CALCULATION OF HENRY'S CONSTANT OF GASES IN HYDROCARBON SOLVENT BY REGULAR SOLUTION THEORY

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The regular solution theory was applied to predict and correlate Henry's constants for hydrogen, nitrogen, methane, ethane, and propane in hydrocarbon solvents. As the system temperature is above the critical temperature of the solute, the liquid properties of the supercritical component are hypothetical. In the present paper, a new method is proposed to estimate such hypothetical liquid properties.

The calculated results represent Henry's constants fairly well over a wide range of temperature, though a slight deviation remained in the region of very low temperatures and in the region near the critical temperature of the solvent. Thus, it was ascertained that the regular solution theory was applicable to predict and correlate Henry's constants for nonpolar molecules. The present estimation for hypothetical liquid properties is considered to be adequate for nonpolar molecules.

Introduction

Henry's constant is important both for the theoretical understanding of dilute liquid solutions and the design of industrial equipment for separation processes. Many proposals based on thermodynamics^{6,16,17,22,28,30} or statistical mechanics^{13,14,19,20,25,29} have been made for the prediction of Henry's constant of a solute gas in a liquid solvent. Most of these proposals, however, are mainly of theoretical interest and are not practical for engineering purposes. Some^{16,19,20}, for example, are restricted to specific systems in their application and others^{6,13,25} require numerous empirical parameters to calculate Henry's constant over a wide range of temperature.

Henry's constant has the following temperature dependency according to the nature of solute and solvent. When the system temperature is not much in excess of the critical temperature of the solute, Henry's constant increases with rising temperature. However, when the system temperature is very much above the critical temperature of the solute, Henry's constant falls with rising temperature. For particular systems, Henry's constant goes through a maximum. It is desirable for practical purposes to

predict this behavior without using numerous empirical parameters.

In the present study, the regular solution theory⁸⁻¹⁰ was applied to predict Henry's constants for hydrogen, nitrogen, methane, ethane, and propane in hydrocarbon solvents, over a wide range of temperature. Because the liquid properties of the solutes become hypothetical when the system temperature is above their critical temperatures, we have proposed below a new method to estimate the hypothetical liquid properties of the supercritical components.

Proposed Model for Calculation of Henry's Constant in a Binary System

Henry's constant of solute 1 in solvent 2 is thermodynamically defined by^{21,23,24}:

$$H_{1,2} = \gamma_1^\infty f_1^{OL} \quad (1)$$

where γ_1^∞ is the infinite dilution activity coefficient and f_1^{OL} denotes the hypothetical pure liquid fugacity of the solute at a reference pressure. Experimentally, Henry's constant is always found at the saturation pressure of the solvent and it is sometimes converted to zero pressure for convenience^{23,24}. Therefore, zero pressure was adopted as the reference pressure and the infinite dilution activity coefficient was assumed to be given by the regular-solution equation²¹. Then, Eq. (1) becomes

$$\ln H_{1,2}^{(P_0)} = V_1^{OL}(\delta_1 - \delta_2)^2/RT + \ln f_1^{OL(P_0)} \quad (2)$$

where V_1^{OL} and δ_1 are respectively the pure liquid

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Table 1 Comparison of observed and calculated coordination numbers in liquid for argon and methane

T[°K]	Ar		T[°K]	CH ₄	
	s^{OL} [—] calc.	obs. ¹²⁾		s^{OL} [—] calc.	obs. ¹⁸⁾
84.4	10.4	10.2~10.9	96	10.4	11.4
126.7	8.1	5.9~6.2	121	9.5	11.1
149.3	5.3	~6	168	7.6	8.8
			186	5.6	7.2

molar volume and the solubility parameter of the solute. The liquid properties of the solute become hypothetical because the solute component cannot exist in a pure liquid state. These hypothetical liquid properties, such as V_1^{OL} , δ_1 , and f_1^{OL} , were estimated as described in the following sections.

i) Hypothetical liquid molar volume

The hypothetical liquid molar volume, V_1^{OL} , was obtained by extrapolation of a generalized function relating reduced volume and reduced temperature proposed in a previous paper²⁶⁾. The results calculated by using this V_1^{OL} gave values for Henry's constant larger than those found experimentally. Zellner *et al.*³¹⁾ have also presented a liquid molar volume-temperature equation which can be used in the region of temperatures exceeding the critical temperature. However, the value of V_1^{OL} calculated from the equation of Zellner *et al.* was also found to be unsuitable for the calculation of Henry's constant, because the value of V_1^{OL} extrapolated was too large. It seems that these correlations of V_1^{OL} cannot be extrapolated far above the critical temperature of the solute. In the present study, V_1^{OL} was estimated on the basis of the concept of free volume.

