Solubilities of Nitrogen in Binary Solutions. Mixtures of Ethanol with Benzene, Ethyl Acetate, and Diethyl Ether

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Experimental data of nitrogen solubilities in binary solvents and those of excess volumes of the solvents are presented; the mixed solvents and temperatures measured are ethanol–benzene at 25 °C, ethanol–ethyl acetate at 40 °C, and ethanol–diethyl ether at 0 °C. It is shown that the curve of the excess quantity of solubility in a mixed solvent against the volume fraction of the solvent is similar to that of the excess volume divided by the ideal volume of mixing for each system.

Gas solubility data are required for the design of gas absorption and stripping columns and certain other pieces of separation equipment. In general, industrial solvents are mixed ones; however, there are few reliable data of gas solubility in mixed solvents. From the viewpoint of molecular thermodynamics, a dissolved inert gas molecule at infinite dilution, in a solvent, is considered to be a probe for detecting intermolecular forces between the gas and the solvent.

In this work experimental data for the solubilities of nitrogen in binary mixtures with ethanol are presented along with data for the excess volumes of the binary solvent mixtures. Benzene, ethyl acetate, and diethyl ether were selected as a component of each liquid mixture because they are known to interact chemically with ethanol.

Apparatus and Procedure

The solubility apparatus and procedures were the same ones as previously described (*3*, *9*), which are similar to those of Horiuti (*2*). The dissolution vessel was 80 cm^3 and immersed in a water bath whose temperature was regulated within 0.05 °C. Mixed solvent of a known composition was first boiled under reflux at atmospheric pressure. It was then transferred to a perviously evacuated dissolution vessel. The change in mixture composition during the degassing operation was within the experimental error (0.7%) of gas chromatographic analysis.

Materials

Merck Uvasol spectral-grade benzene and ethyl acetate were used without further purification. Diethyl ether, guaranteed reagent from Nakarai Chemicals Ltd., was dried with molecular sieve 4A and fractionated. Ethanol was a spectral-grade chemical from Nakarai and used without further purification. Nitrogen gas was superpure grade, 99.99%, from Osaka Oxygen Ltd. and used without further purification.

Solubility Expression and Physicochemical Property

The solubility was expressed in two ways: the Ostwald coefficient L and Henry's constant H

$$L_{\mathrm{R,mix}} = C_{\mathrm{R}}^{\mathrm{L}}/C_{\mathrm{R}}^{\mathrm{G}} \tag{1}$$

$$H_{\mathrm{R,mix}} = p_{\mathrm{R}}/x_{\mathrm{R}} \tag{2}$$

No correction for vapor-phase nonideality was made. Since total pressure P was nearly 1 atm and $x_{\mathrm{R}} << 1$, the partial pressure p_{R} was evaluated by means of Raoult's law as

Table I. Experimental Data of Nitrogen Solubility and Liquid Density for the Mixtures of Ethanol (A) and Benzene (B) at 25 °C

x_{A}	Φ_{A}[a]	P^{S}/mmHg (*10*)	$L_{\mathrm{R,mix}}$	$H_{\mathrm{R,mix}}$/atm	ln $\kappa(L)$	d/g cm^{-3}	v^{E}/cm^3 mol^{-1}
0.0	0.0	95.18	0.1238	2211	0.0	0.87375	0.0
0.1000	0.0679	121.2	0.1262	2245	0.006	0.86685	0.092
0.2000	0.1409	124.5	0.1284	2287	0.010	0.86031	0.100
0.3000	0.2194	124.9	0.1309	2330	0.015	0.85357	0.081
0.4000	0.3042	124.4	0.1317	2408	0.005	0.84616	0.073
0.5000	0.3961	123.5	0.1330	2488	−0.003	0.83830	0.051
0.6000	0.4959	120.8	0.1346	2562	−0.010	0.83016	−0.006
0.7000	0.6048	115.7	0.1379	2615	−0.006	0.82076	−0.021
0.8000	0.7240	106.5	0.1409	2683	−0.007	0.81083	−0.066
0.9000	0.8551	89.5	0.1443	2750	−0.008	0.79897	−0.039
1.0	1.0	59.88	0.1494	2793	0.0	0.78571	0.0

[a] Calculated from $\Phi_{\mathrm{A}} = v_{\mathrm{A}}x_{\mathrm{A}}/(v_{\mathrm{A}}x_{\mathrm{A}} + v_{\mathrm{B}}x_{\mathrm{B}})$.

