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.

Received for review October 24, 1972. Accepted January 15, 1973.

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

Alan M. Phipps[1]
Department of Chemistry, Boston College, Chestnut Hill, Mass. 02167

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,

---

[1] Present address, The Gillette Co., Gillette Park 2T3, So. Boston, Mass. 02106.

approximately 10 ml each, were equilibrated in 50-ml graduated centrifuge tubes immersed in dry ice baths. An acetone–Dry Ice bath maintained a temperature of −74 ± 1°C; temperatures intermediate between this value and −33.3°C (the boiling point of ammonia) were obtained with Dry Ice and mixtures of *o*- and *m*-xylene in various proportions *(8)*. Temperatures were measured with a toluene thermometer. On the basis of the reading obtained when pure ammonia begins to crystallize (−77.7°C), these readings are accurate within ±1°C.

After equilibrating for at least 1 hr with periodic swirling, a 5–7-ml sample of the ammonia phase was obtained by forcing it with dry nitrogen through a U-shaped length of 3-mm i.d. borosilicate glass tubing into a 15-ml graduated centrifuge tube immersed in the same bath. A plug of powdered Pyrex sintered into the end of this tubing reduced the flow rate of the ammonia. The short portion of the tubing outside the centrifuge tubes was cooled with Dry Ice before the transfer *(7, 9)*.

The sample of ammonia measured to the nearest 0.1 ml was quantitatively transferred to a cooled 50-ml Erlenmeyer flask containing a few boiling chips and 7 or 20 ml of carrier solvent, depending on the solvent being investigated. The flask was connected to a water-cooled condenser and the temperature raised to approximately 0°C. A short Drierite column was attached to the condenser to keep out atmospheric moisture. After evaporation of the ammonia, the contents of the flask were transferred to an appropriate volumetric flask, made up to volume with additional carrier solvent, and analyzed chromatographically.

The samples containing ether were injected onto a 12 ft × 0.25 in. o.d. stainless steel column packed with 25% silicone gum rubber S.E.-30 on 60–80-mesh Chromosorb W. Helium flow through the column was 60 cm^3/min and the column temperature was maintained at 80°C for ethyl and isopropyl ether and 125°C for *n*-propyl and *n*-butyl ether. The output of the thermal conductivity detector was monitored with a Honeywell Model Y143X recorder.

A syringe equipped with a Chaney lock was used to inject 30 μl of solution. Very regular peaks were obtained and their area was calculated as height × width at ½ height. One-microliter samples of 2,2,4-trimethylpentane in hexane carrier were separated on a 6 ft × 0.125 in. o.d. column of the same packing material (10% liquid phase) maintained at 80°C. A flame ionization detector (F&M 5750) was employed in conjunction with an Infotronics CRS 11 HSB electronic integrator.

The exact amount of solution injected was determined from the area of the carrier peak. In each case samples were run in sequence with weight/volume standards made up to be of approximately the same concentration as the samples.

The possibility of sample loss during evaporation of the ammonia was investigated by adding 5 ml of liquid ammonia to 25 ml of a cooled standard solution of diethyl ether (the most volatile solvent studied) in 2,2,4-trimethylpentane and evaporating the ammonia as described above. The peak area obtained from the chromatogram of this solution was the same as obtained for the original standard within the uncertainty involved in the measurement, approximately 1%.

Results and Discussion

The solubilities determined for iso-octane and four dialkyl ethers in liquid ammonia at various temperatures in the liquid range at 1 atm are shown in Table I. The values for the ethers were reproducible in a range of ±3%, which is approximately the reliability of the sampling technique.

