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

solute	temp, °C	solubility, wt % lit.[a]	solubility, wt % obsd[b]	dev, %
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.

Acknowledgment

We express our gratitude to Mr. A. Shimomura for his experimental work and Mr. A. Kurata for his useful suggestion.

Registry No. NH_3, 7664-41-7; NH_4I, 12027-06-4; NH_4Br, 12124-97-9.

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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

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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 thermodyanmic 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 wave. 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 enetered 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 cm^3. 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

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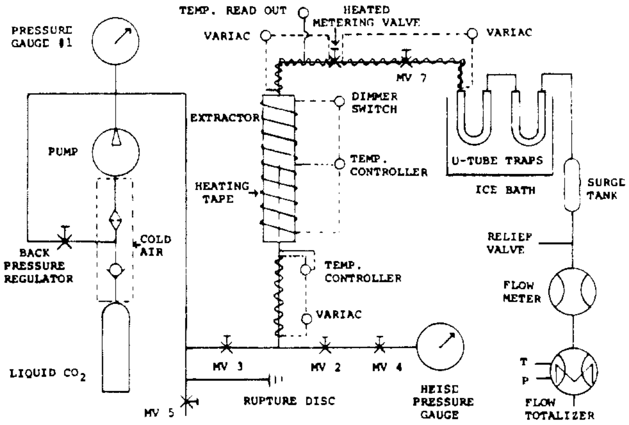

Figure 1. Schematic diagram of the experimental apparatus.

thermocouple located in the center of the tube. The internal temperature was controlled to within approximately ±0.5 K. A calibrated Heise gauge accurate to ±0.35 bar was used to measure the pressure in the extractor vessel.

The supercritical carbon dioxide "picked up" the soluble material as it flowed through the extraction tube. The flow exited through the top of kthe tube into a short length of tubing which was warmed with heating tape to prevent a drop in the flow temperature. The outside wall temperature of this tubing was monitored with a lthermocouple to ensure that excessive heating was also not a problem. (A temperature increase will cause precipitation of the dissolved solid if the operating pressure is within the retrograde region.) The dense fluid was expanded across a heated micrometering valve to ~1 bar. The solids were precipitated in two consecutive tared U-tubes which were immersed in an ice-brine solution. The extractant gas flow rate was measured by a rotameter (used to monitor flow conditions). The total extractant gas volume passed was measured by a calibrated Singer dry test meter. The gas volume could be read to within ±6 cm^3. The dry test meter was equipped with gauges to measure flow temperature and pressure. Pressures in the dry test meter were only slightly above atmospheric pressure. Therefore, pressure was taken as the atmospheric pressure indicated by a mercury barometer.

The mass of solid collected was found by weighing the tared U-tubes on a Mettler balance accurate to ±1 mg. In the case of pure solid, knowledge of the total gas volume and weight of solid collected was sufficient to determine the mole fracture of solid in the supercritical fluid. When dealing the solid mixtures, the composition of the precipitated solid must also be known. NMR spectroscopy was used to determine mixture compositions. The NMR solvent used was deuterated chloroform (99.8% pure, Aldrich Chemical Co.). The equipment used was a GE QE-300 NMR. NMR tests performed on samples of known composition indicated the composition determinations were accurate to within 4.5%.

Before experiments with new chemical compounds were done it was necessary to test the reliability of the equilibrium measurements made by the apparatus. Solubilities of naphthalene in carbon dioxide were measured and found to compare well with the solubility data of Tsekhanskaya et al. (*4*). The average deviation was 4.6%. The tests performed with naphthalene also included determinations of suitable flow rates for our experiments. Experiments were done with flow rates from 0.034 standard cubic meters per hour to 0.087 standard cubic meters per hour with no change in results over this range.

Accurate thermodynamic modeling of solid mixtures requires knowledge of the composition of any solid solutions which may exist in the system. Temperature–composition–melting point curves were experimentally measured for the 1,10-decanediol–benzoic acid system to determine the existence of solid solutions. The melting behavior indicated solid solutions did not form.

Table I. Physical Properties of Benzoic Acid, 1,10-Decanediol, and Carbon Dioxide

	benzoic acid	1,10-decanediol	CO_2
T_c, K	752.0	720.4	304.2
P_c, bar	45.6	23.7	73.76
ω	0.62	1.325	0.225
V^s, $m^3/(K\ mol)$	0.96473	0.1584	

	vapor pressure, Pa	
T, K	benzoic acid	1,10-decanediol
308	0.264	2.97×10^{-3}
318	0.780	1.62×10^{-2}
323		3.64×10^{-2}
328	2.16	7.96×10^{-2}

Further details of the experimental techniques described above are available elsewhere (*5*).

