NITROGEN SOLUBILITY AND VAPOR PRESSURE OF BINARY MIXED SOLVENTS CONTAINING BENZENE, CARBON TETRACHLORIDE, CYCLOHEXANE AND 1-HEXANE

Toshio AKIMOTO, Tomoshige NITTA and Takashi KATAYAMA

Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

Experimental data are presented for vapor pressure and nitrogen solubility at 25°C for three binary nonpolar mixtures: cyclohexane + 1-hexane, cyclohexane + carbon tetrachloride and benzene + carbon tetrachloride. The one-fluid van der Waals model with the Carnahan-Starling equation for a reference fluid expression is applied to represent three thermodynamic excess quantities: the excess Gibbs energy, the excess molar volume and the excess quantity of gas solubility. It is found that agreement of the theory and the experiments is fairly good for mixtures of relatively globular molecules of benzene, cyclohexane and carbon tetrachloride. However, disagreement is found for mixtures of cyclohexane + 1-hexane.

Introduction

Thermodynamic methods for predicting gas solubility in a mixed solvent[16,19] usually require knowledge of the excess Gibbs energy, g^E, of the solvent mixture. On the other hand, some experimental results[14,15,24] indicate a close correlation between the excess molar volume, v^E, of a solvent mixture and the excess quantity of gas solubility, $\ln \kappa(L)$, for the mixture, which suggests that a theory based on the equation of state is required for better understanding of solubility phenomena.

Modern perturbation theories of liquids[4,20,22] gave a new interpretation of the van der Waals (vdW) equation of state, which is composed of two terms: a reference term of repulsive hard-particle fluid and a perturbation term by attractive potential. Among many equations proposed so far for the hard-sphere fluids, the Carnahan-Starling equation[2] is the best one to approximate the Monte Carlo computer experiments. To fluid mixtures the vdW theory has been applied by means of the so-called mixing rules for the vdW constants. A one-fluid vdW model was recommended for mixtures by Leland *et al.*[8] from a theoretical study of equations of state for soft-sphere mixtures.

In the present work, binary nonpolar mixtures of benzene, carbon tetrachloride, cyclohexane and 1-hexane were selected for experiments of nitrogen solubilities and vapor pressures of the mixed solvents. Three excess quantities, g^E, v^E and $\ln \kappa(L)$ calculated from the present data and literature data, are compared with the one-fluid vdW type equation of state with the Carnahan-Starling expression for the reference fluid.

1. Experimental

1.1 Apparatus

The apparatus and procedures were the same as those reported previously.[13] A brief description of the experimental method is as follows. A mixed solvent is degassed thoroughly by a combination of boiling and freezing followed by evacuation. The vapor pressure of the solvent admitted into a dissolution vessel is measured first and then dry nitrogen is introduced; gas solubility is determined by the saturation method. A Digiquartz pressure transducer was used for precise measurements of pressure. Accuracy of temperature is estimated to be within 0.01 K. Reproducibilities of measurements for pure liquids were ± 10 Pa for the vapor pressure P^s and $\pm 0.1\%$ for the Ostwald coefficient L.

1.2 Materials

Benzene, cyclohexane and carbon tetrachloride were guaranteed or spectral-grade reagents from Wako Pure Chemicals Ltd. They were distilled in a laboratory fractionating column and were dried with Molecular Sieve 4A. 1-Hexane, a spectral-grade reagent of Merck (Uvasol), was used without further purification. Nitrogen gas, 99.99% pure, was obtained

from Osaka Oxygen Co., Ltd.

2. Results

Experimental values for the vapor pressure and the solubility of nitrogen at 25°C are compared with literature values in **Table 1** for two pure liquids, 1-hexane and carbon tetrachloride; the same comparison for benzene and cyclohexane was made in the previous paper.[13] The vapor pressure of 1-hexane obtained in the present work is about 70 Pa greater than the value recommended by Riddick and Bunger[21]; the difference is seven times greater than the experimental errors. Therefore, it may be attributed to impurities in reagents used in the present work. All other values for the four pure liquids agree well with the literature.

