K_A = association constant, dm^3 mol^{-1}
m = molality, mol kg^{-1}
S_v = theoretical constant in Equation 4
$y_\pm$ = molar activity coefficient
α = degree of dissociation
Λ = molar conductivity, ohm^{-1} cm^2 mol^{-1}
ϕ_v = apparent molal volume
σ_Λ = standard deviation between observed and calculated values of Λ

Literature Cited

(1) Barlow, R. B., Lowe, B. M., Pearson, J. D. M., Rendall, H. M., Thompson, G. M., *Molec. Pharmacol.*, **7**, 357, (1971).
(2) Conway, B. E., Verall, R. E., Desnoyers, J. E., *Trans. Faraday Soc.*, **62**, 2738 (1966).
(3) Duer, W. C., Robinson, R. A., Bates, R. G., *J. Chem. Soc. Faraday I*, **68**, 716, (1972).
(4) Fernandez-Prini, R., *Trans. Faraday Soc.*, **64**, 2146 (1968).
(5) Fernandez-Prini, R., *ibid.*, **65**, 3311, (1969).
(6) Fernandez-Prini, R., Prue, J. E., *Z. Phys. Chem* (Leipzig), **228**, 373, (1965).
(7) Fuoss, R. M., Hsia, K.-L., *Proc. Nat. Acad. Sci.*, **59**, 1550 (1967).
(8) Hsia, K.-L., Fuoss, R. M., *J. Amer. Chem. Soc.*, **90**, 3055, (1968).
(9) Lind, J. E., Zwolenik, J. J. Fuoss, R. M., *ibid.*, **65**, 1242, (1961).
(10) Lowe, B. M., Rendall, H. M., *J. Chem. Soc. Faraday I*, **68**, 2191, (1972).
(11) Lowe, B. M., Rendall, H. M., *Trans. Faraday Soc.*, **67**, 2318, (1971).
(12) Millero, F. J., *J. Phys. Chem.* **74**, 356 (1970).
(13) Millero, F. J., in "Water and Aqueous Solutions," Ed., R. A. Horne, P. 576, Wiley, New York, N.Y., 1972.
(14) Pitts, E., *Proc. Roy. Soc. A.*, **217**, 43, 1953.
(15) Pitts, E., Tabor, B. E., Daly, J., *Trans Faraday Soc.*, **65**, 849 (1969).
(16) Redlich, O., Meyer, D. M., *Chem. Rev.*, **64**, 221 (1964).
(17) Vaslow, F., *J. Phys. Chem.*, **70**, 2286 (1966).
(18) Vaslow, F., Oak Ridge National Research Laboratory, Oak Ridge, Tenn., private communication, 1972.

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Isothermal Vapor-Liquid Equilibrium Data for System Heptane–2-Pentanone at 90°C

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–2-pentanone system at 90.0°C, using equilibrium samples produced with the aid of a vapor-recirculation equilibrium still. Vaporization equilibrium constants (*K* values) and activity coefficients were calculated from the equilibrium compositions, and the thermodynamic consistency was checked by two methods.

Isothermal vapor–liquid equilibrium data at low pressures are useful for studying the thermodynamics of nonideal solutions and desirable for establishing the vaporization equilibrium constants (*K*-values) used for the design of equilibrium stage processes.

A survey of the literature indicates that no such isothermal data have been published for the system heptane–2-pentanone. Because of this, the equilibrium compositions reported here were determined.

Experimental

A detailed description of the experimental equipment, procedures, and methods has been given by Lodl and Scheller (*5*) and by Scheller et al. (*10*).

Briefly, a modification of the vapor-recirculation equilibrium still described by Hipkin and Myers (*3*) was used. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont (*2*) and measured with a mercury manometer to ±0.1 mm.

Temperature was measured with an iron-constantan thermocouple to ±0.1°C, using a Model 320 Data Technology Corp. digital voltmeter which could be read to the nearest microvolt. The thermocouple was calibrated at the solid-state transition point of sodium sulfate decahydrate (32.384°C) and also against the boiling point of water. Distilled water was placed in the equilibrium still, the pressure was adjusted to the desired value with the aid of the Cartesian manostat, and the system was allowed to operate until a constant millivolt reading was obtained on the potentiometer. The temperature was determined from the measured pressure and the steam tables. Twenty-three experimental points between 85.6 and 690.3 mm of Hg (48.44° and 97.33°C) were used in the calibration. A linear equation of temperature as a function of voltage was fitted to these 23 points by the method of least squares. The absolute average deviation between the experimental and calculated temperatures is 0.13°C. Spot checks of the calibration were made using pure benzene, acetone, and toluene.

