are only a few vapor–liquid (VLE) data for the systems MCH + toluene and MCH + ethylbenzene. The VLE data for MCH + benzene consist of isothermic measurements. There is a complete lack of (either isobaric or isothermal) VLE data for MCH + *o*-xylene, MCH + *p*-xylene, and MCH + propylbenzene. A direct comparison of our results can be made with data of Funk et al. (*2*) for the MCH + ethylbenzene system and less directly, because of differences in temperature, with the data of Schneider (*5*) for the MCH + toluene system. To give a comparison with data obtained at different temperatures, we plotted $Q_{0.5}$, the equimolar value of g^E/RT vs. $1/T$ in Figure 1, giving a straight line in the temperature interval considered. The slope of this line for the MCH + toluene system gives $H^E{}_{0.5} = 507$ J. This average value in the 313–363 K interval agrees well with the data of Wôjcicki (*9*), who obtained $H^E{}_{0.5} = 523$ J at a temperature of 298 K. For the second system the difference between our results and the data of Funk et al. (*2*) is about 5 J. It is evident from Figure 1 that such a difference lies within the limits of experimental error.

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Ammonium Iodide–Potassium Iodide Mixed Crystals in Equilibrium with Aqueous and Aqueous–2-Propanol Solutions

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The equilibria in the systems KI + HN_4I + water and KI + HN_4I + equimolar mixtures of 2-propanol and water have been studied at 25 °C. The two iodides are completely miscible in the solid phase.

Introduction

In a recently proposed cycle for the thermochemical production of hydrogen (*1*, *2*), the water-binding step is the reaction

$$KI + H_2O + NH_3 + CO_2 \rightarrow KHCO_3 + NH_4I$$

This reaction is carried out in an equimolar mixture of water and 2-propanol, potassium bicarbonate precipitates, and the supernatant solution contains a mixture of KI and NH_4I from which the latter must be separated. The present investigation has been undertaken to elucidate the phase behavior of solid KI and NH_4I in equilibrium with such solutions, as well as with purely aqueous solutions of the two salts. We hoped to find a means of precipitating NH_4I from the solutions that would be analogous to the method employed to recover NH_4Cl in the modified Solvay process (*3*).

A study of the NH_4Cl-KCl-H_2O and NH_4Br-KBr-H_2O systems has been reported (*4*). In both of these cases the potassium and ammonium salts exhibit limited mutual solubility. No comparable investigation of the iodide system appears to have been carried out.

Experimental Section

Analytical reagent grade chemicals were used without further purification.

Due to the limited mobility of ions within a solid and the different ratios of K^+/NH_4^+ in the solid and solvent phases, establishment of equilibrium on mixing solid and solvent may be slow. Therefore equilibrium was approached by precipitation of solid from a solvent phase whose composition varied little during the experiment.

Experiments with Equimolar Water–2-Propanol Solutions. Two burets were used to deliver simultaneously over 10 s 3 mL of 2-propanol and about 1.1 mL of aqueous KI-NH_4I solution to a stirred flask thermostated at 25 °C. Volumes were such as to produce a final water/2-propanol mole ratio of 1:1. Precipitation of NH_4I-KI occurred due to reduced solubility in the mixed solvent. The solution and solid were allowed to equilibrate for 30–60 s before the cycle was repeated. Since momentary deviations from equimolar 2-propanol–water on addition and mixing, with resultant inhomogeneity of the solid, are more likely when the solution volume is small, the solid was discarded after addition of the first 24 mL of 2-propanol. Cycles of simultaneous aliquot addition to the retained solution followed by equilibration were continued until sufficient precipitate had collected. The resulting mixture was stirred for 20–24 h, the solution was decanted, the solid was dried, and both phases were analyzed for NH_4^+, K^+, and I^-. The solvent mass loss on drying of the solid was used in conjunction with the density and composition of the mother liquor to correct the composition of the solid for deposition of salts from adhering mother liquor.

Experiments with Aqueous Solutions. A stream of nitrogen was introduced over the surface of a stirred saturated aqueous solution of NH_4I + KI at 25 °C to induce evaporation of water and precipitation. Since solid that formed on the sides of the flask through evaporation would tend to have the composition of evaporated solution, care was taken to avoid contamination of the equilibrium solid phase distributed throughout the liquid with this solid. After the desired amount of precipitate was obtained, the nitrogen stream was stopped, the flask stoppered, and the mixture stirred for 3–20 h. One aliquot of liquid was removed for analysis on initiation of precipitation, and another was taken after the equilibration period. The results were averaged. Since the precipitated solid contained a higher pro-

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Table I. Solid-Solvent Equilibria for KI + NH_4I + Solvent

2-propanol-water[a] $[K^+]/[I^-]$[b]		water $[K^+]/[I^-]$[b]	
solid	liquid	solid	liquid
0.527	0.147	0.0271	0.0269
0.612	0.179	0.0595	0.0535
0.619	0.185	0.103	0.101
0.747	0.260	0.149	0.137
0.748	0.268	0.189	0.151
0.826	0.348	0.285	0.247
0.892	0.457	0.437	0.365
0.948	0.654	0.585	0.493
0.959	0.701	0.731	0.624
0.980	0.827	0.847	0.751
		0.908	0.830
		0.930	0.870

[a] 50 mol % 2-propanol in water. [b] Compositions are mole ratios.