Data Correlation

The modeling of solid–fluid equilibria requires the use of an equation of state. We chose to use the Peng–Robinson equation of state (*6*). Solid solubilities in high-pressure gases have been treated by Prausnitz (*7*). The pertinent relationship for the solubility of a solid component i in the supercritical fluid is

$$y_i = (P_{vp_i}/P)(1/\phi_i)\exp[(P - P_{vp_i})V_i^s/RT] \qquad (1)$$

where y_i denotes the gas phase mole fraction of component i, P_{vp_i} the vapor pressure of i, ϕ_i the fugacity coefficient of i in the gas phase, V_i^s the pure component solid molar volume, T the temperature, and R the gas constant. The equation of state is used to find the vapor-phase fugacity coefficient ϕ_i. For the Peng–Robinson equation this is given by

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln (Z - B) - \frac{A}{2^{1.5}B}\left[2\sum_j (1 - k_{ij})\frac{(a_i a_j)^{1/2}}{a}y_j - \frac{b_i}{b}\right]\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \qquad (2)$$

The interaction parameter, k_{ij}, which appears in eq 2 is characteristic of the binary pair (i and j). It is a purely empirical factor which must be evaluated by regressing eq 1 against experimental data. For a ternary system consisting of solid mixture of components 2 and 3 in a supercritical gas, component 1, the following k_{ij} factors must be determined: k_{12} from binary data for components 1 and 2, k_{13} from binary data for components 1 and 3, and k_{23} from the ternary system solubility data.

The physical properties of 1,10-decanediol, benzoic acid, and carbon dioxide used in our data regression are reported in Table I. The required data for benzoic acid and carbon dioxide were readily available in the literature. However, this was not the case for 1,10-decanediol. It was therefore necessary to estimate the required physical properties. Lydersen's method was used to estimate the critical properties (*8*). The molar volume was available in the literature (*9*). The vapor pressures were determined from a combination of experimental measurements and the application of standard vapor pressure correlations.

Results and Discussion

The experimental solubilities of 1,10-decanediol in carbon dioxide at three temperatures (318, 323, and 328 K) and a range of pressures from 130 to 310 bar are reported in Table II. Except where otherwise noted, the reported solubilities are mean values from at least three independent measurements. The regressed values of the binary interaction parameter at 328

Table II. Equilibrium Solubilities of 1,10-Decanediol (1) in Supercritical Carbon Dioxide (2)

temp, K	press., bar	10^4y^a	95% confidence limits
318	205.3	2.99	*b*
	253.7	3.58	*b*
(k_{12} = 0.142)	307.1	3.95	*b*
323	138.2	1.89	±1.73^c
	154.5	2.60	±0.15
	185.5	3.62	±0.32
(k_{12} = 0.143)	224.4	4.48	±0.25
	263.7	5.43	±0.06
	305.9	6.17	±0.31
328	133.7	1.99	±0.28
	164.7	3.97	±0.19
	195.8	5.24	±0.16
(k_{12} = 0.142)	222.8	5.99	±0.19
	262.8	7.04	±0.32
	307.3	7.89	±0.28

[a] Mole fraction decanediol, mean values. [b] Single data points confidence limits unavailable. [c] Only two data points.

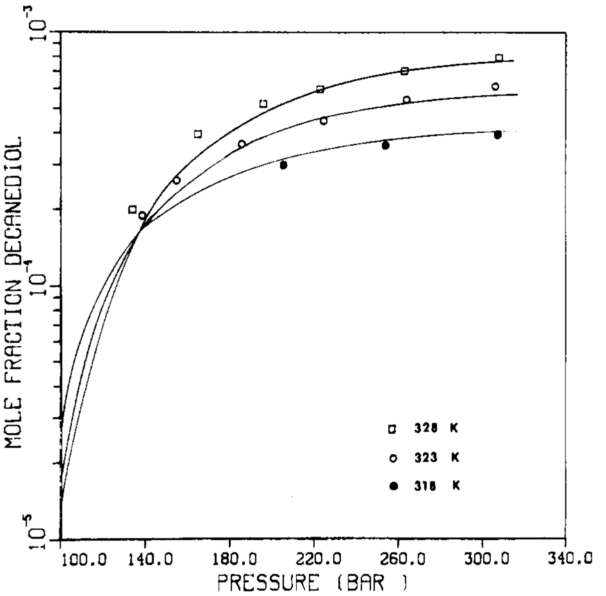

Figure 2. Solubility isotherms of 1,10-decanediol in supercritical carbon dioxide.

and 323 K are also reported in Table II. The value of the interaction parameter shown for 318 K is an average of the two regressed values.