Compositions of equilibrium samples were obtained with the aid of a Perkin-Elmer 880 gas chromatograph with a hot-wire detector, a 194B printing integrator, an L&N Speedomax G strip chart recorder, and a stationary phase of diisodecyl phthalate on 80/90 mesh ABS Anakrom packed in a stainless steel tube $\frac{1}{8}$ in. by 10 ft. long. Helium was used as the elution gas. The chromatograph was calibrated with 12 mixtures of heptane–2-pentanone of known composition by relating the area fraction of the heptane peak to the mole fraction of heptane. The overall precision of the composition analyses was 0.2 mol %.

The heptane and 2-pentanone were obtained from Phillips Petroleum Co. and Eastman Kodak Co., respectively. Because chromatographic analysis indicated small secondary peaks, the reagents were distilled at high reflux in a glass distillation column about 5 ft 6 in. high. A heart cut representing approximately the center 40% of each reagent was collected and displayed no secondary peaks on the chromatograph. Densities, refractive indexes, and normal boiling points were measured and are compared with literature values in Table I.

Discussion of Results

Table II contains the experimental x, y, P equilibrium data obtained at 90.0°C. The vaporization equilibrium constants ($k = y/x$) and activity coefficients were calculated and are also tabulated in Table II. The liquid phase

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activity coefficients were calculated from the relationship:

$$\gamma_i = \frac{(Y_i)}{x_i}\frac{(\phi_i)}{\phi_i^\circ}\frac{P}{P_i^\circ} \qquad (1)$$

If the fugacity coefficient ratio ϕ_i/ϕ_i° is small and B_{12} is assumed to be zero, the ratio can be calculated using the second virial coefficient, B_i, from the equation

$$\ln(\phi_i/\phi_i^\circ) = \frac{B_i(P - P_i^\circ)}{RT} \qquad (2)$$

Second virial coefficients for heptane and 2-pentanone at 90°C were obtained from the data published by McGlashan and Potter (*6*) and by Nickerson et al. (*7*), respectively. The values of ϕ_i/ϕ_i° are included in Table II.

The experimental data indicate the existence of an azeotrope for this system. The azeotropic composition was interpolated by plotting ln α_{hP} against x_h and found to be 58 mol % heptane. The pressure at the azeotrope was found to be 712.8 mm of Hg from an x, y, P plot. Other values at azeotropic conditions were then calculated (Table II). Horsley (*4*) lists the azeotropic composition for this system as 66 wt % (63 mol %) heptane at 760 mm of Hg.

The overall thermodynamic consistency of the experimental equilibrium data was checked by the method of Redlich and Kister (*8*). For an isothermal binary system having a zero volume change on mixing over the entire composition range, the data are consistent if

$$\int_{x_h = 0}^{x_h = x_h^\circ} \ln\frac{(\gamma_h)}{\gamma_P}\,dx_h = \int_{x_h = 1}^{x_h = x_h^\circ} \ln\frac{(\gamma_h)}{\gamma_P}\,dx_h \qquad (3)$$

where x_h° represents the value of x_h for which $\ln(\gamma_h/\gamma_P) = 0$. This relationship is shown in Figure 1 for the heptane-2-pentanone system at 90.0°C. The left side of Equation 3 is 0.283 and the right side 0.264.

Table I. Reagent Properties

Property	Heptane Measured	Heptane Lit.[a]	2-Pentanone Measured	2-Pentanone Lit.[a,b]
Density, 20°C	0.6837	0.6836	0.8090	0.8089
Refractive index, 20°C, n_D	1.3878	1.3877	1.3896	1.3895
Normal boiling point, °C	98.4	98.4	102.3	102.4
Chromatographic analysis	No secondary peaks		No secondary peaks	

[a] Timmermans (*11*). [b] Weast (*12*).