It was assumed that the free volume of the solvent was proportional to its liquid molar volume in the pure state and that that of the solute was proportional to its hypothetical liquid molar volume²⁷⁾,

$$V_i^f = \alpha V_i^{OL} \quad \begin{cases} i=1 \text{ for solute} \\ i=2 \text{ for solvent} \end{cases} \quad (3)$$

where α was assumed to be a universal constant. Further, both the free volume of the solute and of the solvent in a solution was considered to be equal to that in the pure liquid state, because the volume change in mixing was assumed to be negligible. Accordingly, V_i^f can be evaluated by:

$$V_i^f \cong V_i^{OL,f} = V_i^{OL} - V_i^0 \quad (4)$$

where V_i^0 is the solid molar volume for the i -th component. By introducing Eq. (4) into Eq. (3), V_1^{OL} is given as follows:

$$V_1^{OL} = V_2^{OL}(V_1^0/V_2^0) \quad (5)$$

The value of V_1^{OL} calculated by Eq. (5) was used in Eq. (2). As seen from Eq. (5), V_1^{OL} depends not only on the system temperature but also on the kind of

solvent. This is considered to be due to the fact that the supercritical component is condensable only in the presence of a solvent. Since the solid molar volume data were not always available, V^0 was replaced by the solid molar volume at melting point, which was obtained by multiplying the liquid molar volume at melting point by 0.89. This multiplier was determined here from the molar volume data of liquid and solid at melting point compiled in the literature¹⁵⁾. The liquid molar volume at melting point was estimated from Francis' equation^{4,5)}.

ii) Hypothetical liquid fugacity

The hypothetical liquid fugacity converted to zero pressure was estimated by the following equation as derived in the previous paper²⁶⁾.

$$f_1^{OL(P_0)} = f_1^{OL(P_1)} \exp(-V_1^{OL}P_1/RT) \quad (6)$$

where $f_1^{OL(P_1)}$ and P_1 are respectively the fugacity and the pressure of solute at the system temperature, T and at the hypothetical liquid molar volume, V_1^{OL} . The values for $f_1^{OL(P_1)}$ and P_1 were calculated by using the Benedict-Webb-Rubin equation²⁾.

iii) Solubility parameter

The solubility parameter⁸⁻¹⁰⁾ is usually defined as:

$$\delta = \sqrt{U^{OL}/V^{OL}} \quad (7)$$

If the random mixing of molecules is assumed, the internal energy of the molecules in liquid, U^{OL} , can be represented by the following equation:

$$U^{OL} = (1/2)s^{OL}\epsilon N_0 \quad (8)$$

where s^{OL} stands for the coordination number of liquid, ϵ is the pair potential energy, and N_0 is Avogadro's number. According to the hole theory^{1,3)}, it is assumed that the coordination number in liquid decreases with an increase in the number of holes. That is, s^{OL} can be related to the hole fraction, θ , as follows:

$$s^{OL} = (1-\theta)s^0 \quad (9)$$

where the hole fraction is given by³⁾:

$$\theta = (V^{OL} - V^0)/V^{OL} \quad (10)$$

and s^0 is the coordination number in the solid depending on the geometrical structure of the lattice. The geometrical structure of the molecules in solid state was assumed to be a face-centered cubic lattice, and s^0 was set as 12. To test the adequacy of Eq. (9) for the coordination number of liquid, the calculated and experimental values of s^{OL} for methane and argon were compared as in Table 1. Relatively good agreement was found between calculated and experimental values.

From Eqs. (7), (8), (9), and (10), the solubility parameter can be obtained as:

$$\delta = \sqrt{6V^0\epsilon N_0/V^{OL}} \quad (11)$$

This equation was applied to both supercritical com-

Table 2 Pair potential energy parameters determined by solubility parameter

	$(\epsilon/k)_{T_r=0.7} [^\circ\text{K}]$
H ₂	19.45
N ₂	117.8
CH ₄	170.2
C ₂ H ₄	305.8
C ₂ H ₆	336.4
C ₃ H ₆	459.2
C ₃ H ₈	473.0
<i>n</i> -C ₄ H ₁₀	548.6

ponents and solvents.