Table I. Solubility of Organic Solvents in Anhydrous Liquid Ammonia

Compound	Temp,[a] °C	Solubility, mg/ml	Carrier solvent
Diethyl ether	−74	59	25 ml 2,2,4-trimethylpentane
Diisopropyl ether	−74	7.5	25 ml 2,2,4-trimethylpentane
	−62	14	
	−50	21	
	−37	35	
Di-*n*-propyl ether	−74	4.5	10 ml di-*n*-butyl ether
	−61	7.3	
	−48	13	
	−36	21	
Di-*n*-butyl ether	−74	0.77	10 ml 3,3,4-trimethylpentane
	−60	1.2	
	−49	2.1	
	−37	3.7	
2,2,4-Trimethylpentane	−74	0.07 max	10 ml *n*-hexane
	−67	0.11 max	
	−51	0.20 max	

[a] All temperatures ± 1°C.

In general, the larger the aliphatic portion of the compound in a homologous series the less the solubility in liquid ammonia. This was observed qualitatively by Franklin and Kraus *(2)*, who list diethyl ether as miscible and diamyl ether as slightly soluble, both at −33.3°C. We have found no quantitative data reported for the aliphatic ethers. An equal-volume mixture of diethyl ether and liquid ammonia separates into two liquid phases at −42 ± 1°C. A single phase was observed at the lowest temperatures obtainable using the more polar bis-(2-chloroethyl)ether.

The solubilities listed for 2,2,4-trimethylpentane were reproducible to the same degree as the ethers, but the concentrations involved are so low that a susceptibility to several interferences must be considered. All samples were free of emulsion to visual inspection, but the possibility of contamination at this level cannot be ruled out completely for this sampling procedure, given the similarity in the density of the two liquids. Because any error introduced in this way would be positive, the values are listed in Table I as maximum solubilities.

No other data are available in the literature for this system in the temperature range studied. Some data are available, however at higher temperatures: Ishida *(5)* reported a solubility of 1.5 wt % 2,2,4-trimethylpentane in liquid ammonia at 0°C (approximately 9.6 mg/ml) and 3.2 wt % at 20°C. These values, obtained at a pressure of several atmospheres, were determined by difference, the ammonia content of a weighed sample being obtained by a titration method. The upper critical solution temperature for 2,2,4-trimethylpentane and ammonia is 61°C *(1)*. As a point of comparison, McAuliffe *(6)* using a gas chromatographic technique determined the solubility of 2,2,4-trimethylpentane in water to be 2.44 mg/l. at 25°C.

Because of the lack of comparative data in the published literature, it was felt advisable to check the validity of this method through its application to a known system. We have, therefore, determined the solubility of water in diethyl ether using the apparatus, procedure, and sample volumes described in the experimental section of this paper. Absolute ethanol was used as the carrier solvent and the ether was evaporated at approximately 40°C. The gas chromatography in this case was performed on a 6-ft Porapak Q column and thermal conductivity detector. In this way the solubility of water in diethyl ether was determined to be 1.28% (w/w) at 23°C. A value of 1.31% w/w is calculated from the data of Hill *(4)*, who employed a volumetric procedure. This is within the ±3% range assumed for the precision of the sampling technique.

According to other data reported by Hill *(4)*, the solubility of diethyl ether in water at 25°C is 60 mg/ml. Therefore, liquid-liquid extraction with diethyl ether as the organic phase and water at 25°C or ammonia at −74°C as the polar phase provides essentially the same conditions with regard to the solubility of the organic phase in the polar phase.

Literature Cited

(1) Francis, A. W., *Ind. Eng. Chem.*, **36**, 764 (1944).
(2) Franklin, E. C., Krause, C. A., *Amer. Chem. J.*, **20**, 820 (1898).
(3) Hala, J., Tuck, D. G., *J. Chem. Soc.*, **(A) 1970**, 3242.
(4) Hill, A. E., *J. Amer. Chem. Soc.*, **45**, 1143 (1923).
(5) Ishida, K., *Bull. Chem. Soc. Japan*, **31**, 143 (1958).
(6) McAuliffe, C., *J. Phys. Chem.*, **70**, 1267 (1966).
(7) Phipps, A. M., Hume, D. N., *Anal. Chem.*, **39**, 1755 (1967).
(8) Phipps, A. M., Hume, D. N., *J. Chem. Ed.*, **45**, 664 (1968).
(9) Phipps, A. M., McDermott, J. X., *Anal. Chem.*, **43**, 530 (1971).