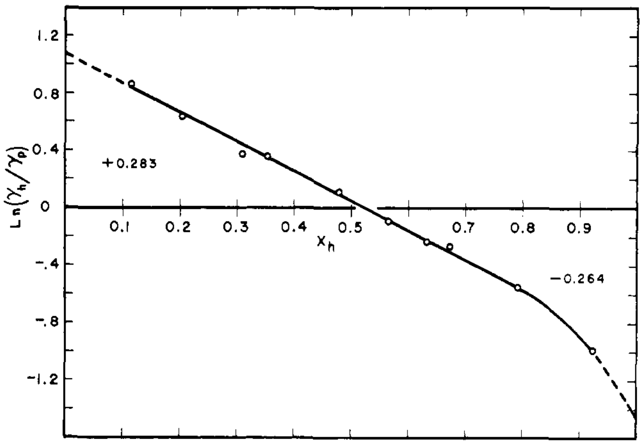

Figure 1. Consistency check of data

The consistency of the data in terms of a temperature deviation were checked by the method of Friend et al. (*1*). With this method all factors contributing to the point by point inconsistency of the data are lumped into a temperature-deviation term. In this case the average absolute deviation from consistency is 1.1°C and the maximum absolute deviation is 1.8°C when integrating over the range of x_h. The point by point results of this check are shown in Table II. When the check is made by integrating over the range of x_P, the average absolute deviation is 0.9°C, and the maximum absolute deviation is 2.1°C.

Nomenclature

B = second virial coefficient, cc/g-mole
K = vaporization equilibrium constant = y/x
P = system pressure, mm of Hg
P° = vapor pressure of pure component, mm of Hg

Table II. Vapor-Liquid Equilibrium for the System Heptane-2-Pentanone at 90°C

P, mm	x_h	y_h	K_h	K_P	α_{hP}	$(\phi/\phi^\circ)_h$[a]	$(\phi/\phi^\circ)_P$[a]	γ_h	γ_P	$\ln\gamma_h/\gamma_P$	$\lvert\epsilon\rvert$
517.1[b]	0.000	0.000	3.368	1.000	3.368	1.0051	1.0000	2.945	1.000	(108)[c]	—
656.2	0.110	0.249	2.264	0.844	2.682	0.9951	0.9895	2.509	1.060	0.862	1.4
693.9	0.202	0.351	1.738	0.813	2.138	0.9925	0.9867	2.030	1.077	0.634	0.8
701.3	0.310	0.424	1.368	0.835	1.638	0.9920	0.9861	1.615	1.116	0.370	0.4
708.1	0.354	0.469	1.325	0.822	1.612	0.9915	0.9856	1.579	1.109	0.353	0.7
710.5	0.478	0.535	1.119	0.891	1.256	0.9914	0.9854	1.338	1.206	0.104	1.3
712.5	0.565	0.572	1.012	0.984	1.028	0.9912	0.9853	1.213	1.336	−0.097	1.4
(712.8)[c]	(0.58)	(0.58)	1.000	1.000	1.000	0.9912	0.9852	1.199	1.358	−0.125	—
702.8	0.638	0.607	0.959	1.071	0.895	0.9919	0.9860	1.134	1.435	−0.235	1.8
698.6	0.674	0.642	0.952	1.098	0.868	0.9923	0.9863	1.120	1.463	−0.267	1.8
687.0	0.792	0.713	0.900	1.380	0.652	0.9930	0.9872	1.042	1.810	−0.552	1.6
670.7	0.923	0.835	0.905	2.143	0.422	0.9942	0.9884	1.024	2.747	−0.987	0.4
589.4[b]	1.000	1.000	1.000	3.761	0.266	1.0000	0.9945	1.000	4.306	(−1.46)[c]	0.9
											Av. 1.1

[a] $B_h = -1620$ cc/g-mol, $B_p = -1720$ cc/g-mol. [b] Literature values: Nickerson et al. (*7*), Rossini (*9*). [c] Numbers in parentheses extrapolated or interpolated values.

t = temperature, °C
T = temperature, K
x = equilibrium mole fraction of a component in the liquid phase
y = equilibrium mole fraction of a component in the vapor phase
α = relative volatility of heptane to 2-pentanone
γ = liquid phase activity coefficient
ϵ = difference between experimental and calculated temperature, °C
ϕ/ϕ° = ratio of the vapor phase fugacity coefficient at system temperature and pressure to that at system temperature and pure component vapor pressure