The potential parameter of molecules, ϵ/k , has usually been obtained from the viscosity data or the second virial coefficient data¹¹. Values of ϵ/k determined from the viscosity and the second virial coefficient do not always agree. Even though the difference is small, it greatly affects the value of Henry's constant calculated from Eq. (2). Thus, the value of ϵ/k should be newly determined. The solubility parameter obtained from Eq. (11) was fitted to the experimental value given by the following equation²⁶:

$$\delta = \sqrt{\left(\frac{\Delta H/RT}{Z^V - Z^L} - 1\right)(Z^V/Z^L)P_s} \quad (12)$$

where ΔH is the heat of vaporization, Z^V and Z^L denote the saturated vapor and liquid compressibility factors respectively, and P_s is the saturated vapor pressure. The pair potential energy parameter could be determined from Eqs. (11) and (12). In the present paper, the value of ϵ/k at a reduced temperature of 0.7 was adopted as a representative value. Eq. (11) with $(\epsilon/k)_{T_r=0.7}$ could well reproduce the experimental solubility parameter from low temperatures to temperatures near the critical region. For examples, the solubility parameters for methane, ethane, and propane are shown in Fig. 1. The values of $(\epsilon/k)_{T_r=0.7}$ for the components studied here are listed in Table 2.

Results and Discussion

In Figs. 2 to 5, the comparisons of calculated and experimental Henry's constants are shown for nitrogen, methane, ethane, and propane in hydrocarbon solvents. From the proposed calculation, Henry's constants for methane, ethane, and propane were predicted accurately, as shown in Figs. 3 to 5. There was, however, a slight discrepancy between calculated and experimental Henry's constants for nitrogen, as shown in Fig. 2. The calculated results, as shown in these figures, were seen to represent the behavior of Henry's constants over a wide range of temperature.

Nakahara *et al.*¹⁶ have also presented a prediction method for Henry's constants based on the dissolution model of gas in liquid. They have adapted the following equation to estimate the hypothetical liquid molar volume:

$$V_1^{OL} = V_2^{OL} - (V_2^0 - V_1^0) \quad (13)$$

where the free volume of solute is assumed to be equal to that of solvent²⁷. As to the propane-*n*-

Fig. 1 Solubility parameters for methane, ethane, and propane

Fig. 2 Comparison of experimental and calculated Henry's constants for nitrogen in methane, ethane, and *n*-butane

Fig. 3 Comparison of experimental and calculated Henry's constants for methane in ethane, propane, and *n*-butane

Fig. 4 Comparison of experimental and calculated Henry's constants for ethane in propane and *n*-butane

Fig. 5 Comparison of experimental and calculated Henry's constants for propane in *n*-butane

Fig. 6 Comparison of experimental and calculated Henry's constants for hydrogen in methane, ethane, and propane

butane system, however, the results calculated by using Eq. (13) instead of Eq. (5) were found to be slightly less than those given by Eq. (5), as shown in Fig. 5.

In the case of a system containing hydrogen, the calculated Henry's constants deviated largely from the experiments when the value of ϵ/k listed in Table 2 was used. The reason for this deviation may be due to the quantum effect for hydrogen. For quantum gases, the potential energy parameter, ϵ/k , depends on temperature as shown by Gunn *et*

Fig. 7 Comparison of experimental and calculated Henry's constants for hydrogen in *n*-butane

Fig. 8 Comparison of experimental and calculated Henry's constants for hydrogen in ethylene and propylene

*al.*⁷⁾. It has been proposed that ϵ/k for hydrogen can be represented by^{7,24)}:

$$\epsilon/k = C_1 / (1 + C_2/T) \quad (14)$$

where C_1 and C_2 are constants. C_1 refers to the potential parameter at the limit of high temperature. In this study, both C_1 and C_2 were determined from experimental Henry's constants. In this case, the value of ϵ/k calculated from Eq. (14) at a reduced temperature of 0.7 was made to coincide with the value listed in Table 2. Values of C_1 and C_2 were finally found to be 36.5 and 20.4, respectively.

Calculated and observed Henry's constants for hydrogen in hydrocarbon solvents are shown in Figs. 6 to 8, together with those calculated from other prediction¹⁰⁾ and correlation methods¹³⁾. Although the present results show a slight discrepancy in the low-temperature region, the agreement found between experimental results and calculations was relatively good.

Conclusion

The regular solution theory was successfully applied to Henry's constant for binary systems consisting of nonpolar molecules. As the system temperature was above the critical temperature of the solute, an estimation method was proposed to calculate hypothetical liquid properties, such as molar volume, solubility parameter, and fugacity of the solute. Thus, it was possible to predict the temperature dependency of Henry's constant.

