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Solubilities of Ammonium Iodide, Ammonium Bromide, and Ammonium Iodide-Ammonium Bromide Mixture in Liquid Ammonia

Hideki Yamamoto,* Junji Tokunaga, and Seiji Sanga

Department of Chemical Engineering, Faculty of Engineering, Kansai University, Osaka, 564, Japan

Solubilities of ammonium iodide and ammonium bromide in liquid ammonia were determined in the temperature range 270.0–350.0 K. Solubilities of these solutes in liquid ammonia increased with the temperature, and the values of weight percent solubility increased from 77.34 to 83.01 wt % for ammonium iodide, and from 88.71 to 73.19 wt % for ammonium bromide. Solubilities of the mixtures of ammonium iodide and ammonium bromide (four weight ratios of $\text{NH}_4\text{I}/\text{NH}_4\text{Br} = 0.37, 0.80, 1.48, \text{ and } 2.95$) in liquid ammonia were also determined in the temperature range 270.0–350.0 K. The relation between temperature and weight percent solubility for ammonium iodide in liquid ammonia was shown by a smooth curve, but a bend point appeared on the solubility curve for ammonium bromide or its mixture with ammonium iodide in liquid ammonia. With increasing weight ratios of ammonium iodide to ammonium bromide, the bend point on the solubility curve gradually moved toward lower temperature.

Introduction

The solubility data of ammonium halides in liquid ammonia are required both for the design of thermal energy storage system utilizing chemical reaction in liquid ammonia solution (1) and for the development of chemical heat pumps that use these solution systems (2).

The purpose of this work is to obtain experimental data for the solubility of ammonium iodide, ammonium bromide, and ammonium iodide-ammonium bromide mixture in liquid ammonia in the temperature range 270.0–350.0 K.

The solubility data for pure ammonium halides in liquid ammonia were reported at 298 K by Hunt (3, 4), and at several temperatures by Kendall and Davidson (5). Solubilities in a wider temperature range, however, have not yet been reported. No data for the solubility of ammonium iodide-ammonium bromide mixture in liquid ammonia are available.

Experimental Section

Materials. Ammonium iodide (NH_4I) and ammonium bromide (NH_4Br) from Wako Junyaku Co. Ltd. were of guaranteed reagent grade and were specified as the pure grade having minimum purities of 99.5% and used without further purification. The powdered crystal was thoroughly dried at 373 K and stored over silica gel in a desiccator.

Ammonia gas of 99.99% purity was provided from Seltetu Kagaku Co. Ltd.

Expression of Solubility. The solubility is presented in weight percent. Weight percent is here defined as the ratio of the mass of solute to that of solution; that is,

$$X = \frac{100S}{S + Vd_1} \quad (1)$$

where X is the weight percent solubility, S is the weight of solute dissolved in liquid ammonia, V is the volume of liquid ammonia, and d_1 is the density of liquid ammonia.

Experimental Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1. The two vessels (I and J) are made of pressure-resistant glass (up to 2 MPa); one is a 20-mL vessel for measuring the volume of liquid ammonia, and the other is a 100-mL vessel for determining the solubility that can be agitated by a magnetic stirrer (B).

These two vessels were immersed in a constant-temperature water bath within 0.05 K. The temperature control of the bath was maintained by using a refrigeration unit combined with a electric relay unit and thermoregulator.

The temperature in the vessels was measured by chromel-alumel thermocouple (F) corrected by a standard mercury thermometer. The temperature in the vessels was regulated within 0.05 K.

The pressure of the liquid ammonia solution was measured by a strain gauge transducer (A) with an accuracy of 0.1% of full scale (2 MPa).

The volume of the solution and the liquid ammonia was measured by a cathetometer (L) within $\pm 0.02\%$ of full volume.

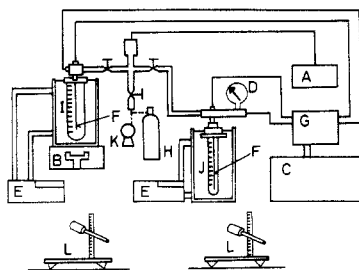


Figure 1. Schematic diagram of the experimental apparatus: A, digital pressure gauge; B, magnetic stirrer; C, recorder; D, Bourdon gauge; E, constant temperature water bath; F, thermocouple; G, selective switch; H, ammonia cylinder; I, reaction vessel; J, ammonia vessel; K, vacuum pump; L, cathetometer.

Table I. Solubility of Ammonium Bromide in Liquid Ammonia

temp, K	solubility, wt %	temp, K	solubility, wt %	temp, K	solubility, wt %
349.7	73.19	314.1	72.03	295.0	70.43
344.3	73.01	308.4	71.92	293.3	70.29
342.2	72.85	307.7	71.87	289.5	69.87
336.9	72.82	306.2	71.67	284.8	69.44
331.7	72.64	304.4	71.46	281.1	69.20
329.4	72.52	303.1	71.27	279.2	69.01
324.9	72.36	299.2	70.90	276.9	68.80
321.6	72.34	299.0	70.85	274.9	68.71
316.0	72.15				

Experimental Method. After a weighed amount of the solid material (about 30–40 g) is charged in the reaction vessel (I), the pipe arrangement and two vessels (I and J) are kept at 350 K under vacuum for 2 h in order to remove moisture from the system. Then, these vessels are cooled down to room temperature. By chilling the vessel (J), liquid ammonia is allowed to be introduced into the ammonia vessel (J) from an ammonia cylinder. Thereafter the ammonia vessel (J) is kept 298 K.

