7.5	71.1 ± 4.4	32.9 ± 1.0	66.4 ± 4.2	222.1 ± 5.0
353.05	0.2476 ± 0.0006	5.861 ± 0.005	2.738 ± 0.009	31.4 ± 4.5	192 ± 12	32.9 ± 0.8	69.1 ± 4.3	325.3 ± 5.0
353.05	0.2476 ± 0.0006	5.867 ± 0.005	3.084 ± 0.016	23.3 ± 3.3	298 ± 20	32.1 ± 0.8	70.4 ± 4.5	424.6 ± 5.0
353.10	0.2475 ± 0.0006	5.869 ± 0.005	3.353 ± 0.025	20.3 ± 2.9	415 ± 32	31.5 ± 0.9	70.6 ± 4.7	538.3 ± 5.0
353.05	0.2475 ± 0.0006	5.872 ± 0.005	3.578 ± 0.037	16.6 ± 2.4	544 ± 47	31.3 ± 1.1	70.3 ± 4.8	663.5 ± 5.0
353.15	0.2483 ± 0.0006	11.955 ± 0.030	0	262 ± 41	0	31.2 ± 1.7	46.0 ± 3.3	339.7 ± 5.0
353.15	0.2482 ± 0.0006	12.000 ± 0.023	1.798 ± 0.001	203 ± 31	8.5 ± 0.6	30.4 ± 1.6	55.9 ± 4.2	296.9 ± 5.0
353.10	0.2479 ± 0.0006	12.049 ± 0.016	4.033 ± 0.003	145 ± 21	63.0 ± 4.1	43.1 ± 1.5	79.6 ± 5.1	331.1 ± 5.0
353.05	0.2479 ± 0.0006	12.075 ± 0.012	4.944 ± 0.006	110 ± 16	127.0 ± 7.9	40.7 ± 1.2	82.9 ± 5.2	361.6 ± 5.0
353.10	0.2478 ± 0.0006	12.099 ± 0.009	5.730 ± 0.010	78 ± 11	232 ± 15	39.1 ± 0.9	84.9 ± 5.4	434.5 ± 5.0
353.05	0.2478 ± 0.0006	12.112 ± 0.007	6.254 ± 0.017	59.3 ± 8.5	349 ± 23	37.9 ± 0.9	85.1 ± 5.5	531.3 ± 5.0
353.05	0.2478 ± 0.0006	12.117 ± 0.007	6.563 ± 0.024	51.6 ± 7.4	443 ± 32	36.4 ± 1.0	83.9 ± 5.6	615.5 ± 5.0
353.15	0.4912 ± 0.0014	6.058 ± 0.019	0	140 ± 22	0	26.6 ± 1.8	84.8 ± 8.6	251.3 ± 5.0
353.15	0.4910 ± 0.0014	6.092 ± 0.013	1.096 ± 0.002	100 ± 15	43.2 ± 2.8	25.3 ± 0.9	93.7 ± 8.6	262.6 ± 5.0
353.10	0.4910 ± 0.0014	6.120 ± 0.009	2.110 ± 0.008	66.7 ± 9.6	156 ± 10	25.3 ± 0.7	99.0 ± 9.1	347.1 ± 5.0
353.15	0.4909 ± 0.0014	6.130 ± 0.008	2.498 ± 0.014	56.1 ± 8.1	249 ± 17	25.4 ± 0.7	104 ± 10	434.6 ± 5.0
353.15	0.4909 ± 0.0014	6.136 ± 0.007	2.785 ± 0.021	48.4 ± 7.0	333 ± 25	25.9 ± 0.7	104 ± 10	512.1 ± 5.0
353.15	0.4909 ± 0.0014	6.141 ± 0.007	3.050 ± 0.030	41.7 ± 6.1	432 ± 37	25.5 ± 0.8	104 ± 10	604.3 ± 5.0
353.15	0.4909 ± 0.0014	6.146 ± 0.006	3.232 ± 0.041	36.5 ± 5.3	519 ± 50	24.7 ± 0.9	105 ± 11	685.5 ± 5.0
353.10	0.4990 ± 0.0014	11.914 ± 0.043	0	324 ± 56	0	23.1 ± 1.6	73.8 ± 7.6	421.4 ± 5.0
353.05	0.4989 ± 0.0014	11.989 ± 0.029	2.157 ± 0.002	229 ± 37	26.9 ± 2.0	21.1 ± 1.1	86.9 ± 9.1	364.4 ± 5.0
353.10	0.4987 ± 0.0014	12.058 ± 0.017	4.113 ± 0.006	144 ± 22	108.6 ± 7.2	21.1 ± 0.7	100 ± 11	373.4 ± 5.0
353.05	0.4987 ± 0.0014	12.078 ± 0.014	4.727 ± 0.009	121 ± 18	170 ± 12	21.8 ± 0.7	107 ± 12	419.4 ± 5.0
353.05	0.4987 ± 0.0014	12.091 ± 0.013	5.189 ± 0.013	105 ± 15	234 ± 17	21.6 ± 0.6	108 ± 12	468.4 ± 5.0
353.10	0.4987 ± 0.0014	12.101 ± 0.011	5.652 ± 0.019	93 ± 14	330 ± 24	26.5 ± 0.7	112 ± 11	561.8 ± 5.0
353.05	0.4987 ± 0.0014	12.110 ± 0.010	6.001 ± 0.026	82 ± 12	417 ± 33	27.3 ± 0.8	112 ± 11	638.4 ± 5.0
353.05	0.7501 ± 0.0024	5.937 ± 0.028	0	172 ± 30	0	15.6 ± 1.4	117 ± 21	304.7 ± 5.0
353.10	0.7500 ± 0.0024	5.956 ± 0.022	0.511 ± 0.002	151 ± 24	32.0 ± 2.4	15.7 ± 0.8	120 ± 20	318.9 ± 5.0
353.05	0.7500 ± 0.0024	5.967 ± 0.020	0.833 ± 0.004	138 ± 21	62.2 ± 4.5	15.0 ± 0.7	122 ± 21	337.5 ± 5.0
353.05	0.7501 ± 0.0024	5.979 ± 0.018	1.202 ± 0.007	124 ± 19	110.8 ± 7.8	16.6 ± 0.6	118 ± 19	368.8 ± 5.0
353.05	0.7500 ± 0.0024	5.997 ± 0.015	1.650 ± 0.013	104 ± 16	181 ± 14	15.1 ± 0.6	127 ± 23	427.3 ± 5.0
353.10	0.7499 ± 0.0024	6.012 ± 0.013	2.071 ± 0.023	88 ± 13	276 ± 25	14.4 ± 0.5	129 ± 24	507.8 ± 5.0
353.10	0.7499 ± 0.0024	6.017 ± 0.012	2.278 ± 0.032	82 ± 12	333 ± 35	13.9 ± 0.5	130 ± 26	559.4 ± 5.0
353.10	0.7499 ± 0.0024	6.027 ± 0.011	2.622 ± 0.053	71 ± 11	449 ± 58	14.1 ± 0.6	130 ± 26	664.6 ± 5.0
353.15	0.7509 ± 0.0024	11.711 ± 0.078	0	393 ± 91	0	13.4 ± 1.6	100 ± 20	506.4 ± 5.0
353.15	0.7509 ± 0.0024	11.741 ± 0.061	0.669 ± 0.001	355 ± 71	11.8 ± 1.1	14.0 ± 1.0	102 ± 17	483.7 ± 5.0
353.10	0.7508 ± 0.0024	11.772 ± 0.055	1.354 ± 0.002	318 ± 63	27.8 ± 2.4	12.6 ± 0.9	105 ± 20	463.8 ± 5.0
353.15	0.7508 ± 0.0024	11.809 ± 0.044	2.117 ± 0.004	274 ± 51	50.4 ± 4.1	12.8 ± 0.8	110 ± 21	446.8 ± 5.0
353.00	0.7508 ± 0.0024	11.848 ± 0.035	3.062 ± 0.007	228 ± 40	96.7 ± 7.6	12.0 ± 0.6	112 ± 22	448.8 ± 5.0
353.05	0.7507 ± 0.0024	11.876 ± 0.029	3.682 ± 0.010	195 ± 33	137 ± 11	11.7 ± 0.5	116 ± 24	460.2 ± 5.0
353.05	0.7507 ± 0.0024	11.908 ± 0.023	4.324 ± 0.016	160 ± 26	201 ± 18	11.6 ± 0.5	122 ± 27	494.3 ± 5.0
353.00	0.7507 ± 0.0024	11.924 ± 0.020	4.781 ± 0.023	141 ± 22	265 ± 27	11.7 ± 0.5	123 ± 27	541.3 ± 5.0
353.05	0.7507 ± 0.0024	11.938 ± 0.018	5.151 ± 0.035	125 ± 20	332 ± 41	11.2 ± 0.5	125 ± 29	593.5 ± 5.0
353.10	0.7507 ± 0.0024	11.948 ± 0.016	5.401 ± 0.046	113 ± 18	388 ± 53	11.3 ± 0.5	126 ± 30	638.2 ± 5.0
353.10	0.7506 ± 0.0024	11.952 ± 0.016	5.584 ± 0.058	109 ± 17	434 ± 68	10.7 ± 0.6	127 ± 32	680.6 ± 5.0
353.10	0.9458 ± 0.0033	6.002 ± 0.018	0	193 ± 19	0	4.9 ± 1.6	154.2 ± 4.5	352.4 ± 5.0
353.10	0.9458 ± 0.0033	6.020 ± 0.016	0.435 ± 0.002	174 ± 17	44.4 ± 1.6	4.7 ± 1.6	157.4 ± 4.0	380.2 ± 5.0
353.10	0.9458 ± 0.0033	6.039 ± 0.014	0.874 ± 0.003	153 ± 14	106.4 ± 3.6	5.2 ± 1.6	159.0 ± 3.3	423.6 ± 5.0