Table II. Experimental Data of Nitrogen Solubility and Liquid Density for the Mixtures of Ethanol (A) and Ethyl Acetate (B) at 40 °C

x_{A}	Φ_{A}[a]	P^{S}/mmHg[b]	$L_{\mathrm{R,mix}}$	$H_{\mathrm{R,mix}}$/atm	ln $\kappa(L)$	d/g cm^{-3}	v^{E}/cm^3 mol^{-1}
0.0	0.0	187.9	0.2059	1242	0.0	0.876 13	0.0
0.1000	0.0618	205.8	0.2052	1297	0.013	0.868 70	0.117
0.2000	0.1291	213.6	0.2010	1382	0.010	0.861 12	0.182
0.3000	0.2026	216.4	0.1983	1465	0.016	0.853 23	0.207
0.4000	0.2832	216.2	0.1953	1559	0.021	0.844 39	0.251
0.5000	0.3721	213.4	0.1908	1677	0.021	0.835 07	0.255
0.6000	0.4706	209.2	0.1863	1810	0.023	0.825 20	0.218
0.7000	0.5804	201.4	0.1801	1979	0.018	0.813 94	0.203
0.8000	0.7033	188.1	0.1727	2190	0.009	0.801 32	0.189
0.9000	0.8421	166.8	0.1653	2437	0.001	0.787 89	0.108
1.0	1.0	135.2	0.1584	2767	0.0	0.772 94	0.0

[a] Calculated from $\Phi_{\mathrm{A}} = x_{\mathrm{A}}v_{\mathrm{A}}/(x_{\mathrm{A}}v_{\mathrm{A}} + x_{\mathrm{B}}v_{\mathrm{B}})$. [b] Calculated from the literature (*5*).

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Table III. Experimental Data of Nitrogen Solubility and Liquid Density for the Mixtures of Ethanol (A) and Diethyl Ether (B) at 0 °C

x_A	$\Phi_A{}^a$	P^S/mmHg (*6*)	$L_{R,mix}$	$H_{R,mix}$/atm	ln $\kappa(L)$	d/g cm^{-3}	ν^E/cm^3 mol^{-1}
0.0	0.0	185.3	0.2668	835.1	0.0	0.73638	0.0
0.1000	0.0593	176.4	0.2562	909.0	−0.001		
0.2000	0.1243	167.5	0.2429	1004	−0.012	0.7488	−0.45
0.3000	0.1956	159.8	0.2330	1099	−0.006		
0.4000	0.2745	152.9	0.2180	1236	−0.021	0.7610	−0.57
0.5000	0.3621	143.0	0.2035	1397	−0.032		
0.5672	0.4263					0.7724	−0.58
0.6000	0.4598	129.2	0.1923	1563	−0.024		
0.7000	0.5698	112.9	0.1778	1797	−0.029		
0.8000	0.6942	90.8	0.1637	2081	−0.030	0.7898	−0.37
0.9000	0.8363	57.4	0.1500	2431	−0.023		
1.0	1.0	12.14	0.1378	2847	0.0	0.80696	0.0

[a] Calculated from $\Phi_A = \nu_A x_A/(\nu_A x_A + \nu_B x_B)$.

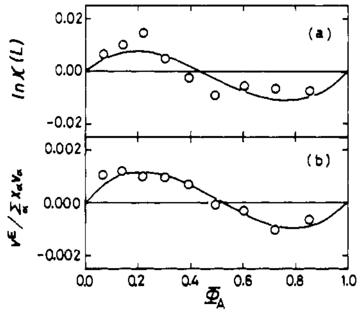

Figure 1. Excess quantities of ln $\kappa(L)$ and $\nu^E/\sum_\alpha x_\alpha \nu_\alpha$ against volume fraction Φ_A for the mixture of ethanol (A) and benzene (B) at 25 °C.

$$p_R = P - P^S_{solvent}(1 - x_R) \tag{3}$$

A small increase of liquid volume due to gas absorption was evaluated from the average value of 0.0022 for the coefficients of dilatation by absorption, determined by Horiuti (*2*).