Experimental data for the total pressure and the solubility of nitrogen at 25°C are summarized in **Table 2** for three binary solvents. The values for the mole fraction x_A and the volume fraction Φ_A of solvent-component A are given on solute-free basis. The volume fraction is calculated as $\Phi_A = v_A x_A / (v_A x_A + v_B x_B)$ where v_A and v_B are the molar volumes of pure components A and B, respectively. The activity coefficients, γ_A and γ_B, were calculated by means of the three-constant Redlich-Kister equation, the constants of which were determined from fitting to the vapor pressures of the mixed solvent by use of a nonlinear least square method. The activity coefficients given in Table 2 are called the "experimental" values in the present work.

For cyclohexane and 1-hexane mixtures, the total vapor pressures at 25°C were reported by Martin and Youings[12] and Li, Lu and Chen.[10] The excess Gibbs energies calculated from the experimental activity coefficients are compared with the literature in **Fig. 1**. Agreement between the curve of Martin and Youings and that of the present work is satisfactory. Markuzin et al.[11] reported the total pressure data for benzene and carbon tetrachloride mixtures, but their values differ from the present data by about 700 Pa. No literature values have been found for the total vapor pressure of a binary mixture of cyclohexane and carbon tetrachloride at 25°C.

Two expressions for nitrogen solubility, the Ostwald coefficient L and Henry's constant H, are given in Table 2. Calculations of L and H are based on the following equations.

$$L = C_R^l / C_R^g \tag{1}$$

$$H = f_R / x_R \tag{2}$$

where C_R is the concentration of solute, nitrogen, in $\text{mol} \cdot \text{m}^{-3}$; f_R and x_R are the fugacity and the mole fraction of solute, respectively.

Table 1. Experimental values of vapor pressure and nitrogen solubility in pure liquids, 1-hexane and carbon tetrachloride, at 25°C

	P^s [kPa]		L [—]	
1-hexane	20.246	(exptl.)	0.2599	(exptl.)
	20.17	21)	0.261	3)
	20.179	25)	0.256	6)
	20.153	12)		
	20.124	1)		
CCl$_4$	15.220	(exptl.)	0.1634	(exptl.)
	15.22	21)	0.164	5)
	15.195	1)		

Table 2. Experimental values of nitrogen solubilities and total pressures of three mixed solvents at 25°C