Table 1. Continued

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	kPa	kPa	kPa
353.10	0.9458 ± 0.0033	6.050 ± 0.013	1.208 ± 0.005	140 ± 13	161.7 ± 5.3	4.8 ± 1.6	160.1 ± 2.9	467.2 ± 5.0
353.10	0.9458 ± 0.0033	6.062 ± 0.012	1.513 ± 0.007	127 ± 12	222.4 ± 7.3	4.6 ± 1.6	160.8 ± 2.6	515.5 ± 5.0
353.05	0.9458 ± 0.0033	6.070 ± 0.011	1.725 ± 0.008	118 ± 11	271.8 ± 9.1	4.5 ± 1.6	161.0 ± 2.5	555.3 ± 5.0
353.15	0.9458 ± 0.0033	6.080 ± 0.011	2.017 ± 0.011	107 ± 10	349 ± 12	4.5 ± 1.7	162.1 ± 2.4	623.2 ± 5.0
353.15	0.9457 ± 0.0033	6.087 ± 0.010	2.229 ± 0.014	99 ± 9	412 ± 15	4.6 ± 1.7	163.0 ± 2.4	679.1 ± 5.0
353.20	0.9590 ± 0.0033	11.906 ± 0.040	0	449 ± 46	0	4.6 ± 1.4	137.9 ± 5.1	591.8 ± 5.0
353.15	0.9590 ± 0.0033	11.941 ± 0.036	0.771 ± 0.001	404 ± 40	26.4 ± 1.1	4.8 ± 1.4	140.0 ± 4.8	577.4 ± 5.0
353.20	0.9590 ± 0.0033	11.986 ± 0.031	1.476 ± 0.002	350 ± 35	41.0 ± 1.7	4.4 ± 1.5	142.0 ± 4.5	537.4 ± 5.0
353.10	0.9589 ± 0.0033	12.027 ± 0.026	2.073 ± 0.002	302 ± 29	54.1 ± 2.1	3.8 ± 1.5	145.7 ± 4.3	505.1 ± 5.0
353.00	0.9589 ± 0.0033	12.064 ± 0.023	2.663 ± 0.003	258 ± 25	74.2 ± 2.8	3.6 ± 1.5	148.2 ± 4.0	483.1 ± 5.0
353.10	0.9589 ± 0.0033	12.104 ± 0.019	3.292 ± 0.003	213 ± 20	107.4 ± 3.8	4.4 ± 1.6	153.7 ± 3.6	478.5 ± 5.0
353.10	0.9589 ± 0.0033	12.138 ± 0.016	3.936 ± 0.005	175 ± 17	163.5 ± 5.5	3.8 ± 1.6	155.7 ± 3.1	498.8 ± 5.0
353.05	0.9589 ± 0.0033	12.166 ± 0.013	4.446 ± 0.007	144 ± 14	232.5 ± 7.7	3.9 ± 1.6	159.8 ± 2.7	540.9 ± 5.0
353.10	0.9589 ± 0.0033	12.188 ± 0.011	4.891 ± 0.010	121 ± 11	320 ± 11	3.5 ± 1.7	163.0 ± 2.4	607.7 ± 5.0
353.05	0.9589 ± 0.0033	12.195 ± 0.011	5.079 ± 0.012	113 ± 11	364 ± 13	3.7 ± 1.7	162.9 ± 2.4	643.6 ± 5.0
353.15	0.9589 ± 0.0033	12.200 ± 0.010	5.215 ± 0.013	107 ± 10	404 ± 15	3.9 ± 1.7	164.3 ± 2.4	679.4 ± 5.0
353.05	1 − 0.0036	6.292 ± 0.017	0	210 ± 18	0	1.9 ± 2.1	161.6 ± 4.8	373.5 ± 5.0
353.05	1 − 0.0036	6.299 ± 0.018	0.173 ± 0.001	202 ± 19	15.3 ± 0.6	2.3 ± 1.7	162.8 ± 4.6	382.1 ± 5.0
353.05	1 − 0.0036	6.312 ± 0.017	0.492 ± 0.002	187 ± 18	53.5 ± 1.9	2.7 ± 1.7	164.2 ± 4.1	407.1 ± 5.0
353.05	1 − 0.0036	6.335 ± 0.015	1.039 ± 0.004	161 ± 15	133.7 ± 4.5	2.2 ± 1.7	166.5 ± 3.3	463.4 ± 5.0
353.05	1 − 0.0036	6.351 ± 0.013	1.481 ± 0.006	143 ± 13	213.2 ± 7.0	2.1 ± 1.7	167.5 ± 2.8	526.0 ± 5.0
353.10	1 − 0.0036	6.370 ± 0.012	1.890 ± 0.009	122 ± 11	303 ± 10	2.5 ± 1.7	168.6 ± 2.5	596.3 ± 5.0
353.10	1 − 0.0036	6.380 ± 0.011	2.168 ± 0.012	111 ± 10	369 ± 13	2.2 ± 1.7	169.9 ± 2.5	652.5 ± 5.0
353.10	1 − 0.0036	6.388 ± 0.010	2.348 ± 0.014	103 ± 10	420 ± 15	2.3 ± 1.7	170.7 ± 2.5	696.0 ± 5.0
353.20	1 − 0.0036	11.913 ± 0.026	0	468 ± 76	0	0.6 ± 0.8	151.8 ± 8.8	621.1 ± 5.0
353.15	1 − 0.0036	11.937 ± 0.022	1.071 ± 0.002	387 ± 63	41.3 ± 4.3	0.6 ± 0.8	154.7 ± 8.0	584.1 ± 5.0
353.30	1 − 0.0036	11.964 ± 0.018	2.004 ± 0.003	307 ± 50	65.8 ± 6.7	0.6 ± 0.9	163.1 ± 7.5	536.4 ± 5.0
353.25	1 − 0.0036	11.993 ± 0.014	2.981 ± 0.004	224 ± 37	111 ± 11	0.5 ± 0.9	169.7 ± 6.5	505.3 ± 5.0
353.25	1 − 0.0036	12.015 ± 0.011	3.781 ± 0.006	163 ± 28	186 ± 18	0.6 ± 1.0	175.9 ± 5.6	525.8 ± 5.0
353.25	1 − 0.0036	12.034 ± 0.008	4.598 ± 0.011	110 ± 21	324 ± 31	0.6 ± 1.0	178.7 ± 5.4	613.4 ± 5.0
353.25	1 − 0.0036	12.048 ± 0.007	5.417 ± 0.020	71 ± 16	569 ± 56	0.6 ± 1.0	180.7 ± 6.1	822.8 ± 5.0
353.25	1 − 0.0036	12.059 ± 0.005	6.163 ± 0.032	40 ± 9	913 ± 93	0.6 ± 1.0	181.4 ± 7.1	1140 ± 10
353.20	1 − 0.0036	12.063 ± 0.005	6.924 ± 0.049	30.5 ± 7.0	1369 ± 144	0.5 ± 1.0	186.0 ± 7.9	1594 ± 10
353.25	1 − 0.0036	12.067 ± 0.004	7.621 ± 0.071	21.9 ± 5.1	1878 ± 207	0.6 ± 1.1	194.6 ± 8.8	2106 ± 10
353.25	1 − 0.0036	12.071 ± 0.004	8.407 ± 0.100	14.4 ± 3.3	2529 ± 295	0.8 ± 1.1	207 ± 10	2767 ± 10
353.25	1 − 0.0036	12.075 ± 0.004	9.193 ± 0.136	7.4 ± 1.7	3230 ± 400	1.1 ± 1.2	217 ± 11	3476 ± 10
353.25	1 − 0.0036	12.080 ± 0.004	9.976 ± 0.177	0	3986 ± 524	1.1 ± 1.2	229 ± 13	4241 ± 10
353.25	1 − 0.0036	12.085 ± 0.004	11.06 ± 0.23	0	5068 ± 690	1.1 ± 1.5	270 ± 16	5370 ± 10
393.00	0	5.930 ± 0.003	0	303.0 ± 4.4	0	166.2 ± 3.5	0	469.6 ± 5.0
393.05	0	5.947 ± 0.005	0.9754 ± 0.0007	236 ± 14	77.9 ± 1.7	155.1 ± 2.3	0	469.3 ± 5.0
393.10	0	5.970 ± 0.004	1.9524 ± 0.0024	144.0 ± 9.7	300.4 ± 9.1	172.6 ± 4.3	0	618.5 ± 5.0
393.05	0	5.985 ± 0.004	2.818 ± 0.011	92.7 ± 7.2	876 ± 42	218.8 ± 9.4	0	1194 ± 10
393.00	0	5.992 ± 0.004	3.518 ± 0.069	58.0 ± 7.3	2128 ± 254	169 ± 18	0	2373 ± 10
393.10	0	5.995 ± 0.004	3.93 ± 0.21	44.1 ± 9.0	3454 ± 747	142 ± 28	0	3669 ± 10
393.10	0	11.884 ± 0.003	0	598.8 ± 7.7	0	170.4 ± 6.7	0	762.3 ± 5.0
393.05	0	11.882 ± 0.013	1.0175 ± 0.0006	597 ± 61	19.7 ± 1.1	184.4 ± 4.2	0	800.4 ± 5.0
393.05	0	11.883 ± 0.013	2.0015 ± 0.0010	582 ± 60	71.0 ± 4.0	208.1 ± 5.5	0	861.7 ± 5.0