The liquid ammonia is transferred to the vessel (I) from the vessel (J) so as to dissolve most of ammonium halides in the reaction vessel.

The temperature of the reaction vessel (I) is then raised at the rate of 0.5 K/min to dissolve the ammonium halide in it. When the solution of ammonium halide in liquid ammonia is nearing saturation, the rate is decreased to 0.2 K/min or less. The temperature and the pressure are read at the point where the last crystal disappears. The liquid level in the reaction vessel is also read immediately. Then, the solution in the reaction vessel is cooled down gradually from a higher temperature than the saturated point, and the temperature at which the first crystal appears is recorded. The average of these two temperatures was recorded against the solubility of ammonium halides in liquid ammonia.

If the temperature in the pipe arrangement was lower than that of ammonia vessel, ammonia gas condensed in it and liquid ammonia remained. In order to prevent the condensation of ammonia gas, a heating coil was rolled around the pipe arrangement, and it was kept at constant temperature. The correction for the weight of ammonia in the pipe arrangement was calculated by using the equation of state for ammonia gas by Meyer and Jessup (6).

Results and Discussion

The solubilities of ammonium bromide and ammonium iodide in liquid ammonia are summarized in Tables I and II.

The solubilities of the mixtures of ammonium iodide and ammonium bromide with four weight ratios ($\text{NH}_4\text{I}/\text{NH}_4\text{Br} = 0.37, 0.80, 1.48$ and 2.95) in liquid ammonia were measured at the temperature range from 270.0 to 350.0 K and the experimental data are listed in Table III.

Table II. Solubility of Ammonium Iodide in Liquid Ammonia

temp, K	solubility, wt %	temp, K	solubility, wt %	temp, K	solubility, wt %
341.7	83.01	316.7	80.12	297.9	78.63
337.5	82.54	314.1	79.91	293.1	78.25
337.1	82.44	311.9	79.66	288.7	77.93
332.2	81.72	308.1	79.36	288.0	78.05
328.7	81.28	307.7	79.40	287.1	77.88
323.6	80.81	307.2	79.31	283.2	77.61
322.2	80.67	303.4	79.01	279.3	77.37
318.4	80.22	298.4	78.65		

Table III. Solubility of Ammonium Iodide–Ammonium Bromide Mixture^a in Liquid Ammonia

temp, K	solubility, wt %	temp, K	solubility, wt %
$\text{NH}_4\text{I}:\text{NH}_4\text{Br} = 0.37$			
348.7	74.28	341.1	76.80
337.4	73.91	330.1	76.40
331.2	73.73	324.5	75.97
329.7	73.60	317.4	75.78
321.9	73.38	312.4	75.56
318.1	73.24	308.8	75.34
313.1	73.14	301.7	75.13
307.8	72.99	292.6	74.82
302.8	72.89	287.9	74.56
298.0	72.51	282.9	74.01
294.1	71.83	279.2	73.59
289.5	71.45		
283.5	70.90	$\text{NH}_4\text{I}:\text{NH}_4\text{Br} = 2.95$	
277.6	70.40	343.9	79.53
		339.5	79.30
$\text{NH}_4\text{I}:\text{NH}_4\text{Br} = 0.80$			
348.0	75.33	331.2	78.82
339.8	74.87	324.1	78.45
326.1	74.44	318.3	78.14
316.1	73.99	314.1	77.84
305.8	73.74	308.1	77.53
295.9	73.30	303.1	77.26
287.4	72.37	298.2	77.04
283.9	72.07	290.1	76.64
281.5	71.71	283.1	76.19
		279.7	75.76

^a Weight ratio.

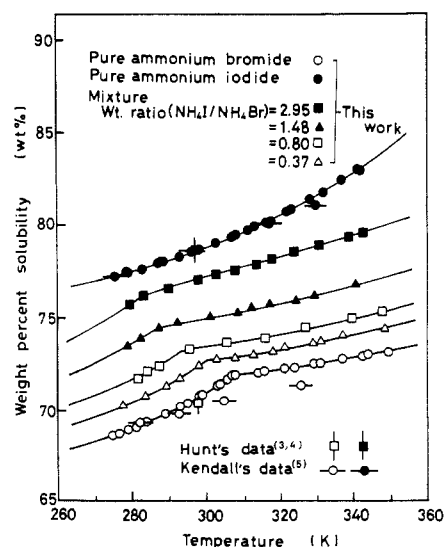


Figure 2. Solubility curves of ammonium iodide, ammonium bromide, and ammonium iodide–ammonium bromide mixture in liquid ammonia.