x_A [a]	Φ_A [b]	P [kPa]	$\ln \gamma_A$ [c]	$\ln \gamma_B$ [c]	L	H [MPa]
Cyclohexane (A) + 1-Hexane (B)
0.0	0.0	20.246	0.1088	0.0	0.2599	72.48
0.1013	0.0852	19.662	0.0848	0.0012	0.2520	76.10
0.1940	0.1659	19.086	0.0689	0.0040	0.2446	79.70
0.2887	0.2512	18.475	0.0564	0.0079	0.2377	83.41
0.4098	0.3646	17.691	0.0436	0.0148	0.2280	88.89
0.5065	0.4589	17.038	0.0345	0.0225	0.2201	93.77
0.6084	0.5621	16.317	0.0251	0.0344	0.2108	99.85
0.7058	0.6647	15.606	0.0165	0.0512	0.2016	106.4
0.8135	0.7828	14.743	0.0078	0.0788	0.1916	114.4
0.8955	0.8763	14.042	0.0028	0.1087	0.1831	121.7
1.0	1.0	13.012	0.0	0.1615	0.1702	133.9
Cyclohexane (A) + CCl$_4$ (B)
0.0	0.0	15.220	0.1999	0.0	0.1634	156.4
0.0966	0.1070	15.225	0.1217	0.0037	0.1656	152.4
0.1963	0.2148	15.152	0.0728	0.0119	0.1675	148.8
0.2964	0.3206	14.953	0.0457	0.0205	0.1689	145.9
0.4065	0.4341	14.736	0.0313	0.0282	0.1700	143.0
0.5042	0.5325	14.531	0.0251	0.0333	0.1709	140.7
0.6103	0.6369	14.307	0.0204	0.0392	0.1713	138.7
0.7085	0.7314	14.021	0.0153	0.0492	0.1714	137.2
0.8070	0.8241	13.731	0.0090	0.0694	0.1714	135.7
0.8998	0.9096	13.445	0.0032	0.1044	0.1709	134.8
1.0	1.0	13.012	0.0	0.1689	0.1702	133.9
Benzene (A) + CCl$_4$ (B)
0.0	0.0	15.220	0.1567	0.0	0.1634	156.4
0.0871	0.0808	15.167	0.1187	0.0017	0.1606	160.2
0.1895	0.1772	15.048	0.0883	0.0064	0.1573	164.9
0.2969	0.2800	14.866	0.0672	0.0131	0.1530	170.9
0.3970	0.3775	14.708	0.0533	0.0205	0.1493	176.6
0.5028	0.4822	14.456	0.0414	0.0302	0.1452	183.2
0.6035	0.5836	14.229	0.0309	0.0433	0.1410	190.2
0.7057	0.6883	13.913	0.0204	0.0634	0.1368	197.7
0.8011	0.7876	13.604	0.0111	0.0923	0.1327	205.5
0.9068	0.8996	13.208	0.0029	0.1409	0.1278	215.3
1.0	1.0	12.706	0.0	0.2040	0.1238	224.0

[a] Mole fraction on solute-free basis.
[b] $\Phi_A = x_A v_A / (x_A v_A + x_B v_B)$.
[c] Calculated from Barker's total pressure method by use of 3-constant Redlich-Kister equation. Second virial coefficients were evaluated from the O'Connell and Prausnitz correlation.[17]
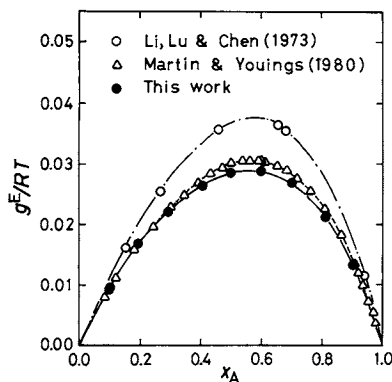
Fig. 1. Comparison of excess Gibbs energies for cyclohexane (A) and 1-hexane (B) mixtures at 25°C.

3. Discussion

The vdW type equation of state with the cut-off Lennard-Jones potential is expressed[20] by

$$\frac{P}{\rho kT} = Z^{hs} - \frac{16}{9} \cdot \frac{\pi \rho}{kT} \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \tag{3}$$

where ρ is the number density; k the Boltzmann constant; T temperature; ε and σ are the Lennard-Jones force constants. The Carnahan-Starling equation is used for the hard sphere reference fluid.

$$Z^{hs} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \tag{4}$$

where

$$\xi = \frac{\pi}{6} \rho \langle \sigma^3 \rangle \tag{5}$$

According to the one-fluid model, the mixing rule for σ is given as

$$\langle \sigma^3 \rangle = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \sigma_{\alpha\beta}^3 \tag{6}$$

Then the chemical potential of component A is expressed by

$$\frac{\mu_A}{kT} = \frac{\mu_A^{hs}}{kT} - \frac{32}{9} \cdot \frac{\pi \rho}{kT} \sum_{\alpha} x_{\alpha} \varepsilon_{A\alpha} \sigma_{A\alpha}^3 \tag{7}$$

where

$$\frac{\mu_A^{hs}}{kT} = \ln(\rho_A \Lambda_A^3) + \frac{\xi(4 - 3\xi)}{(1 - \xi)^2}$$

$$+ (Z^{hs} - 1)\left(2 \sum_{\alpha} x_{\alpha} \sigma_{A\alpha}^3 \Big/ \langle \sigma^3 \rangle - 1 \right) \tag{8}$$