Table 1. Continued

T	X_4'	m_1	m_2	p_1	p_2	p_3	p_4	p
K		mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	kPa	kPa	kPa
392.90	0	11.928 ± 0.003	0	619.9 ± 7.8	0	175.7 ± 6.9	0	797.1 ± 5.0
392.95	0	11.958 ± 0.010	2.9757 ± 0.0019	461 ± 49	153.2 ± 9.2	202.7 ± 6.8	0	814.7 ± 5.0
392.95	0	11.989 ± 0.008	4.4517 ± 0.0075	307 ± 35	504 ± 37	211 ± 12	0	1024 ± 10
392.90	0	12.017 ± 0.006	5.823 ± 0.032	160 ± 23	1364 ± 160	203 ± 21	0	1736 ± 10
393.00	0	12.030 ± 0.005	6.568 ± 0.078	97 ± 17	2403 ± 383	203 ± 29	0	2721 ± 10
392.90	0	12.036 ± 0.004	7.22 ± 0.18	65 ± 14	4001 ± 847	203 ± 39	0	4302 ± 10
393.15	0.0490 ± 0.0001	6.146 ± 0.005	0	268 ± 20	0	212.2 ± 5.7	51.0 ± 5.6	531.1 ± 5.0
393.25	0.0490 ± 0.0001	6.157 ± 0.004	0.769 ± 0.001	217 ± 15	56.0 ± 1.3	216.9 ± 3.7	54.5 ± 5.9	545.0 ± 5.0
393.15	0.0490 ± 0.0001	6.169 ± 0.004	1.533 ± 0.001	165 ± 11	191.0 ± 4.0	244.1 ± 3.0	57.1 ± 6.1	657.6 ± 5.0
393.20	0.0490 ± 0.0001	6.174 ± 0.003	2.207 ± 0.003	143 ± 10	518 ± 11	231.3 ± 2.2	67.3 ± 7.2	963.4 ± 5.0
393.15	0.0489 ± 0.0001	6.180 ± 0.003	2.807 ± 0.007	115 ± 8	1088 ± 30	231.7 ± 2.7	72.6 ± 7.8	1516 ± 10
393.15	0.0489 ± 0.0001	6.186 ± 0.003	3.159 ± 0.015	86.8 ± 5.9	1705 ± 67	206.9 ± 3.2	79.9 ± 8.6	2096 ± 10
393.25	0.0489 ± 0.0001	6.186 ± 0.003	3.384 ± 0.023	87.4 ± 6.0	2202 ± 100	223.9 ± 4.1	80.5 ± 8.7	2610 ± 10
393.20	0.0489 ± 0.0001	6.189 ± 0.003	3.621 ± 0.039	73.9 ± 5.2	2920 ± 164	232.1 ± 5.3	75.2 ± 8.2	3321 ± 10
393.15	0.0489 ± 0.0001	6.192 ± 0.003	3.792 ± 0.061	62.4 ± 4.5	3582 ± 254	224.1 ± 6.5	84.4 ± 9.4	3981 ± 10
393.20	0.0489 ± 0.0001	6.195 ± 0.003	3.956 ± 0.123	45.6 ± 3.6	4659 ± 507	194.5 ± 8.6	79.2 ± 9.3	4989 ± 10
393.10	0.0491 ± 0.0001	11.847 ± 0.011	0	561 ± 56	0	253.1 ± 9.7	45.3 ± 5.2	861.3 ± 5.0
393.15	0.0491 ± 0.0001	11.859 ± 0.008	1.102 ± 0.001	485 ± 41	37.9 ± 1.1	257.5 ± 6.4	46.3 ± 5.1	827.2 ± 5.0
393.25	0.0491 ± 0.0001	11.868 ± 0.007	2.061 ± 0.001	438 ± 35	104.5 ± 2.8	270.7 ± 5.5	48.6 ± 5.3	861.8 ± 5.0
393.20	0.0491 ± 0.0001	11.877 ± 0.006	3.081 ± 0.001	382 ± 29	239.7 ± 5.7	258.2 ± 4.2	51.9 ± 5.6	934.2 ± 5.0
393.20	0.0490 ± 0.0001	11.885 ± 0.006	4.110 ± 0.002	336 ± 25	487 ± 12	226.5 ± 3.4	60.9 ± 6.6	1113 ± 10
393.30	0.0490 ± 0.0001	11.900 ± 0.004	4.971 ± 0.005	257 ± 18	954 ± 26	208.2 ± 2.5	76.9 ± 8.3	1505 ± 10
393.20	0.0489 ± 0.0001	11.918 ± 0.004	5.718 ± 0.016	161 ± 11	1718 ± 81	164.7 ± 3.0	90.6 ± 9.9	2150 ± 10
393.30	0.0489 ± 0.0001	11.917 ± 0.004	6.314 ± 0.029	169 ± 12	2589 ± 150	198.3 ± 4.5	84.5 ± 9.3	3069 ± 10
393.20	0.0490 ± 0.0001	11.916 ± 0.004	6.695 ± 0.058	162 ± 12	3535 ± 291	186.3 ± 6.3	76.7 ± 8.6	3998 ± 10
393.25	0.0490 ± 0.0001	11.925 ± 0.003	7.012 ± 0.099	118 ± 9	4724 ± 493	195.8 ± 8.6	68.1 ± 7.9	5136 ± 10
393.15	0.2462 ± 0.0006	5.938 ± 0.006	0	276 ± 22	0	182.4 ± 5.2	211 ± 24	669.6 ± 5.0
393.20	0.2462 ± 0.0006	5.952 ± 0.005	0.718 ± 0.001	222 ± 16	139.6 ± 3.5	210.1 ± 3.9	214 ± 24	787.5 ± 5.0
393.15	0.2460 ± 0.0006	5.958 ± 0.005	1.352 ± 0.003	201 ± 14	440 ± 11	181.7 ± 3.1	240 ± 27	1065 ± 10
393.15	0.2459 ± 0.0006	5.968 ± 0.004	1.990 ± 0.007	166 ± 11	944 ± 28	177.9 ± 2.5	261 ± 29	1558 ± 10
393.15	0.2458 ± 0.0006	5.976 ± 0.004	2.525 ± 0.019	135 ± 9	1669 ± 73	177.1 ± 3.0	275 ± 31	2273 ± 10
393.20	0.2458 ± 0.0006	5.983 ± 0.004	2.955 ± 0.045	109 ± 8	2549 ± 164	172.4 ± 4.3	282 ± 32	3134 ± 10
393.15	0.2456 ± 0.0006	5.988 ± 0.004	3.251 ± 0.076	95.5 ± 7	3336 ± 274	175.4 ± 5.7	304 ± 35	3938 ± 10
393.25	0.2456 ± 0.0006	5.991 ± 0.003	3.477 ± 0.104	88.5 ± 6.7	3954 ± 373	180.1 ± 6.8	316 ± 37	4579 ± 10
393.10	0.2455 ± 0.0006	5.993 ± 0.003	3.644 ± 0.138	82.4 ± 6.5	4573 ± 489	183.4 ± 7.9	336 ± 40	5218 ± 10
393.15	0.2502 ± 0.0006	11.708 ± 0.013	0	553 ± 66	0	197.0 ± 8.2	225 ± 26	976.2 ± 5.0
393.10	0.2501 ± 0.0006	11.719 ± 0.011	0.979 ± 0.001	486 ± 54	82.1 ± 2.8	183.6 ± 5.4	242 ± 27	994.9 ± 5.0
393.20	0.2499 ± 0.0006	11.730 ± 0.010	1.905 ± 0.001	432 ± 47	201.4 ± 6.5	163.8 ± 4.5	277 ± 32	1077 ± 10
393.15	0.2499 ± 0.0006	11.738 ± 0.009	2.818 ± 0.002	394 ± 40	376 ± 11	158.8 ± 3.6	292 ± 33	1225 ± 10
393.15	0.2497 ± 0.0006	11.762 ± 0.006	3.716 ± 0.005	281 ± 23	743 ± 23	150.1 ± 2.6	323 ± 37	1501 ± 10
393.25	0.2498 ± 0.0006	11.764 ± 0.005	4.579 ± 0.010	264 ± 21	1273 ± 51	152.0 ± 2.5	298 ± 34	1997 ± 10
393.10	0.2498 ± 0.0006	11.773 ± 0.005	5.165 ± 0.021	223 ± 17	1872 ± 99	156.2 ± 3.1	307 ± 35	2565 ± 10
393.15	0.2497 ± 0.0006	11.779 ± 0.004	5.630 ± 0.037	195 ± 15	2568 ± 180	159.0 ± 4.2	319 ± 37	3249 ± 10
393.10	0.2496 ± 0.0006	11.784 ± 0.004	5.933 ± 0.056	181 ± 14	3156 ± 266	160.4 ± 5.2	340 ± 40	3844 ± 10
393.10	0.2495 ± 0.0006	11.797 ± 0.004	6.187 ± 0.076	133 ± 10	3713 ± 356	166.6 ± 6.2	368 ± 44	4387 ± 10
393.15	0.2495 ± 0.0006	11.792 ± 0.004	6.427 ± 0.109	153 ± 12	4418 ± 508	164.4 ± 7.5	367 ± 45	5109 ± 10
393.10	0.4943 ± 0.0014	6.075 ± 0.008	0	278 ± 24	0	153.9 ± 5.2	368 ± 44	808.2 ± 5.0
393.05	0.4941 ± 0.0014	6.081 ± 0.007	0.648 ± 0.003	259 ± 22	280.0 ± 9.0	136.5 ± 3.6	401 ± 49	1079 ± 10
393.20	0.4938 ± 0.0014	6.088 ± 0.007	1.287 ± 0.007	241 ± 20	705 ± 25	127.4 ± 2.8	460 ± 59	1540 ± 10