Figure 2 shows the data for 1,10-decanediol plotted for comparison with the correlating equation. The 328 and 323 K isotherms correlate the data well. The average deviation of 323 K isotherm from the data is only 3.7%. The average deviation of the 328 K isotherm form the data is 9.0% with a maximum deviation of 23% at 134 bars. The equation of state tends to become less accurate as the critical pressure of the solvent gas is approached. However, it is clear that the Peng–Robinson equation is a good model of the behavior of this binary system. The question now is whether the equation can yield reasonable predictions of the solubilities at other temperatures. The isotherm predicted at 318 K is also shown in Figure 2. From the three solubility measurements made at 318 K, it is clear that the use of an average interaction parameter leads to overestimation of the solubility. However, the error is small, only about 12%, and over a narrow temperature range satisfactory estimates can be made. This fact supports the use of the average 1,10-decanediol–carbon dioxide interaction parameter in the ternary system.

The results of the solubility measurements on the 1,10-decanediol–benzoic acid–carbon dioxide system at 318 and 308 K are presented in Table III. The regressed values of the solute–solute interaction parameters, k_{ij}, along with the values of the two solute–solvent interaction parameters used in the regression are also reported in Table III. The 1,10-decanediol–carbon dioxide interaction parameter was obtained as described prevously. The benzoic acid–carbon dioixde interaction parameters were obtained by regressing the data of Kurnik (*10*). Our values are within 4% of the values reported by Kurnik. If the solubility data for the ternary system is compared with the solubility data of the 1,10-decanediol–carbon dioxide and benzoic acid–carbon dioxide component binary systems, it is apparent there has been an enhancement of the component solubilities. On the average, 1,10-decanediol shows a solubility increase of 32% and benzoic acid shows a solubility increase of 3.6% Kurnik and Reid (*2*) reported the same enhancement effect in a number of ternary systems. Generally, the enhancements they observed were larger. The enhancement appears to decrease with decreasing solubilities.

Figures 3 and 4 show the Peng–Robinson isotherms plotted with the ternary system experimental solubilities of benzoic acid and 1,10-decanediol, respectively. Overall, the Peng–Robinson equation gives a fair approximation to the data. The average deviations of the Peng–Robinson isotherms from the benzoic acid solubilities are 15% and 9.8% for the 318 and 308 K isotherms, respectively. The results are better for the decanediol solubilities. The 318 K isotherm displays an average deviation of 9.1%. The 308 K isotherm gives a good approximation to the true (measured) solubilities, missing the data by

Table III. Equilibrium Solubilities of a 1,10-Decanediol (1), Benzoic Acid (2) Mixture in Supercritical Carbon Dioxide (3)

temp, K	press., bar	10^4y 1,10-decanediol	10^3y benzoic acid
308	163.8	1.81 ± 0.13	2.34 ± 0.15
	186.4	2.36 ± 0.14	2.69 ± 0.16
(k_{13} = 0.143)	230.9	2.54 ± 0.23	3.25 ± 0.14
(k_{12} = −0.142)	265.1	2.88 ± 0.15	3.43 ± 0.17
(k_{23} = 0.0187)	306.4	3.06 ± 0.24	3.87 ± 0.17
318	163.8	3.41 ± 0.10	2.76 ± 0.08
	186.8	3.49 ± 0.42	3.20 ± 0.07
(k_{13} = 0.143)	226.1	4.11 ± 0.19	3.84 ± 0.12
(k_{12} = 0.144)	267.6	4.13 ± 0.21	4.58 ± 0.11
(k_{23} = 0.0104)	307.1	5.34 ± 0.31	4.84 ± 0.18

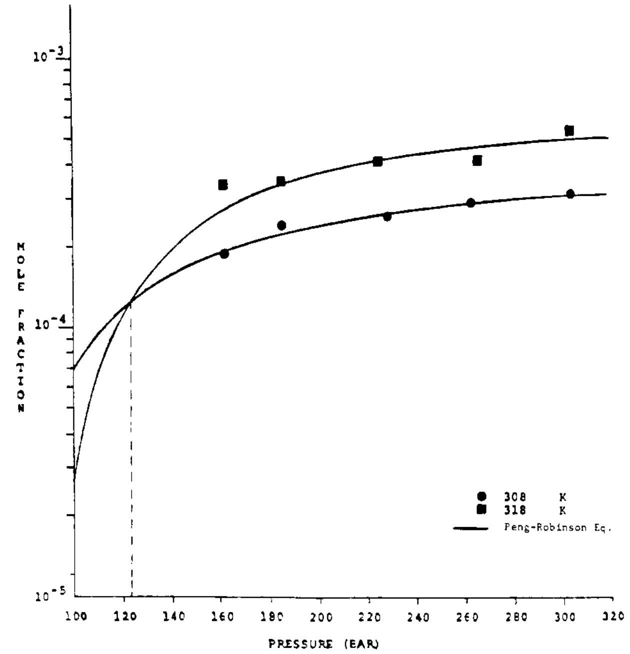

Figure 3. Solubility isotherms of benzoic acid from a solid mixture of benzoic acid and 1,10-decanediol in supercritical carbon dioxide.