Subscripts

h = heptane
P = pentanone
i = a component

Literature Cited

(1) Friend, J., Scheller, W. A., Weber, J. H., *Ind. Eng. Chem., Process Des. Develop.*, **9**, 144 (1970).
(2) Gilmont, R., *Ind. Eng. Chem., Anal. Ed.*, **18**, 663 (1946).
(3) Hipkin, H., Myers, H. S., *Ind. Eng. Chem.*, **46**, 2524 (1954).
(4) Horsley, L. H., *Advan. Chem. Ser.*, **6**, 141 (1952).
(5) Lodl, S. J., Scheller, W. A., *J. Chem. Eng. Data*, **12**, 485 (1967).
(6) McGlashan, J. L., Potter, D. J. B., *Proc. Roy. Soc., Ser.* **A, 267,** 478 (1962).
(7) Nickerson, J. K., Kobe, K. A., McKetta, J. J., *J. Phys. Chem.* **65,** 1037 (1961).
(8) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(9) Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimental, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," p 341, Carnegie Press, Pittsburgh, Pa., 1953.
(10) Scheller, W. A., Torres-Soto, A. R., Daphtary, K. J., *J. Chem. Eng. Data*, **14**, 17 (1969).
(11) Timmermans, J., "Physico-Chemical Constants for Pure Organic Compounds," Vol. I, pp 60, 64, 362, Elsevier, New York, N.Y., 1950.
(12) Weast, R. C., Ed., "Handbook of Chemistry and Physics," 51st ed., p C414, Chemical Rubber Co., Cleveland, Ohio, 1970.

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Solubility of Iso-octane and Four Aliphatic Ethers in Liquid Ammonia

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The solubilities of 2,2,4-trimethylpentane and diethyl, di-*n*-propyl, diisopropyl, and di-*n*-butyl ether in liquid ammonia were determined by means of a carrier solvent-gas chromatographic method. Values were obtained in the temperature range −74° to −36°C. Two immiscible liquid phases are observed in this range, except for the case of diethyl ether which exhibits an upper critical solution temperature of −42 ± 1°C.

A series of investigations was carried out in this laboratory involving liquid-liquid extraction of various types using liquid ammonia as the polar phase. Because these investigations are performed at 1-atm pressure and the liquid range of ammonia is −77.7° to −33.3°C, the choice of organic solvents is much more limited than in analogous aqueous systems. The low-melting chlorohydrocarbons are miscible, as is ethyl acetate. Acetone forms an insoluble solid ammoniate, while other low melting ketones and aromatic solvents are too soluble to be useful. Tri-*n*-butyl phosphate forms an immiscible solvent pair with liquid ammonia and this system has been investigated by Hala and Tuck *(3)*. Alkanes are only slightly soluble in liquid ammonia, but below octane the densities are so close to that of ammonia that clean phase separations are difficult to obtain. Above octane the melting points become too high; *n*-octane, saturated with ammonia, solidifies at −51°C. Iso-octane and the lower aliphatic ethers are the only low boiling "inert" and "participating" solvents which we have found to be of practical use for distribution studies with liquid ammonia.

Mutual solubility data are required for these systems, but very few quantitative data are in the literature despite the extensive use of liquid ammonia in many areas over the last 70 years. Liquid ammonia has frequently been used for the extraction of aromatic and olefinic compounds from petroleum. This technique generally employs additional solvents and temperatures above the boiling point of ammonia. The solubility and physical data available concerning these procedures reflect these conditions.

The solubility of ammonia in the organic solvent is readily determinable by titration, while the solubility of the organic solvent in liquid ammonia has presented more of a problem. Recently, however, gas chromatography has been found to offer a means of obtaining quantitative data in applications of this type. McAuliffe, for example, employing a gas chromatographic technique, has determined the solubility of 65 hydrocarbons in water *(6)*.

A gas chromatographic investigation has therefore been made of the solubility of some useful extraction solvents in liquid ammonia over its liquid range at 1 atm.

Reagents

ACS reagent grade anhydrous diethyl ether and 99.99% minimum purity anhydrous ammonia (Matheson Co.) were used without further treatment. Reagent grade *n*-hexane, 2,2,4-trimethylpentane, and di-*n*-propyl ether were dried by equilibration with molecular sieves (Linde 4A). Diisopropyl ether and di-*n*-butyl ether were extracted four times with equal volumes of 1:1 ammonium hydroxide, twice with deionized water, and dried with molecular sieves.

Gas chromatograms at minimum attenuation using the conditions described below were obtained for solvents used as carriers. No impurities were detectable with retention times similar to those of the solvents being studied. The sensitivity of the detectors is such that the error introduced by impurities is less than 0.01 mg/ml for any of the solubilities reported.

Procedure

The general procedures used for equilibrium and sampling have been described *(7, 9)*. The two liquid phases,

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