Table 1. Continued

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	kPa	kPa	kPa	kPa	kPa
393.10	0.4939 ± 0.0014	6.102 ± 0.005	1.801 ± 0.018	191 ± 14	1324 ± 61	133.1 ± 2.6	436 ± 54	2087 ± 10
393.10	0.4938 ± 0.0014	6.109 ± 0.005	2.233 ± 0.035	171 ± 13	1902 ± 117	134.8 ± 3.1	456 ± 57	2668 ± 10
393.15	0.4937 ± 0.0014	6.112 ± 0.005	2.665 ± 0.067	162 ± 13	2523 ± 219	126.9 ± 4.0	469 ± 61	3294 ± 10
393.05	0.4937 ± 0.0014	6.121 ± 0.005	3.019 ± 0.089	138 ± 11	3132 ± 290	144.5 ± 5.1	492 ± 63	3915 ± 10
393.20	0.4936 ± 0.0014	6.124 ± 0.005	3.314 ± 0.120	132 ± 10	3748 ± 390	153.6 ± 6.1	518 ± 67	4558 ± 10
393.10	0.4935 ± 0.0014	6.133 ± 0.004	3.564 ± 0.170	102 ± 9	4309 ± 551	143.5 ± 7.2	520 ± 70	5080 ± 10
392.80	0.4983 ± 0.0014	11.643 ± 0.027	0	601 ± 111	0	149.3 ± 7.1	424 ± 54	1174 ± 10
392.95	0.4982 ± 0.0014	11.661 ± 0.022	0.964 ± 0.003	511 ± 90	237 ± 10	130.5 ± 5.2	423 ± 54	1303 ± 10
393.30	0.4981 ± 0.0014	11.680 ± 0.017	2.009 ± 0.005	430 ± 65	544 ± 20	121.0 ± 3.4	426 ± 54	1519 ± 10
393.35	0.4981 ± 0.0014	11.694 ± 0.013	2.927 ± 0.010	371 ± 50	949 ± 41	113.7 ± 2.6	439 ± 57	1876 ± 10
393.25	0.4981 ± 0.0014	11.712 ± 0.009	3.758 ± 0.018	295 ± 33	1317 ± 72	108.2 ± 2.4	429 ± 56	2152 ± 10
393.30	0.4980 ± 0.0014	11.722 ± 0.007	4.359 ± 0.033	265 ± 27	1824 ± 130	109.6 ± 2.9	458 ± 61	2660 ± 10
393.30	0.4978 ± 0.0014	11.730 ± 0.007	4.952 ± 0.059	244 ± 23	2493 ± 232	112.9 ± 3.8	493 ± 68	3348 ± 10
393.25	0.4978 ± 0.0014	11.743 ± 0.006	5.415 ± 0.096	198 ± 18	3199 ± 375	115.0 ± 5.1	501 ± 70	4015 ± 10
393.30	0.4976 ± 0.0014	11.749 ± 0.006	5.752 ± 0.136	191 ± 18	3803 ± 527	115.8 ± 6.1	544 ± 80	4657 ± 10
393.30	0.4976 ± 0.0014	11.751 ± 0.006	6.018 ± 0.159	194 ± 18	4250 ± 614	123.9 ± 6.9	562 ± 82	5135 ± 10
393.25	0.7498 ± 0.0024	5.737 ± 0.018	0	409 ± 56	0	56.4 ± 4.9	459 ± 61	924.7 ± 5.0
393.15	0.7497 ± 0.0024	5.741 ± 0.014	0.687 ± 0.008	406 ± 43	448 ± 25	65.0 ± 1.7	527 ± 55	1449 ± 10
393.20	0.7496 ± 0.0024	5.742 ± 0.014	1.177 ± 0.015	409 ± 43	855 ± 48	69.8 ± 1.6	584 ± 61	1921 ± 10
393.05	0.7495 ± 0.0024	5.761 ± 0.012	1.642 ± 0.025	354 ± 37	1371 ± 78	75.3 ± 1.6	622 ± 65	2426 ± 10
392.20	0.7494 ± 0.0024	5.755 ± 0.013	2.151 ± 0.037	380 ± 40	1919 ± 115	77.4 ± 1.7	675 ± 73	3054 ± 10
392.75	0.7493 ± 0.0024	5.766 ± 0.012	2.445 ± 0.050	351 ± 37	2480 ± 157	76.0 ± 1.8	704 ± 79	3603 ± 10
393.00	0.7493 ± 0.0024	5.774 ± 0.011	2.668 ± 0.060	329 ± 34	2868 ± 188	79.0 ± 1.9	729 ± 82	4008 ± 10
393.00	0.7492 ± 0.0024	5.775 ± 0.012	2.988 ± 0.073	331 ± 35	3320 ± 229	80.1 ± 2.1	762 ± 87	4497 ± 10
393.05	0.7491 ± 0.0024	5.779 ± 0.011	3.302 ± 0.088	323 ± 34	3804 ± 275	82.1 ± 2.2	795 ± 93	5009 ± 10
393.00	0.7471 ± 0.0024	11.985 ± 0.037	0	961 ± 148	0	52.6 ± 4.8	411 ± 55	1425 ± 10
393.10	0.7470 ± 0.0024	11.983 ± 0.033	0.789 ± 0.003	959 ± 127	200 ± 13	50.1 ± 2.0	453 ± 52	1663 ± 10
393.20	0.7470 ± 0.0024	11.994 ± 0.030	1.201 ± 0.006	909 ± 115	359 ± 22	52.5 ± 1.8	467 ± 52	1788 ± 10
393.25	0.7469 ± 0.0024	11.998 ± 0.030	2.066 ± 0.011	889 ± 113	677 ± 41	48.8 ± 1.5	508 ± 63	2125 ± 10
393.20	0.7468 ± 0.0024	12.016 ± 0.027	2.835 ± 0.017	822 ± 102	1044 ± 63	48.7 ± 1.3	550 ± 71	2467 ± 10
393.15	0.7467 ± 0.0024	12.049 ± 0.022	3.642 ± 0.026	704 ± 81	1559 ± 97	53.7 ± 1.3	586 ± 74	2907 ± 10
393.05	0.7466 ± 0.0024	12.064 ± 0.021	4.437 ± 0.041	660 ± 76	2187 ± 153	50.5 ± 1.3	636 ± 89	3536 ± 10
393.15	0.7465 ± 0.0024	12.081 ± 0.019	4.971 ± 0.058	605 ± 69	2738 ± 213	50.3 ± 1.4	673 ± 100	4070 ± 10
393.10	0.7466 ± 0.0024	12.114 ± 0.014	5.495 ± 0.057	493 ± 52	3059 ± 214	73.0 ± 1.8	691 ± 80	4325 ± 10
393.00	0.7465 ± 0.0024	12.125 ± 0.014	6.055 ± 0.079	472 ± 51	3781 ± 294	70.6 ± 2.0	746 ± 93	5073 ± 10
393.10	0.9464 ± 0.0033	5.786 ± 0.023	0	492 ± 85	0	13.6 ± 3.1	548 ± 22	1054 ± 10
393.10	0.9463 ± 0.0033	5.790 ± 0.024	0.711 ± 0.013	495 ± 88	490 ± 47	13.9 ± 3.6	662 ± 20	1664 ± 10
393.10	0.9463 ± 0.0033	5.785 ± 0.025	1.398 ± 0.027	522 ± 93	1079 ± 104	15.5 ± 3.9	706 ± 21	2329 ± 10
393.15	0.9463 ± 0.0033	5.792 ± 0.024	2.079 ± 0.044	501 ± 91	1775 ± 172	15.0 ± 4.0	718 ± 22	3024 ± 10
393.15	0.9463 ± 0.0033	5.793 ± 0.024	2.739 ± 0.061	504 ± 92	2458 ± 241	15.2 ± 4.1	749 ± 25	3732 ± 10
393.15	0.9463 ± 0.0033	5.800 ± 0.023	3.404 ± 0.076	487 ± 92	3122 ± 309	17.1 ± 4.4	799 ± 27	4434 ± 10
393.10	0.9463 ± 0.0033	5.804 ± 0.022	4.078 ± 0.094	475 ± 91	3897 ± 391	16.9 ± 4.4	800 ± 29	5198 ± 10
393.00	0.9526 ± 0.0033	11.626 ± 0.051	0	1013 ± 165	0	10.3 ± 2.9	527 ± 27	1556 ± 10
393.15	0.9526 ± 0.0033	11.640 ± 0.049	0.896 ± 0.011	968 ± 157	366 ± 37	9.6 ± 3.2	586 ± 24	1932 ± 10
393.15	0.9526 ± 0.0033	11.645 ± 0.047	1.745 ± 0.025	936 ± 150	805 ± 79	10.2 ± 3.2	578 ± 21	2334 ± 10
393.20	0.9526 ± 0.0033	11.670 ± 0.043	2.620 ± 0.036	854 ± 138	1182 ± 115	12.3 ± 3.3	602 ± 20	2658 ± 10
393.15	0.9526 ± 0.0033	11.680 ± 0.043	3.460 ± 0.051	831 ± 136	1664 ± 162	13.1 ± 3.6	653 ± 21	3168 ± 10
393.05	0.9526 ± 0.0033	11.706 ± 0.039	4.235 ± 0.067	748 ± 124	2186 ± 214	14.7 ± 3.7	678 ± 22	3630 ± 10