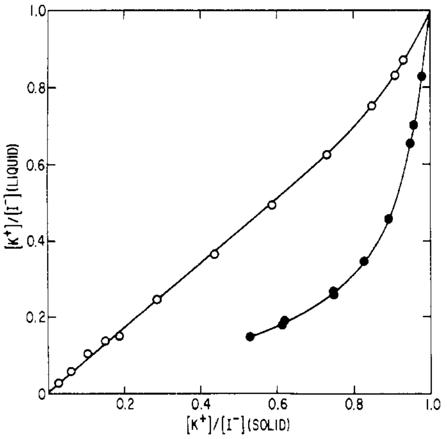

Figure 1. Distribution of K^+ between solid and liquid phases in the potassium iodide-ammonium iodide system: (○) solvent is H_2O; (●) solvent is equimolar mixture of water and 2-propanol. Compositions are mole ratios.

portion of K^+ than the liquid, the second analysis was systematically higher in $[NH_4^+]$ and lower in $[K^+]$; the average increase in $[NH_4^+]$ was 0.8%. Analyses of the solid were corrected for the presence of mother liquor.

Chemical Analysis. Iodide was determined by titration with standard silver nitrate using 0.5% Eosine Y indicator. The Kjeldahl method was used for ammonium ion. Potassium was determined either by atomic absorption spectroscopy or by addition of excess tetraphenyl boron and back-titration with a quaternary ammonium bromide solution in the presence of Clayton Yellow indicator (*5*).

X-ray Analysis. Cell dimensions were obtained from Debye-Scherrer powder patterns taken with Cu Kα radiation, using a Straumanis mounting.

Results and Discussion

Composition data for the 2-propanol-water and water systems are given in Table I. The data are shown graphically in Figure 1.

The KI-NH_4I-H_2O system exhibits one degree of freedom over the entire composition range at 25 °C and atmospheric pressure. For any given concentration of K^+ in the solid, the K^+ concentration in the liquid is fixed. The phase rule predicts two coexistent phases in a three-component system (KI, NH_4I, and solvent of fixed composition) with one degree of freedom. One solvent phase is present, so KI and NH_4I must form a solid solution at all compositions. Since the thermodynamic stability of the solid phase is independent of solvent (assuming no incorporation of solvent into the solid), the 2-propanol-water system verifies the conclusion over the composition range studied. Continuous solid solution formation is also indicated by X-ray powder patterns of the solid. The unit cell lengths of the cubic structures are shown in Table II and Figure 2. The dimensions for the solid solutions are intermediate between those of pure KI and pure NH_4I (*6*). The cell dimensions that we have obtained for pure NH_4I and KI are respectively 0.014 and 0.073% lower than those of the literature values (*6*). This discrepancy is negligible, however, compared to the ca. 1% uncertainty in $[K^+]/[I^-]$ for the solid solutions.

Table II. Unit Cell Lengths of NH_4I-KI Mixed Crystals as a Function of Composition

unit cell length, Å	$[K^+]/[I^-]$[b]
7.258 (1)[a]	0
7.225 (1)	0.185
7.181 (4)	0.398
7.144 (1)	0.594
7.102 (1)	0.802
7.060 (2)	1.00

[a] Uncertainties are standard deviations. [b] Compositions are mole ratios.

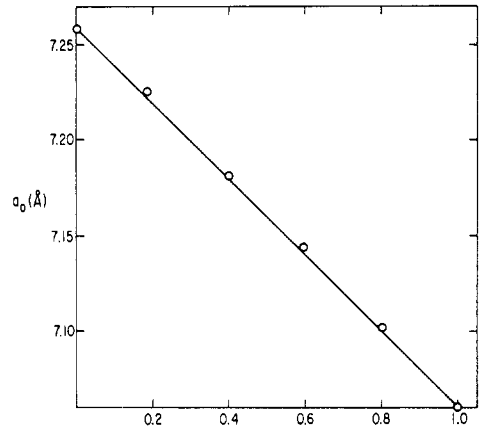

Figure 2. Dependence of the cubic unit cell length (a_0) on the composition of mixed crystals of potassium and ammonium iodides. Compositions are mole ratios.