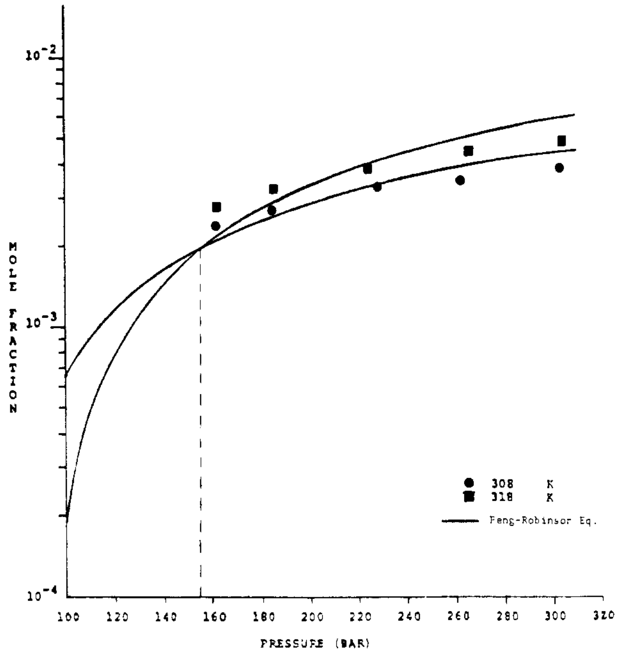

Figure 4. Solubility isotherms of 1,10-decanediol from a solid mixture of benzoic acid and 1,10-decanediol in supercritical carbon dioxide.

an average of 3.8%. In summation, the Peng–Robinson equation of state provides a reasonable correlation of the benzoic acid and 1,10-decanediol solubilities at 308 K. The correlation at 318 K is not as good but is still acceptable.

Glossary

a_i	parameter in equation of state, component *i*
A	parameter in equation of state
b_i	parameter in equation of state, component *i*
B	parameter in equation of state
k_{ij}	binary interaction parameter, components, *i*–*j*
P	pressure
T	temperature
V_i^s	solid-phase molar volume, component *i*
y_i	gas-phase mole fraction, component *i*
Z	compressibility factor

Greek Letters

ϕ	fugacity coefficient, component *i*

Subscripts

vp	vapor pressure

Registry No. CO_2, 124-38-9; 1,10-decanediol, 112-47-0; benzoic acid, 65-85-0.

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Volumetric Properties of Molten Hydrated Salts. 7. Mixtures of Ferric Nitrate Nonahydrate with Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

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Volumetric behavior of molten mixtures of ferric nitrate nonahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates has been studied at different temperatures and compositions by using a manometric densimeter. Density and molar volumes varied linearly with composition. Molar volumes were additive except for Mg^{2+} mixtures. Variations of thermal expansion coefficient and molar expansivity have been discussed in terms of changes in hydration of Fe^{3+} ions and the van der Waals volume.

Introduction

In continuation of our studies on the behavior of molten hydrated salts and mixtures (*1–6*), volumetric behavior of mixtures of molten ferric nitrate nonahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates are reported.

Experimental Section

Salts were of AnalaR (BDH) grade or equivalent purity. The number of moles of water per mole of the electrolyte (*R*), determined by volumetric titration using EDTA, was found with a precision of ±0.01 mol/mol of cation. For the samples used, *R* was 9.08 for ferric nitrate, 4.12 for calcium nitrate, 4.15 for cadmium nitrate, 6.22 for zinc nitrate, and 6.02 for magnesium nitrate. Calibration of densimeter, dilation correction, sample preparation, etc. have been described earlier (*1*). Temperature was controlled and known with a precision of ±0.05 °C.

Results and Discussion

Densities (ρ) of different binary mixtures were measured over a range of composition limited by solubility and at temperatures ranging between 288.2 and 353.2 K at ca. 5-deg intervals (Table I) in both heating and cooling cycles. The data in different sets were reproducible within ±0.0003 g cm^{-3}. Molar volumes were calculated by using mean molecular mass (*M*) of the mixture. Densities and molar volumes varied linearly with

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