Table 1. Continued

T	X'_4	m_1	m_2	p_1	p_2	p_3	p_4	p
K		mol·kg^{-1}	mol·kg^{-1}	kPa	kPa	kPa	kPa	kPa
393.10	0.9526 ± 0.0033	11.751 ± 0.033	5.069 ± 0.081	604 ± 104	2623 ± 259	20.8 ± 3.8	675 ± 23	3933 ± 10
393.10	0.9526 ± 0.0033	11.756 ± 0.033	5.840 ± 0.104	598 ± 104	3355 ± 335	20.6 ± 4.0	714 ± 25	4698 ± 10
393.05	0.9526 ± 0.0033	11.767 ± 0.032	6.573 ± 0.130	578 ± 103	4152 ± 420	21.6 ± 4.2	755 ± 28	5520 ± 10
393.05	1 − 0.0036	5.748 ± 0.036	0	514 ± 88	0	1.1 ± 3.0	546 ± 23	1062 ± 10
393.10	1 − 0.0036	5.743 ± 0.038	0.800 ± 0.022	539 ± 93	563 ± 54	1.2 ± 3.4	633 ± 20	1743 ± 10
393.20	1 − 0.0036	5.767 ± 0.033	1.526 ± 0.054	475 ± 83	1412 ± 137	0.9 ± 3.2	593 ± 19	2492 ± 10
393.35	1 − 0.0036	5.771 ± 0.031	2.240 ± 0.085	459 ± 80	2218 ± 219	0.9 ± 3.0	545 ± 19	3238 ± 10
392.90	1 − 0.0036	12.116 ± 0.049	0	837 ± 142	0	1.2 ± 7.2	794 ± 34	1636 ± 10
392.85	1 − 0.0036	12.033 ± 0.055	0.866 ± 0.011	1032 ± 163	339 ± 31	0.0 ± 9.1	673 ± 8	2049 ± 10
392.90	1 − 0.0036	12.037 ± 0.055	1.749 ± 0.020	1008 ± 162	624 ± 60	2.2 ± 7.0	681 ± 20	2322 ± 10
392.80	1 − 0.0036	12.048 ± 0.052	2.558 ± 0.038	954 ± 153	1161 ± 112	1.6 ± 6.3	644 ± 16	2767 ± 10
392.80	1 − 0.0036	12.057 ± 0.050	3.370 ± 0.058	910 ± 147	1722 ± 172	2.7 ± 5.6	616 ± 21	3258 ± 10
392.90	1 − 0.0036	12.088 ± 0.046	3.965 ± 0.069	827 ± 136	2041 ± 206	4.7 ± 6.0	666 ± 22	3548 ± 10
392.90	1 − 0.0036	12.095 ± 0.046	4.748 ± 0.090	816 ± 135	2579 ± 265	4.6 ± 6.4	708 ± 24	4118 ± 10
392.90	1 − 0.0036	12.119 ± 0.043	5.511 ± 0.114	753 ± 127	3210 ± 338	5.2 ± 6.8	746 ± 27	4724 ± 10
392.95	1 − 0.0036	12.141 ± 0.039	6.251 ± 0.142	682 ± 117	3870 ± 423	9.4 ± 6.7	737 ± 29	5314 ± 10

[a] T = temperature; X'_4 = mole fraction of methanol in the liquid on a gas-free basis; m_1 = stoichiometric molality of gas i in the liquid = amount of substance of gas i per kilogram of solvent mixture of (water + methanol); p_i = partial pressure of component i; p = total pressure.

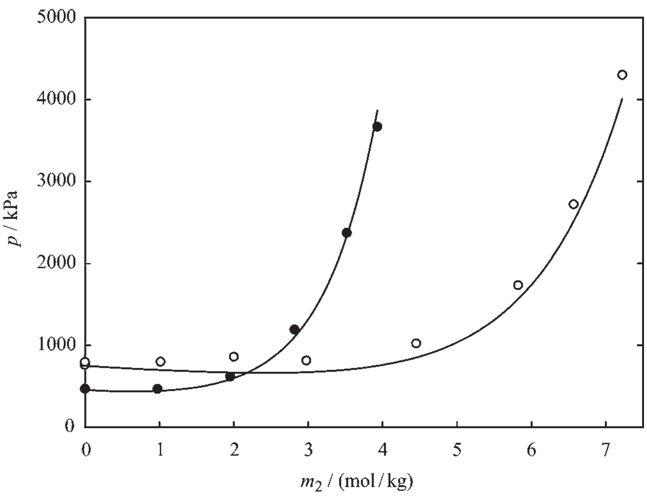

Figure 1. Total pressure above liquid mixtures of NH_3 (1) + CO_2 (2) + H_2O (3) at $T \approx 393$ K. Symbols show experimental results from this work: ●, $m_1 \approx 6$ mol·kg^{-1}; ○, $m_1 \approx 12$ mol·kg^{-1}. Solid curves show results calculated using the model of Lichtfers and Rumpf.[18]

are given in the Appendix. The amounts of every single component in the liquid phase were determined from those results and the known amounts and the composition of the feed, accounting for the small amounts of the volatile components previously withdrawn from the cell for analysis.

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 pressures. They were repeatedly calibrated against a high-precision pressure gauge (Desgranges & Huot, Aubervilliers, France). For pressures below 0.1 MPa, a mercury manometer was used for calibration. The absolute uncertainty of the measured pressure amounted to ± 5 kPa for pressures up to 1 MPa and ± 10 kPa for pressures up to 10 MPa.

The temperature was determined using a coated, calibrated platinum-resistance thermometer placed inside the cell and in contact with the liquid phase. The absolute uncertainty of the measured temperature was ± 0.1 K.

The vapor-phase volume was determined as follows: From the top, a rod was inserted into the equilibrium cell. The rod and the cell were electrically isolated from each other, and a small voltage was applied between them. The rod was then slowly moved down until it contacted the surface of the liquid, which resulted in a small electric current that was detected using an ammeter. The position of the rod was then read from a dial meter. The relation between the rod position and the vapor-phase volume was determined from isothermal calibration measurements with liquid water and a tiny amount of salt, as the temperature-dependent volume of the cell had been previously determined by means of a high-precision displacement pump (type M118, Leukert Instruments, Adendorf, Germany). The uncertainty in the experimental results for the vapor-phase volume was estimated to be below ± 5 cm^3.