The average reproducibility of weight percent solubilities obtained in this work was within 0.03%.

Experimental data for pure ammonium halides were compared with the literature values in Table IV. The solubilities of ammonium iodide in liquid ammonia were in agreement within

Table IV. Comparison of Experimental Solubilities of Ammonium Bromide and Ammonium Iodide in Liquid Ammonia with Literature Values

solute	temp, °C	solubility, wt %		dev, %
		lit. ^a	obsd ^b	
ammonium bromide	9.2	69.3 (5)	69.29	-0.01
	20.0	69.7 (5)	70.22	+0.74
	32.6	70.4 (5)	71.59	+1.70
	53.6	71.2 (5)	72.34	+1.60
	25	70.4 (3)	70.75	+0.50
ammonium iodide	2.5	77.2 (5)	77.17	-0.04
	22.6	78.6 (5)	78.47	-0.17
	44.2	80.0 (5)	79.34	-0.83
	57.0	80.9 (5)	81.50	+0.74
	25	78.7 (4)	78.64	-0.09

^a (5) Kendall's data; (3) and (4) Hunt's data. ^b Smoothed value from observed data.

1% with the data of Hunt (4) and Kendall (5). But the values of ammonium bromide in liquid ammonia at 32.6 and 53.6 °C were 1.7 and 1.6% larger than those of Kendall (5).

No literature data have been available for mixtures of ammonium halides in liquid ammonia.

The solubility curves against temperature are shown in Figure 2. The solubility of ammonium iodide is shown by a smoothed increasing curve. However, it was found that the solubility-temperature curve for ammonium bromide and its mixture of ammonium iodide had a bend point on the solubility curve. With increasing weight ratio of ammonium iodide, the solubility increased and the bend point on the solubility curve gradually moved toward lower temperature.

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Solubilities of Solid 1,10-Decanediol and a Solid Mixture of 1,10-Decanediol and Benzoic Acid in Supercritical Carbon Dioxide

Kenneth J. Pennisi and Eldred H. Chlmowitz*

Department of Chemical Engineering, University of Rochester, Rochester, New York 14627

A flow system was used to measure the equilibrium solubilities of 1,10-decanediol in supercritical carbon dioxide at three temperatures and a range of pressures. The equilibrium solubilities of a binary, solid mixture of 1,10-decanediol and benzoic acid were also experimentally determined. The data were correlated with a thermodynamic model based on the Peng-Robinson equation of state.

Introduction

Experimentally determined equilibrium solubilities of 1,10-decanediol in carbon dioxide are presented. The equilibrium solubilities of a binary solid mixture of 1,10-decanediol and benzoic acid in carbon dioxide are also presented. Data on solid mixtures is scarce. The only other data available in the literature for ternary systems were reported by Van Gunst (1) and Kurnik et al. (2). It was our intention to measure solubilities for a solid mixture of two hydrogen-bonding components which had significantly different vapor pressures. At 308 K the vapor pressure of benzoic acid is nearly 2 orders of magnitude greater than the vapor pressure of 1,10-decanediol. Benzoic acid was selected as the second component of the solid mixture on this basis.

In addition to presenting the experimental solubilities, we use a thermodynamic model based on the Peng-Robinson equation of state to correlate the data.

Experimental Section

The carbon dioxide used as the extractant gas was Air Products and Chemicals' CP grade (99.8%) purity. Aldrich

Chemical Co. supplied the 1,10-decanediol (99+ % purity). Baker Chemical Co. supplied the benzoic acid (crystals) which was 99+ % pure. All chemicals were used without further purification. The benzoic acid was granulated to improve its mechanical properties.

Experimental data were obtained by using a flow apparatus similar to the system used by Kurnik et al. (3). A schematic diagram of the apparatus is shown in Figure 1. Liquid carbon dioxide was compressed to the desired operating pressure by a Milton Roy liquid pump. Pressure was controlled to within ± 1.5 bar with a back-pressure regulator valve. The high-pressure carbon dioxide flowed through the preheater where it was warmed to within ± 1 K of the operating temperature. The fluid flow then entered the vertical extraction tube.

The extraction tube was packed with a uniform mixture consisting of equal volumes of the solid and 3-mm glass beads. The glass beads were used primarily to reduce caking of the solid during operation of the system. When dealing with a solid mixture of 1,10-decanediol and benzoic acid, equal weights of the solids were combined in a uniform mixture with an equal volume of glass beads. Experiments were also performed in which the extractor was packed with equal volumes rather than equal weights of benzoic acid and 1,10-decanediol (for example: 20 mL (14 g) of granulated benzoic acid, 20 mL (10 g) of 1,10-decanediol, and 28 mL of glass beads). There was no change in the results. A glass wool plug at the outlet of the extraction tube prevented entrainment of the solid.

The extraction tube was 1.75 cm in diameter (inside) and 30.5 cm long with a volume of 73 cm³. It was wrapped with heating tape which was connected to an on-off temperature controller. The controller's reference thermocouple was mounted on the outside wall of the extractor vessel under the heating tape. The internal temperature was monitored with a