The Ostwald coefficient L is calculated from the condition of thermal equilibrium, $\mu_R^l = \mu_R^g$; where $\mu_R^g = kT \ln(\Lambda_R^3 \rho_R^g)$ for ideal gas assumption. Taking a limit that x_R approaches zero, one finds

$$\ln L = -\frac{\xi(4 - 3\xi)}{(1 - \xi)^2} - (Z^{hs} - 1)\left(2 \sum_{\alpha} x_{\alpha} \sigma_{R\alpha}^3 \Big/ \langle \sigma^3 \rangle - 1 \right)$$

$$+ \frac{32}{9} \cdot \frac{\pi \rho}{kT}\left(\sum_{\alpha} x_{\alpha} \varepsilon_{R\alpha} \sigma_{R\alpha}^3 \right) \tag{9}$$

The force constants of ε and σ were determined from the experimental values of v^l and P^s for each solvent. They are summarized in **Table 3**. A simultaneous fit to both the vapor pressure P and the excess molar volume v^E of a binary mixture requires two binary constants, $k_{\alpha\beta}$ and $l_{\alpha\beta}$, defined by

$$\varepsilon_{\alpha\beta} = (1 - k_{\alpha\beta})(\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta})^{1/2} \tag{10}$$

$$\sigma_{\alpha\beta} = \frac{1}{2}(1 + l_{\alpha\beta})(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}) \tag{11}$$

In **Table 4** are listed the values of k_{AB} and l_{AB} for four binary systems. Experimental data of the excess molar volume were taken from the literature.[7,9,18,23] A binary system of cyclohexane and benzene is included, the data of which were reported previously.[13] **Figures 2** and **3** show the excess Gibbs energy, g^E, and the excess molar volume, v^E; the keys are the experimental data points, and the solid lines show the calculations by means of k_{AB} and l_{AB} given in Table 4. Agreement between the theory and the experiments is fairly good except for v^E of cyclohexane and 1-hexane mixtures, the experimental v^E curve of which is highly asymmetric, showing a peak in the cyclohexane-rich region.

In calculation of the Ostwald coefficient L by Eq. (9) the values of cross constants $\varepsilon_{R\alpha}$ and $\sigma_{R\alpha}$ are needed but ε_{RR} and σ_{RR} for nitrogen are not necessary. Since the solubility datum in a pure solvent gives one equation through Eq. (9), only one parameter is determined. Therefore, $\varepsilon_{R\alpha}$ was selected as a fitting parameter, being determined from the solubility in pure solvent α, and another parameter $\sigma_{R\alpha}$ was calculated from the arithmetic assumption.

$$\sigma_{R\alpha} = \frac{1}{2}(\sigma_{RR} + \sigma_{\alpha\alpha}) \tag{12}$$

The value of 0.38 nm for σ_{RR} was chosen after several values were assumed in the solubility calculations. **Figure 4** shows the excess quantity of nitrogen solubility, $\ln \kappa(L)$, defined by

$$\ln \kappa(L) = \ln L_{R,\text{mix}} - \sum_{\alpha} \Phi_{\alpha} \ln L_{R,\alpha} \tag{13}$$

The keys are the experimental data points, and the solid lines are the calculated values; they are predictions in the sense that no adjustable parameters are used in the calculation of gas solubilities in mixed solvents. The filled circles show the experimental points for cyclohexane + 1-hexane mixtures, which deviate from the calculated line (numbered 2). It is

Table 3. Force constants of pure liquids determined from v^l and P^s at 25°C

|	σ [nm]	ε/k [K]
Cyclohexane	0.5464	641.9
Benzene	0.5134	654.4
1-Hexane	0.5766	605.8
CCl₄	0.5258	639.7