A gas chromatograph (HP Agilent model 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 were the peak areas of ammonia, carbon dioxide, water, and methanol. The following relation between the peak areas A_i and A_j and the mole fractions y_i and y_j of any two components i and j holds:

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

Before, during, and after the series of VLE experiments, the proportionality factors α_{ij} were determined from calibration

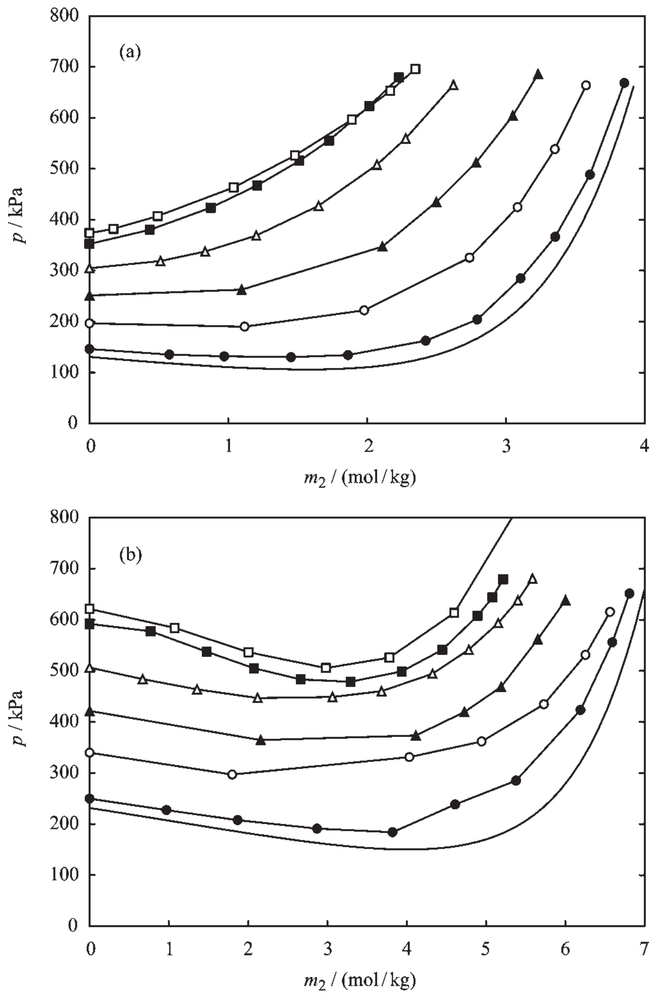

Figure 2. Total pressure above liquid mixtures of NH_3 (1) + CO_2 (2) + H_2O (3) + CH_3OH (4) at $T \approx 353$ K: (a) $m_1 \approx 6$ mol·kg^{-1}; (b) $m_1 \approx 12$ mol·kg^{-1}. Symbols show experimental results from this work: ●, $X'_4 \approx 0.05$; ○, $X'_4 \approx 0.25$; ▲, $X'_4 \approx 0.5$; △, $X'_4 \approx 0.75$; ■, $X'_4 \approx 0.95$; □, $X'_4 \approx 1$ (symbols are connected by lines for better visualization). Solid curves show results for $X'_4 = 0$ calculated using the model of Lichtfers and Rumpf.[18]

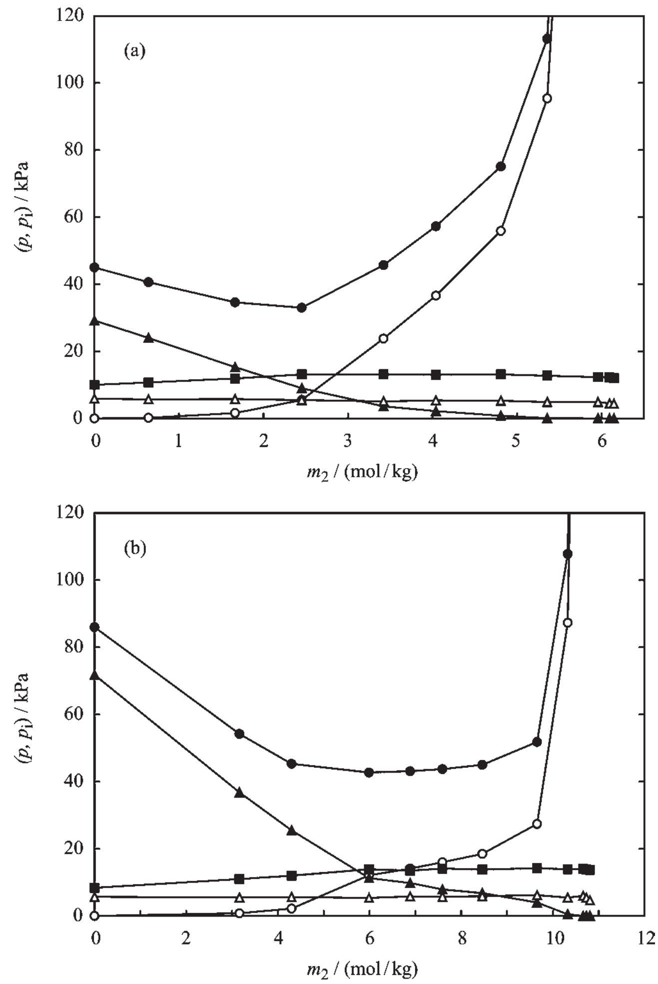

Figure 3. Total and partial pressures above liquid mixtures of NH_3 (1) + CO_2 (2) + H_2O (3) + CH_3OH (4) at $T \approx 313$ K and $X'_4 \approx 0.25$: (a) $m_1 \approx 6$ mol·kg^{-1}; (b) $m_1 \approx 12$ mol·kg^{-1}. Symbols show experimental results from this work: ●, p; ▲, p_1; ○, p_2; △, p_3; ■, p_4 (symbols are connected by lines for better visualization).

measurements on binary gaseous mixtures of (ammonia + water), (carbon dioxide + water), (ammonia + methanol), and (carbon dioxide + methanol) as well as on binary liquid mixtures of (water + methanol). In the different calibration series, α_{ij} was reproduced within a maximum scattering of ± 5 %. For more details on the experimental procedure, etc., see ref 20.

Materials and Sample Pretreatment. Ammonia (UHP, mole fraction ≥ 0.99999) and carbon dioxide (4.5, mole fraction ≥ 0.99999) were both purchased from Messer-Griesheim (Ludwigshafen, Germany). Methanol (p.a., mass fraction ≥ 0.998) was purchased from Merck KGaA (Darmstadt, Germany). Methanol and doubly distilled water were degassed before use.

■ EXPERIMENTAL RESULTS

Table 1 lists the experimental results for the simultaneous solubility of ammonia (1) and carbon dioxide (2) in solvent mixtures of water (3) and methanol (4). Seven gas-free solvent mixture compositions were considered (with methanol mole fractions on a gas-free basis, X'_4, of approximately 0, 0.05, 0.25, 0.5, 0.75, 0.95, and 1). The measurement temperatures, T, were approximately (313.15, 353.15, and 393.15) K. The stoichiometric molality of ammonia, m_1, in the solvent mixture of (water + methanol) was approximately 6 and 12 mol·(kg of solvent mixture)$^{-1}$, respectively. The carbon dioxide loading (i.e., the ratio of the stoichiometric molalities of carbon dioxide and ammonia in the liquid phase, m_2/m_1) ranged up to 1.07. The total pressure, p, ranged up to 5.5 MPa. Table 1 reports the experimental results for the total pressure p and the partial pressures p_1, p_2, p_3, and p_4 of ammonia (component 1), carbon dioxide (component 2), water (component 3), and methanol (component 4), respectively. As usual, the partial pressure of a component is the product of its vapor-phase mole fraction and the total pressure.

The absolute uncertainties of the experimental results for the liquid-phase composition (X'_4, m_1, m_2) as given in Table 1 were estimated from the sample purities and the filling and sampling procedures as described before. The absolute uncertainties of the experimental results for the partial pressures (p_1, p_2, p_3, and p_4) as given in Table 1 were determined as follows: Five samples were taken and analyzed. Average values

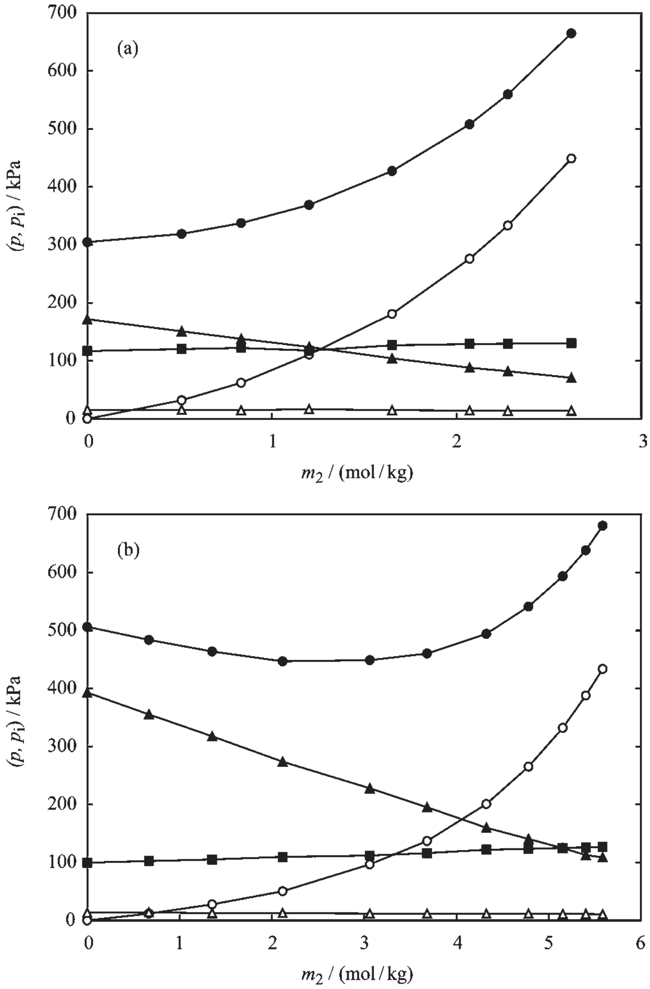

Figure 4. Total and partial pressures above liquid mixtures of NH_3 (1) + CO_2 (2) + H_2O (3) + CH_3OH (4) at $T \approx 353$ K and $X_4' \approx 0.75$: (a) $m_1 \approx 6$ mol·kg^{-1}; (b) $m_1 \approx 12$ mol·kg^{-1}. Symbols show experimental results from this work: ●, p; ▲, p_1; ○, p_2; △, p_3; ■, p_4 (symbols are connected by lines for better visualization).