Accurate values for vapor pressure of liquid mixtures, $P^S_{solvent}$ in eq 3, are essential in measuring the gas solubility. The solubility experiments were performed at different temperatures for the three liquid mixtures because there were only limited data of $P^S_{solvent}$ for the systems available in literature. Data sources and temperatures chosen in this work are as follows: the data of Smith and Robinson (*10*) at 25 °C for the ethanol and benzene system, those of Murti and Van Winkle (*5*) at 40 °C for the ethanol and ethyl acetate system, those of Nagai and Ishii (*6*) at 0 °C for the ethanol and diethyl ether system.

The densities of the liquid mixtures were measured in this experiment by use of a mechanical oscillator densimeter, Type SS-D-200, Shibayama Scientific Co. Ltd.

Experimental Results and Discussion

Solubility data for nitrogen in the three binary mixtures of ethanol with benzene, ethyl acetate, and diethyl ether are summarized in Tables I–III. The experimental values of solubility in pure solvents at each temperature are in good agreement with those reported previously by other investigators (*1–4, 9*). Reproducibilities of solubility data were within ±0.3% for pure solvents and within ±0.8% in the worst case, usually within ±0.5%, for mixed solvents.

Among several expressions for the excess quantity of gas solubility in mixed solvents, ln $\kappa(L)$ defined by eq 4 was shown

$$\ln \kappa(L) = \ln L_{R,mix} - \sum_{\alpha=A}^{B} \Phi_\alpha \ln L_{R,\alpha} \tag{4}$$

to have the advantage of subtracting the contribution of the term due to the difference of molecular sizes (*8*). The experimental excess quantities of ln $\kappa(L)$ for the systems studied are shown in Figures 1a, 2a, and 3a. The excess quantities ln $\kappa(L)$ calculated from a linear association model (A_iB_1 model (*7*)) have large positive values for all three systems; therefore, they are not shown in the figures.

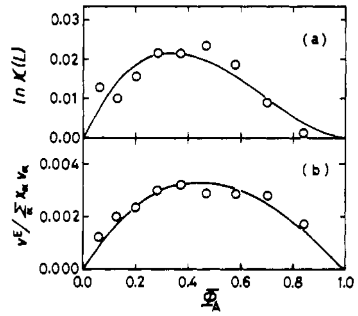

Figure 2. Excess quantities of ln $\kappa(L)$ and $\nu^E/\sum_\alpha x_\alpha \nu_\alpha$ against volume fraction Φ_A for the mixture of ethanol (A) and ethyl acetate (B) at 40 °C.

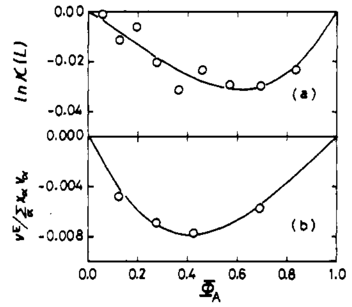

Figure 3. Excess quantities of ln $\kappa(L)$ and $\nu^E/\sum_\alpha x_\alpha \nu_\alpha$ against volume fraction Φ_A for the mixture of ethanol (A) and diethyl ether (B) at 0 °C.

Recently Tokunaga (*11*) pointed out the qualitative similarity between the curve ln $\kappa(L)$ and that of $\nu^E/\sum_\alpha x_\alpha \nu_\alpha$ against Φ_A for the solubilities of inert gases in aqueous alcohol mixtures.

$$\nu^E = \nu - \sum_{\alpha=A}^{B} x_\alpha \nu_\alpha \tag{5}$$

The experimental data of mixture density are listed in Tables I–III along with the excess molar volume ν^E. Reproducibilities of density data were ±0.1 × 10^{-4} g/cm^3 for pure liquids and ±0.8 × 10^{-4} g/cm^3 for mixed solvents except for the ethanol–diethyl ether system where the reproducibilities were 1.5 times poorer.

The reliabilities of excess molar volume ν^E were estimated to be ±0.008 cm^3/mol for the ethanol–benzene and ±0.012 cm^3/mol for the ethanol–diethyl ether system.