Table 4. Binary constant k_{AB} and l_{AB} determined from a best fit to P and v^E at 25°C

System	k_{AB}	l_{AB}	Data source P	Data source v^E
Cyclohexane (A) + Benzene (B)	0.02434	0.00160	13)	23)
Cyclohexane (A) + 1-Hexane (B)	0.00308	0.00158	*	18)
Cyclohexane (A) + CCl₄ (B)	0.00623	0.00042	*	7)
Benzene (A) + CCl₄ (B)	0.00612	−0.00069	*	9)

* Present work.
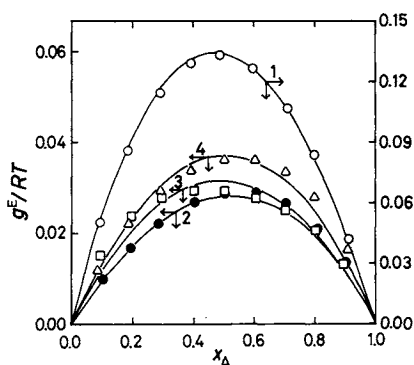
Fig. 2. Excess Gibbs energy for binary mixtures at 25°C: 1) cyclohexane (A) + benzene (B) (○); 2) cyclohexane (A) + 1-hexane (B) (●); 3) cyclohexane (A) + CCl₄ (B) (□); 4) benzene (A) + CCl₄ (B) (△).
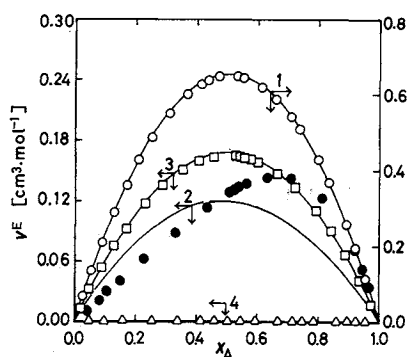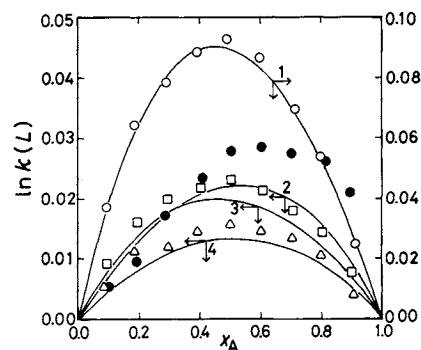
Fig. 3. Excess molar volume for binary mixtures at 25°C. Number and keys are the same as in Fig. 2.

interesting to see the same trends in the two excess quantities v^E and $\ln \kappa(L)$ as shown in Figs. 3 and 4.

Concluding Remarks

The one-fluid vdW model perturbed from the hard-

Fig. 4. Excess quantity of nitrogen solubility for binary mixtures at 25°C. Number and keys are the same as in Fig. 2.

sphere reference fluid can represent fairly well the excess quantities g^E, v^E and $\ln \kappa(L)$ for three binary mixtures formed by benzene, cyclohexane and carbon tetrachloride; all three are relatively globular molecules. Disagreement between the theory and the experiments for mixtures of cyclohexane and 1-hexane may be attributed to the difference in shape of 1-hexane, a rod-like molecule.

Nomenclature

C	= concentration	[mol·m⁻³]
f	= fugacity	[Pa]
H	= Henry's constant	[Pa]
k	= Boltzmann constant	[J·K⁻¹]
$k_{\alpha\beta}$	= binary energy parameter	[—]
L	= Ostwald coefficient	[—]
$l_{\alpha\beta}$	= binary size parameter	[—]
P	= total pressure	[Pa]
P^s	= vapor pressure of pure liquid	[Pa]
R	= gas constant	[J·mol⁻¹·K⁻¹]
T	= temperature	[K]
v	= molar volume	[m³·mol⁻¹]
x	= mole fraction	[—]
Z	= compressibility factor	[—]
γ	= activity coefficient	[—]
ε	= potential well parameter	[J]
$\kappa(L)$	= excess quantity of gas solubility	[—]
Λ	= thermal de Broglie wavelength	[m]
μ	= chemical potential	[J]
ξ	= packing density	[—]
ρ	= number density	[m⁻³]
σ	= collision diameter	[m]
Φ	= volume fraction	[—]