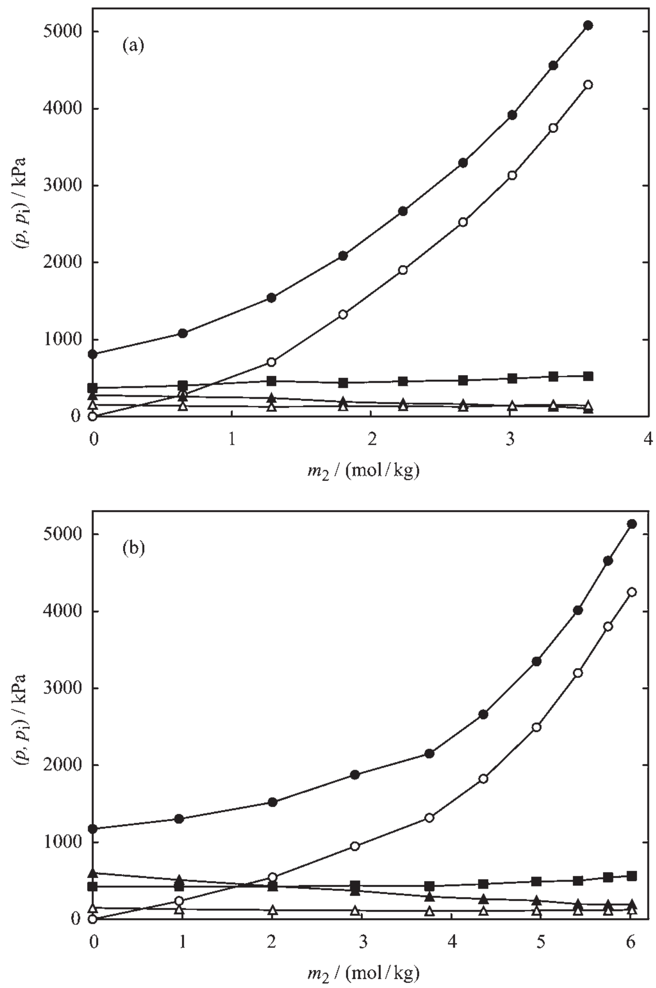

Figure 5. Total and partial pressures above liquid mixtures of NH_3 (1) + CO_2 (2) + H_2O (3) + CH_3OH (4) at $T \approx 393$ K and $X_4' \approx 0.5$: (a) $m_1 \approx 6$ mol·kg^{-1}; (b) $m_1 \approx 12$ mol·kg^{-1}. Symbols show experimental results from this work: ●, p; ▲, p_1; ○, p_2; △, p_3; ■, p_4 (symbols are connected by lines for better visualization).

for p_i are reported, and the given absolute uncertainty in p_i corresponds to the maximum deviation from the average value.

In aqueous solutions of ammonia and carbon dioxide, deposition of solid ammonium bicarbonate may occur (e.g., see ref 15):

$$H_2O(l) + NH_3(aq) + CO_2(aq) \rightleftarrows NH_4HCO_3(s) \qquad (2)$$

In addition, in liquid mixtures of methanol, ammonia, and carbon dioxide, precipitation of solid ammonium carbamate may occur:

$$2NH_3(aq) + CO_2(aq) \rightleftarrows NH_4COONH_2(s) \qquad (3)$$

However, the experimental arrangement did not allow precipitation of a salt to be clearly identified. Therefore, no indication of salt precipitation is given in Table 1.

In Figure 1, the experimental results from the present work for the total pressure above methanol-free liquid mixtures of ammonia (1), carbon dioxide (2), and water (3) at $T \approx 393$ K and $m_1 \approx$ (6 and 12) mol·kg^{-1} (cf. Table 1) are plotted versus the stoichiometric molality of carbon dioxide in the liquid phase, m_2. The following well-known qualitative behavior was observed (e.g., see Kurz et al.[15]). At first, the total pressure slightly decreased when carbon dioxide was added to an aqueous ammoniacal solution at constant temperature. After passing a minimum, the total pressure steeply increased. That behavior is due to chemical reactions in the liquid phase. The partial pressure of ammonia decreased with increasing amount of the acidic gas in the liquid phase as more and more ammonia (a gas with basic character in water) was converted into ionic, nonvolatile species (ammonium and carbamate ions). The partial pressure of carbon dioxide at first was very small, since carbon dioxide was almost completely dissolved chemically (as bicarbonate, carbonate, and carbamate ions), but it increased rapidly when ammonia had been spent in the liquid phase by chemical reactions. The solid lines in Figure 1 show calculated results for the simultaneous solubility of (NH_3 + CO_2) in water obtained using the model developed by Lichtfers and Rumpf.[18] That model covers a wide range of temperatures, pressures, and liquid-phase compositions, including the range of the experimental data shown in Figure 1. The new experimental results satisfactorily agree with the calculated results.

Figure 2 illustrates the experimental results for the solubility of (NH_3 and CO_2) in aqueous solvent mixtures of (water + methanol) and in pure methanol at $T \approx 353$ K. To guide the eyes, in Figure 2 (as well as in all of the following figures) the new experimental results for neighboring data points (i.e., before and

dx.doi.org/10.1021/je1010505 | J. Chem. Eng. Data 2011, 56, 1084–1095

after a new addition of carbon dioxide) are connected by straight lines. The pressure was always below 700 kPa. The mole fraction of methanol in the gas-free solvent was varied between (5 and 100) %. The molality of ammonia was about 6 mol·(kg of gas-free solvent)$^{-1}$ in the upper diagram in Figure 2 and about 12 mol·kg^{-1} in the lower diagram (cf. Table 1). The total pressure is plotted versus the stoichiometric molality of carbon dioxide in the liquid phase, m_2. For comparison, calculated results for the total pressure above the corresponding aqueous (methanol-free) ammoniacal solutions as obtained using the model of Lichtfers and Rumpf[18] are included in Figure 2. Obviously, the presence of small amounts of methanol in the solvent does not qualitatively affect the pressure development. However, as the amount of methanol in the solvent mixture increases, the influence of chemical reactions decreases, resulting in a pure "physical gas solubility" in the absence of water. This can be nicely observed from the experimental series shown in the upper diagram of Figure 2 (for a 6 mol·kg^{-1} ammoniacal solution). However, in the experimental series shown in the lower diagram of Figure 2 (i.e., for a 12 mol·kg^{-1} ammoniacal solution) and for the solutions containing large amounts of methanol ($X'_4 \approx 0.95$ and 1), a somewhat surprising effect was observed. Again, when carbon dioxide was added to the liquid, the pressure decreased to a minimum and afterward increased again. This behavior may be caused by the precipitation of ammonium carbamate. Such a precipitation would reduce the amount of dissolved ammonia and carbon dioxide, and a behavior similar to that caused by chemical reactions in the liquid phase would be observed.

Figures 3 to 5 are intended only to illustrate the "chemical effects" occurring in liquid mixtures of ammonia, carbon dioxide, water, and methanol. In these figures, some of the new experimental results for the total and partial pressures above those solutions are plotted versus the stoichiometric molality of carbon dioxide in the liquid, m_2, at constant T, X'_4, and m_1. The partial pressure of ammonia (p_1) decreased almost linearly with m_2. The partial pressure of carbon dioxide (p_2) increased with m_2, and the slope of that curve became larger with increasing amount of carbon dioxide in the liquid. The partial pressures of water and methanol remained almost unchanged.

CONCLUSIONS

In continuation of extensive experimental investigations of the simultaneous solubility of ammonia and acidic gases in water as well as of the influence of strong electrolytes on that solubility, this paper reports new experimental results for the simultaneous solubility of ammonia and carbon dioxide in liquid mixtures of (water + methanol) at about (313, 353, and 393) K. The whole range of solvent mixture composition from pure water to pure methanol is covered in the present work.

In an upcoming paper, the experimental database will be extended to include the influence of the single strong electrolytes sodium chloride and sodium sulfate on the simultaneous solubility of ammonia and carbon dioxide in (water + methanol).