The complete miscibility of KI and NH_4I in the solid phase contrasts with the behavior of the chloride and bromide systems, which exhibit limited mutual solubility, resulting in two solid phases when the solubility of one component in the other is exceeded (*4*). Since KI and NH_4I exist in the same crystalline form at 25 °C, while the chloride and bromide pairs do not (*6*), greater mutual solubility is expected in the iodide system. The complete miscibility and identical crystalline forms of KI and NH_4I are probably due to the greater interstitial volume created by iodide ions as compared with the smaller chloride and bromide ions.

With regard to the original motivation of the study, our results indicate that it will not be possible to isolate NH_4I by selective precipitation from solutions containing both NH_4I and KI. Hence the cycle for thermochemical hydrogen generation to which we referred earlier will have to rely on other means of separation.

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Vapor–Liquid Equilibrium for the Binary Systems Propionitrile + Ethylbenzene and Acetonitrile + Ethyl Acetate, + Ethyl Alcohol, and + Toluene

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Total pressure vapor-liquid equilibrium data were measured for the following four binaries: ethyl acetate + acetonitrile at 313.15, 353.15, and 393.15 K; ethyl alcohol + acetonitrile at 293.15, 343.15, and 393.15 K; acetonitrile + toluene at 293.15, 343.15, and 393.15 K; propionitrile + ethylbenzene at 313.15, 353.15, and 393.15 K. The P,T,x data were reduced to y, γ, and G^E values by the Mixon-Gumowski-Carpenter method. The virial equation of state truncated after the second coefficient was used to calculate the vapor-phase fugacity coefficients. The Tsonopoulos correlation was used to predict the second virial coefficients. For comparison purposes, the data for the acetonitrile + toluene system were also reduced by the Barker method using a four-suffix Margules equation.

Introduction

The selection of the systems covered in this paper was based on the group interaction parameter grid of the UNIFAC correlation scheme outlined by Fredenslund et al. (*1*). The aim was to fill in places in the grid where either sparse or no data were available. Data were measured at three temperatures for each of the four systems. Maher and Smith (*2*, *3*) have reported similar data previously for binary systems containing chlorobenzene and aniline.

Experimental Apparatus and Techniques

The apparatus used for this study has been described previously (*4*). Fifteen discrete cells are loaded with the two pure components and thirteen intermediate binary mixtures. The mass of each component loaded in a cell is determined by the use of an analytical balance. The cells are attached to a low-volume manifold, and the contents are degassed in situ by successive freezing-evacuation-thawing cycles. When the degassing is completed, the manifold assembly is placed in a constant-temperature bath. Pressure measurements are made by opening each cell in turn to a differential pressure transducer used as a nulling device. The nitrogen pressure used to balance the cell vapor pressure is measured by using a separate transducer that is calibrated frequently vs. a dead weight gauge. The bath temperature is measured with a platinum resistance thermometer that is calibrated vs. a local platinum resistance temperature standard using the IPTS-68 temperature scale.

Table I. Chemicals Used

component	vendor	stated purity, %
acetonitrile	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9
ethyl alcohol	U.S. Industrial Chemicals	200 proof
ethylbenzene	El Paso Products Co.	99.96
propionitrile	Aldrich	99.0
toluene	Burdick and Jackson	99.9

The uncertainties in the measured temperatures and mole fractions are ±0.03 K and ±0.0005, respectively. The estimated uncertainties for the three reported variables (P, T, and x) due to resolution limits in the instrumentation were summed to give an expression for the total effect on the reported vapor pressures. The total possible resolution error in kPa is given by

$$\text{total possible resolution error} = 0.03\left(\frac{\partial P}{\partial T}\right)_x + 0.0005\left|\frac{\partial P}{\partial x}\right|_T + 0.00035P + 0.003 + 6.89476[(2.5)(\text{resolution for 572})]$$

where P = experimental pressure, $(\partial P/\partial T)_x$ = temperature derivative of pressure at constant composition, and $(\partial P/\partial x)_T$ = absolute value of the composition derivative of pressure at constant temperature. The first two terms provide the uncertainty in the pressure measurement due to the possible temperature and mole fraction errors. The last three terms are related to the uncertainty in the measurement of pressure with a Datametrics 572 transducer. That transducer reads out psia and the "resolution" at various pressure levels is as follows: 0.0001 below 4 psia, 0.001 below 40 psia, 0.01 below 400 psia, etc.

The error in the reported vapor pressures, as computed by the above equation, will be referred to as the "Resolution Error Band" (REB) to distinguish it from the total possible experimental error which will include other factors such as residual gas, residual water, and chemical reaction. The width of the REB is usually about ±0.1% or less of the system pressure.

Chemicals Used

Table I lists the chemicals used and their stated purity. All chemicals except propionitrile were available in at least 99.9% purity. Activated Linde molecular sieves (either 3A or 4A) were put in the containers with the chemicals as they were received. Prior to being loaded in the metal cells, the chemicals were distilled over freshly activated molecular sieves through a Vigreaux column (25 mm o.d. and 470 mm long) with the first and last portions being discarded. The distilled samples were

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