⟨Subscripts⟩

A, B	= solvent component A or B
R	= gas component
R, α	= R in pure liquid α
R, mix	= R in mixed solvent
αβ	= pair of α − β

⟨Superscripts⟩

E	= excess quantity
hs	= hard sphere
g	= gas phase
l	= liquid phase

Literature Cited

1) Bissell, T. G. and A. G. Williamson: *J. Chem. Thermodyn.*, **7**, 131 (1975).
2) Carnahan, N. F. and K. E. Starling: *J. Chem. Phys.*, **51**, 635 (1969).
3) Gjaldbaek, J. C. and J. H. Hildebrand: *J. Am. Chem., Soc.*, **71**, 3147 (1949).
4) Hansen, J. P. and I. R. McDonald: "Theory of Simple Liquids," Academic Press, London (1976).
5) Horiuti, J.: *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **17**, 125 (1931).
6) Katayama, T. and T. Nitta: *J. Chem. Eng. Data*, **21**, 194 (1976).
7) Kiyohara, O. and G. C. Benson: *J. Chem. Thermodyn.*, **9**, 807 (1977).
8) Leland, T. W., J. S. Rowlinson and G. A. Sather: *Trans. Faraday Soc.*, **64**, 1447 (1968).
9) Levien, B. J. and K. N. Marsh: *J. Chem. Thermodyn.*, **2**, 227 (1970).
10) Li, I. P.-C., B. C.-Y. Lu and E. C. Chen: *J. Chem. Eng. Data*, **18**, 305 (1973).
11) Markuzin, N. P., V. V. Gomerova and T. M. Lesteva: *J. Appl. Chem. USSR*, **39**, 1878 (1966).
12) Martin, M. L. and J. C. Youings: *Austr. J. Chem.*, **33**, 2133 (1980).
13) Nitta, T., T. Akimoto, A. Matsui and T. Katayama: *J. Chem. Eng. Japan*, **16**, 352 (1983).
14) Nitta, T., J. Fujio and T. Katayama: *J. Chem. Eng. Data*, **23**, 157 (1978).
15) Nitta, T., Y. Nakamura, H. Ariyasu and T. Katayama: *J. Chem. Eng. Japan*, **13**, 97 (1980).
16) Nitta, T., A. Tatsuishi and T. Katayama: *J. Chem. Eng. Japan*, **6**, 475 (1973).
17) O'Connell, J. P. and J. M. Prausnitz: *Ind. Eng. Chem. Process Des. Develop.*, **6**, 245 (1967).
18) Ott, J. B., K. N. Marsh and R. H. Stokes: *J. Chem. Thermodyn.*, **12**, 1139 (1980).
19) Prausnitz, J. M.: "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Englewood Cliffs, N. J. (1969).
20) Reed, T. M. and K. E. Gubbins: "Applied Statistical Mechanics," McGraw-Hill, New York (1973).
21) Riddick, J. A. and W. B. Bunger: "Organic Solvents, Physical Properties and Methods of Purification," 3rd ed., John Wiley & Sons (1970).
22) Rowlinson, J. S. and F. L. Swinton: "Liquids and Liquid Mixtures," 3rd ed., Butterworth (1982).
23) Stokes, R. H., B. J. Levien and K. N. Marsh: *J. Chem. Thermodyn.*, **2**, 43 (1970).
24) Tokunaga, J.: *J. Chem. Eng. Japan*, **8**, 7 (1975).
25) Wolf, H. and A. Shadiakhy: *Fluid Phase Equilibria*, **7**, 309 (1981).