Nomenclature

C_1, C_2	= constants in Eq. (14)	[°K]
f	= fugacity	[atm]
H	= Henry's constant	[atm]
ΔH	= heat of vaporization	[l · atm/g-mole]
k	= Boltzmann's constant	[erg/°K]
N_0	= Avogadro's number	[molecules/g-mole]
P	= pressure	[atm]
R	= gas constant, 0.08205	[l · atm/g-mole · °K]
s	= coordination number	[—]
T	= temperature	[°K]
U	= internal energy	[l · atm/g-mole]
V	= molar volume	[l/g-mole]
Z	= compressibility factor	[—]
α	= proportional constant in Eq. (3)	[—]
γ	= activity coefficient	[—]
δ	= solubility parameter	[atm ^{1/2}]
ϵ	= pair potential energy	[erg]
θ	= hole fraction	[—]

<Subscripts and Superscripts>

0	= solid state
1	= solute
2	= solvent
f	= free volume
i	= component i
L	= liquid phase
OL	= pure liquid
P_0	= zero pressure
r	= reduced value
s	= saturation
V	= vapor phase
∞	= infinite dilution

Literature Cited

- 1) Barker, J. A.: "Lattice Theories of The Liquid State", Pergamon Press (1963).
- 2) Benedict, M., G. B. Webb and L. C. Rubin: *Chem. Eng. Progr.*, **47**, 419, 449 (1951).

- 3) Eyring, H. and M. S. Jhon: "Significant Liquid Structures", John Wiley and Sons (1969).
- 4) Francis, A. W.: *Ind. Eng. Chem.*, **49**, 1779 (1957).
- 5) Francis, A. W.: *Chem. Eng. Sci.*, **10**, 37 (1959).
- 6) Funk, E. W. and J. M. Prausnitz: *Ind. Eng. Chem., Process Design and Develop.*, **10**, 405 (1971).
- 7) Gunn, R. D., P. L. Chueh and J. M. Prausnitz: *AIChE J.*, **12**, 937 (1966).
- 8) Hildebrand, J. H. and R. L. Scott: "Regular Solutions", Prentice-Hall (1962).
- 9) Hildebrand, J. H. and R. L. Scott: "The Solubility of Nonelectrolytes", Dover Publications (1964).
- 10) Hildebrand, J. H., J. M. Prausnitz and R. L. Scott: "Regular and Related Solutions", Van Nostrand Reinhold (1970).
- 11) Hirschfelder, J. O., C. F. Curtiss and R. B. Bird: "Molecular Theory of Gases and Liquids", John Wiley and Sons (1967).
- 12) Kruh, R. F.: *Chem. Revs.*, **62**, 319 (1962).
- 13) Miller, R. C. and J. M. Prausnitz: *Ind. Eng. Chem., Fundamentals*, **8**, 449 (1969).
- 14) Miller, R. C.: *J. Chem. Phys.*, **55**, 1613 (1971).
- 15) Moelwyn-Hughes, E. A.: "Physical Chemistry", 2nd Ed., (1961) (translated into Japanese by Y. Miyahara, Baifukan (1967)).
- 16) Nakahara, T. and M. Hirata: *J. Chem. Eng. Japan*, **2**, 137 (1969).
- 17) Orentlicher, M. and J. M. Prausnitz: *Chem. Eng. Sci.*, **19**, 775 (1964).
- 18) Petz, J. I.: *J. Chem. Phys.*, **43**, 2238 (1965).
- 19) Pierotti, R. A.: *J. Phys. Chem.*, **67**, 1840 (1963).
- 20) Pierotti, R. A.: *ibid.*, **69**, 281 (1965).
- 21) Prausnitz, J. M.: "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall (1969).
- 22) Prausnitz, J. M. and F. H. Shair: *AIChE J.*, **7**, 682 (1961).
- 23) Prausnitz, J. M., C. A. Eckert, R. V. Orye and J. P. O'Connell: "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Prentice-Hall (1967).
- 24) Prausnitz, J. M. and P. L. Chueh: "Computer Calculations for High-Pressure Vapor-Liquid Equilibria", Prentice-Hall (1968).
- 25) Preston, G. T. and J. M. Prausnitz: *Ind. Eng. Chem., Fundamentals*, **10**, 389 (1971).
- 26) Sagara, H., Y. Yokobori and S. Saito: *J. Chem. Eng. Japan*, **7**, 8 (1974).
- 27) Shinoda, K.: "Yoeki to Yokaido (Solution and Solubility)", (in Japanese), Maruzen (1966).
- 28) Singh, S. P. and P. K. Mukhopadhyay: *AIChE J.*, **18**, 1171 (1972).
- 29) Snider, N. S. and T. M. Herrington: *J. Chem. Phys.*, **47**, 2248 (1967).
- 30) Yen, L. C. and J. J. McKetta: *AIChE J.*, **8**, 501 (1962).
- 31) Zellner, M. G., L. C. Claitor and J. M. Prausnitz: *Ind. Eng. Chem., Fundamentals*, **9**, 549 (1970).