For the three systems investigated in this work, curves (a) and (b) of Figures 1–3 show that there is a qualitative similarity between the curve of ln $\kappa(L)$ and that of $\nu^E/\sum_\alpha x_\alpha \nu_\alpha$ as in the case of aqueous alcohol solutions. This observation may suggest that the relative excess volume in a mixed solvent corresponds to the excess space for accommodating dissolved inert gas molecules.

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Glossary

C	molar concentration, mol cm^{-3}
d	liquid density, g cm^{-3}
H	Henry's constant, atm
L	Ostwald coefficient
P	total pressure, atm
P^S	vapor pressure of pure liquid or liquid mixture, atm
p	partial pressure, atm
v	molar volume, cm^3 mol^{-1}
x	mole fraction
$\kappa(L)$	excess quantity of gas solubility defined in eq 4
Φ	volume fraction

Subscripts

A, B	solvents of A and B, respectively
R	gas component
R,mix	R in mixed solvents
R,α	R in pure solvent of α
α	pure solvent of A or B

Superscripts

E	excess quantity
G	gas phase
L	liquid phase

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Vapor–Liquid Equilibrium Data for the Systems 2-Propanol–Isopropylbenzene, Allyl Alcohol–Isopropylbenzene, 2-Methoxyethanol–Isopropylbenzene, and 2-Ethoxyethanol–Isopropylbenzene

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Vapor–liquid equilibrium data were obtained experimentally for the binary systems, 2-propanol–isopropylbenzene, allyl alcohol–isopropylbenzene, 2-methoxyethanol–isopropylbenzene, and 2-ethoxyethanol–isopropylbenzene at 760 mmHg pressure. Vapor-phase nonideality was taken into account to calculate the activity coefficients. The data were found to be thermodynamically consistent by the application of the tests of Herington, Norrish-Twigg, and Black. The correlations of Wilson and NRTL fit the activity coefficient–composition data well.

Isobaric vapor–liquid equilibrium data for the binary systems 2-propanol–isopropylbenzene, allyl alcohol–isopropylbenzene, 2-methoxyethanol–isopropylbenzene, and 2-ethoxyethanol–isopropylbenzene were obtained at 760 ± 2 mmHg pressure using a vapor recirculating type equilibrium still reported earlier (*8*). The wide boiling systems, 2-propanol–isopropylbenzene and allyl alcohol–isopropylbenzene formed no azeotropes as has been reported in literature (*6*), whereas the systems 2-methoxyethanol–isopropylbenzene and 2-ethoxyethanol–isopropylbenzene formed minimum boiling azeotropes. The azeotropic conditions for these systems are 122.2 °C and 79.5 mol % 2-methoxyethanol and 133.1 °C and 73.5 mol % 2-ethoxyethanol, respectively, whereas the values reported in the literature (*6*) are 122.4 °C and 81.5 mol % 2-methoxyethanol and 133.2 °C and 73.1 mol % 2-ethoxyethanol, respectively.

Experimental Section

2-Methoxyethanol and 2-ethoxyethanol were purified as described earlier (*8*). 2-Propanol obtained from British Drug Houses was initially dried by refluxing for about 4 h with pure quicklime. Allyl alcohol obtained from Riedel was refluxed for 4 h with chemically pure anhydrous potassium carbonate. Isopropylbenzene obtained from British Drug Houses was kept overnight in contact with pure magnesium sulfate for preliminary drying. These were finally purified by distillation as described earlier for 2-methoxyethanol and 2-ethoxyethanol. The details of apparatus and the experimental procedure used for obtaining the vapor–liquid equilibrium data have been described earlier (*8*). The refractive index method was used for the analysis of the equilibrium samples.

Results and Discussion

The activity coefficients were calculated using eq 1 and 2 described earlier (*8*). Table I gives the vapor–liquid equilibrium data along with activity coefficients for these systems.

On the basis of the recommendations made elsewhere (*7, 11*), the pure component properties were chosen. For isopropylbenzene, the vapor pressures were estimated by the RPME equation (*9, 10*), second virial coefficients by the Pitzer–Curl correlation (*15*), and liquid molar volumes by the surface tension method (*4*). For allyl alcohol, the Thek–Stiel equation (*17, 18*) was used to estimate the vapor pressures and the O'Connell–Prausnitz correlation (*14*) for estimating second virial

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