Received for review December 8, 1972. Accepted December 16, 1972. Work supported in part by Grant GP-7501 of the National Science Foundation.

Effect of Pressure and Temperature on the Liquid Densities of Pure Hydrocarbons

Homer E. Rea
Union Research Center, Brea, Calif. 92621

Calvin F. Spencer and Ronald P. Danner[1]
Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa. 16802

Two different approaches were taken to improve the methods of predicting the effect of pressure and temperature on the liquid densities of pure compounds. First, the Rackett equation for obtaining the saturated liquid density was introduced into two correlations previously given in the literature. Second, a set of generalized polynomials was developed to predict the correlating parameter of the Lu chart which is frequently used to evaluate the density variation with temperature and pressure. These correlations were evaluated for a set of 2590 data points for 32 compounds, mainly hydrocarbons. The regression of the Lu chart is shown to be quite accurate and the most general of the methods. A modification of the Chueh-Prausnitz approach is the most accurate when the specific constant of the Rackett equation is available.

At pressures higher than the vapor pressure, liquid densities increase with increasing pressure, provided, of course, the temperature remains constant. A number of correlations have been presented in the literature to predict this change in the liquid densities.

In a 1966 review of such correlations *(16)*, the methods of Watson *(35)*, Lu *(21)*, Lydersen et al. *(23)*, and Ritter et al. *(26)* were evaluated. The methods are all graphical in nature, and, while they may be convenient for obtaining a few predicted values, they are tedious for obtaining a large number of values and are not easily adaptable for use in computer programs. In the above review the following average percent errors in the predicted liquid densities were found for a data set consisting of approximately 150 points: Watson (2.06), Lu (1.57), Lydersen et al. (3.51), Ritter et al. (2.76). The Lu chart thus emerged from this study as the most accurate and was also commended for its general applicability.

Of these methods therefore only the method of Lu was considered in the present study. For this purpose a set of polynomial equations was developed to substitute for the graph normally used in the Lu procedure.

In addition, two newer methods, those of Yen and Woods *(36)* and of Chueh and Prausnitz *(4)*, were considered. Both of these methods require a saturated liquid density value at the temperature of interest. In addition to examining these methods as originally presented, an evaluation was made of the effect of introducing into them the modified Rackett equation *(31)* for predicting the saturated liquid density.

Approximately 2600 experimental data points for 32 compounds, mainly hydrocarbons, were used for these evaluations. The literature sources of these data are indicated in Table I.

Analytical Form of Lu Chart

The graphical method of Lu *(21)* is based on the approach recommended by Watson *(35)*:

$$\rho_1 = \left(K_1/K_R\right) \rho_R \qquad (1)$$

where ρ_1 and ρ_R are the desired density and the density at some reference condition, respectively, and K_1 and K_R are the corresponding values of the correlating parameter. Watson defined K as an empirical factor depending on T_r and P_r, while Lu defined it as $(Z_c^{0.77}/V_r)$. In both cases, the K factors are given in graphical form as a function of the reduced temperature and reduced pressure. The Lu chart covers a reduced temperature range of 0.5 to 1.0 and reduced pressures from saturation to 30.0.

Ewbank and Harden *(9)* revised a portion of the Lu chart. They expanded the scale in the range of reduced pressures less than 3.0 and reduced temperatures less than 0.76.

In the present study the correlating parameter of the Lu chart, as revised by Ewbank and Harden, has been represented by a set of generalized polynomials in T_r and P_r. A regression analysis of the Lu coefficient as a function of reduced temperature was made for each of the

---

[1] To whom correspondence should be addressed.