The new experimental data will be used to validate a thermodynamic model[21] that allows for (a) the correlation of the solubility of chemically reactive gases in mixed solvents and (b) the prediction of salt effects on this solubility.

APPENDIX: SECOND VIRIAL COEFFICIENTS

The correlation equations for the second virial coefficients were taken from previous publications (see Table A1). As that information is distributed over several publications, the details are summarized below.

Table A1. References for Second Virial Coefficient Equations

	H_2O	NH_3	CO_2	CH_3OH
H_2O	1			
NH_3	3	3		
CO_2	1	23	1	
CH_3OH	21	10	21	10

Table A2. Values of Coefficients in Equation A1

i	a_i	b_i	c_i	d_i
H_2O	−53.527	−39.287	647.3	4.277
NH_3	4.059	−117.713	405.6	2.5
CO_2	65.703	−184.854	304.16	1.36
CH_3OH	−59.649	−103.781	513.2	5.7

Table A3. Values of Pure-Component Parameters

i	$T_{c,i}$/K	$p_{c,i}$/atm	μ_i/D	$R_{D,i}$/Å
H_2O	647.3	218.4	1.83	0.615
NH_3	405.6	111.3	1.447	0.8533
CO_2	241.0	53.096	0	0.9918
CH_3OH	513.2	78.5	1.66	1.536

Table A4. Values of Association Parameters ($\eta_{i,j} = \eta_{j,i}$)

	i			
j	H_2O	NH_3	CO_2	CH_3OH
H_2O	1.7			
NH_3	0.2	0		
CO_2	0.3	0.2	0.16	
CH_3OH	0	0	0.32	1.63

The second virial coefficient $B_{i,i}$ of each pure component was calculated as

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

Values of the coefficients a_i, b_i, c_i, and d_i are given in Table A2.

Mixed second virial coefficients $B_{i,j}$ were calculated as proposed by Hayden and O'Connell.[22] That method requires parameters for each pure component i (characteristic temperature $T_{c,i}$, characteristic pressure $p_{c,i}$, molecular dipole moment μ_i, and mean radius of gyration $R_{D,i}$) as well as association parameters $\eta_{i,j}$ for interactions between species i and j. The parameters used here are given in Tables A3 and A4.

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Funding Sources

The authors appreciate financial support of this investigation by the German Government (BMBF Grant-No. 01/RK9808/8) and several industrial partners (BASF AG, Bayer AG, Degussa AG, Lurgi Oel Gas Chemie GmbH, Lurgi Energie und Entsorgung GmbH, and Siemens-Axiva GmbH & Co. KG).

REFERENCES

(1) Rumpf, B.; Maurer, G. An experimental and theoretical investigation on the solubility of carbon dioxide in aqueous solutions of strong electrolytes. *Ber. Bunsen-Ges.* **1993**, *97*, 85–97.

(2) Rumpf, B.; Nicolaisen, H.; Öcal, C.; Maurer, G. Solubility of carbon dioxide in aqueous solutions of sodium chloride: Experimental results and correlation. *J. Solution Chem.* **1994**, *23*, 431–448.

(3) Rumpf, B.; Maurer, G. Solubility of ammonia in aqueous solutions of sodium sulfate and ammonium sulfate at temperatures from 333.15 to 433.15 K and pressures up to 3 MPa. *Ind. Eng. Chem. Res.* **1993**, *32*, 1780–1789.

(4) Rumpf, B.; Weyrich, F.; Maurer, G. Enthalpy of dilution in aqueous systems of single solutes ammonia, sodium sulfate and ammonium sulphate: Experimental results and modeling. *Thermochim. Acta* **1997**, *303*, 77–91.

(5) Sing, R.; Rumpf, B.; Maurer, G. Solubility of ammonia in aqueous solutions of single electrolytes sodium chloride, sodium nitrate, sodium acetate, and sodium hydroxide. *Ind. Eng. Chem. Res.* **1999**, *38*, 2098–2109.

(6) Weyrich, F.; Rumpf, B.; Maurer, G. Enthalpy of mixing of aqueous solutions of NH_3 with aqueous solutions of Na_2SO_4 or $(NH_4)_2SO_4$ at temperatures between 313 and 373 K. *Thermochim. Acta* **2000**, *359*, 11–22.

(7) Xia, J.; Jödecke, M.; Pérez-Salado Kamps, Á.; Maurer, G. Solubility of CO_2 in $(CH_3OH + H_2O)$. *J. Chem. Eng. Data* **2004**, *49*, 1756–1759.

(8) Pérez-Salado Kamps, Á.; Jödecke, M.; Xia, J.; Vogt, M.; Maurer, G. Influence of salts on the solubility of carbon dioxide in (water + methanol). Part I: sodium chloride. *Ind. Eng. Chem. Res.* **2006**, *45*, 1505–1515.

(9) Pérez-Salado Kamps, Á.; Jödecke, M.; Vogt, M.; Xia, J.; Maurer, G. Influence of salts on the solubility of carbon dioxide in (water + methanol). Part II: sodium sulfate. *Ind. Eng. Chem. Res.* **2006**, *45*, 3673–3677.

(10) Schäfer, D.; Xia, J.; Vogt, M.; Pérez-Salado Kamps, Á.; Maurer, G. Experimental investigation of the solubility of ammonia in methanol. *J. Chem. Eng. Data* **2007**, *52*, 1653–1659.

(11) Schäfer, D.; Vogt, M.; Pérez-Salado Kamps, Á.; Maurer, G. Solubility of ammonia in liquid mixtures of (water + methanol). *Fluid Phase Equilib.* **2007**, *261*, 306–312.

(12) Schäfer, D.; Vogt, M.; Pérez-Salado Kamps, Á.; Maurer, G. Influence of a single salt ($NaCl/Na_2SO_4$) on the solubility of ammonia in liquid mixtures of (water + methanol). *Ind. Eng. Chem. Res.* **2008**, *47*, 5112–5118.

(13) Müller, G.; Bender, E.; Maurer, G. Das Dampf-Flüssigkeitsgleichgewicht des ternären Systems Ammoniak−Kohlendioxid−Wasser bei hohen Wassergehalten im Bereich zwischen 373 und 473 K. *Ber. Bunsen-Ges.* **1988**, *92*, 148–160.

(14) Göppert, U.; Maurer, G. Vapor−liquid equilibria in aqueous solutions of ammonia and carbon dioxide at temperatures between 333 and 393 K and pressures up to 10 MPa. *Fluid Phase Equilib.* **1988**, *41*, 153–185.

(15) Kurz, F.; Rumpf, B.; Maurer, G. Vapor−liquid−solid equilibria in the system $NH_3-CO_2-H_2O$ from around 310 to 470 K: New experimental data and modelling. *Fluid Phase Equilib.* **1995**, *104*, 261–275.

(16) Bieling, V.; Kurz, F.; Rumpf, B.; Maurer, G. Simultaneous solubility of ammonia and carbon dioxide in aqueous solutions of sodium sulfate in the temperature range 313−393 K and pressures up to 3 MPa. *Ind. Eng. Chem. Res.* **1995**, *34*, 1449–1460.

(17) Kurz, F.; Rumpf, B.; Sing, R.; Maurer, G. Vapor−liquid and vapor−liquid−solid equilibria in the system ammonia−carbon dioxide−sodium chloride−water at temperatures from 313 to 393 K and pressures up to 3 MPa. *Ind. Eng. Chem. Res.* **1996**, *35*, 3795–3802.

(18) Lichtfers, U.; Rumpf, B. An Infrared Spectroscopic Investigation on the Species Distribution in the System $NH_3 + CO_2 + H_2O$. In *Thermodynamic Properties of Complex Fluid Mixtures*; Maurer, G., Ed.; Research Report, Deutsche Forschungsgemeinschaft (DFG); Wiley-VCH: Weinheim, Germany, 2004; pp 92−119.

(19) Maurer, G.; Pérez-Salado Kamps, Á. Solubility of Gases in Ionic Liquids, Aqueous Solutions, and Mixed Solvents. In *Developments and Applications in Solubility*; Letcher, T., Ed.; Royal Society of Chemistry: Cambridge, U.K., 2007; Chapter 4.

(20) Schäfer, D. Untersuchungen zur Löslichkeit von Ammoniak und Kohlendioxid in organisch-wässrigen Lösungsmittelgemischen. Doctoral Dissertation, University of Kaiserslautern, Kaiserslautern, Germany, 2003.

(21) Pérez-Salado Kamps, Á. Model for the Gibbs excess energy of mixed-solvent (chemical-reacting and gas-containing) electrolyte systems. *Ind. Eng. Chem. Res.* **2005**, *44*, 201–225.

(22) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–216.

(23) Pérez-Salado Kamps, Á.; Sing, R.; Rumpf, B.; Maurer, G. Influence of NH_4Cl, NH_4NO_3, and $NaNO_3$ on the simultaneous solubility of ammonia and carbon dioxide in water. *J. Chem. Eng. Data* **2000**, *45*, 796–809.