Correlation for Solubilities of Water in Compressed Nonpolar Gases

Hironori MIYAHARA*, Satoru SUZUTA* and Yasuhiko ARAI*

By using a perturbed-hard-sphere equation of state, a useful procedure has been proposed for estimating the equilibrium moisture content in compressed gases resulting from some processes.

The solubility of water, expressed in mole fraction, in compressed nitrogen, argon, carbon dioxide, methane, and ethane can be well correlated in the range from 25° to 100°C and up to 100 atm by introducing two characteristic binary constants into the mixing rules for a_m and c_m .

1. Introduction

In recent years, much attention has been paid to the correlation of water solubility in compressed nonpolar gases. The solubility information is very important to evaluate the equilibrium moisture content in compressed gases, such as inert gases and light hydrocarbon gases resulting from some processes.

De Santis *et al.*¹⁾ have shown that the Redlich-Kwong equation of state is useful to correlate the solubility of water in compressed *n*-butane gas by adjusting the constant a reflecting the intermolecular attraction. De Santis and Marrelli²⁾ have adopted a perturbed-hard-sphere equation of state (the repulsion term is given by Carnahan and Starling's expression³⁾ and the attraction term is approximated by that of the Redlich-Kwong equation of state) to correlate the solubility of water in compressed air. More recently, Luks *et al.*⁴⁾ have found that the modified Redlich-Kwong equation of state of Heidemann and Prausnitz⁵⁾ is useful for correlating the water content of combustion gases saturated with moisture.

In a previous paper⁶⁾, the perturbed-hard-sphere equation of state proposed by Nakamura *et al.*⁷⁾ has been found to be successful to represent both the p - v - T relations and the second and third virial coefficients for water vapor. In the present study, the equation of state is applied to correlate the solubility of water in several compressed nonpolar gases.

2. Equation of State

The perturbed-hard-sphere equation of state proposed by Nakamura *et al.*⁷⁾ has the following form:

Received Aug. 31, 1981.

* Department of Chemical Engineering, Kyushu University (6-10-1, Hakozaki, Higashi-ku, Fukuoka 812)

$$z = \frac{pv}{RT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} - \frac{a}{RT(v + c)} \quad (1)$$

where

$$\xi = \frac{b}{4v} \quad (2)$$

Parameter b reflects the hard-core size of the molecule and parameter a reflects the strength of attractive forces. Parameter c is empirically introduced to successfully represent the p - v - T relations of strongly polar components. In a previous study⁶⁾, all parameters, a , b , and c , have been found dependent on temperature to accurately represent both the p - v - T relations and the virial coefficients of water vapor. The parameters a , b , and c expressed in the reduced forms are as follows:

$$\frac{a}{RT_c v_c} = \sum_{i=0}^3 a^{(i)} T_r^{-i} \quad (3)$$

$$\frac{b}{v_c} = \sum_{i=0}^4 b^{(i)} T_r^i \quad (4)$$

$$\frac{c}{v_c} = \sum_{i=0}^6 c^{(i)} T_r^{-i} \quad (5)$$

The coefficients in Eqs. (3) to (5) for water vapor, presented in **Table 1**, have been determined in a previous study by use of the p - v - T relations and the second and third virial coefficients. These coefficients are found here to be very successful in calculating the molar volume, fugacity coefficients, and enthalpies of water vapor, including saturated regions, by comparing the calculated results with experimental data⁸⁾.

The values of coefficients $a^{(i)}$, $b^{(i)}$, and $c^{(i)}$ of several nonpolar gases have been determined and they are shown in **Table 1**. In the present determination, the p - v - T data^{9)~11)} are firstly used. That is, the deviations between calculated and experimental values for $(z-1)v$ have been minimized. Then, the second and third virial coefficient data¹²⁾ are adopted to fit more precisely

Table 1 Parameters for a Perturbed-Hard-Sphere Equation of State

Range	Nitrogen	Argon	Carbon Dioxide	Methane	Ethane	Water
	166-450K up to 100 atm	130-600K up to 5,000 atm	223-423K up to 200 atm	273-373K up to 400 atm	240-500K up to 700 atm	300-870K up to 290 atm
$a^{(0)}$	-2.5015486	2.3859247	0.65108680	1.3726333	0.95659009	1.966
$a^{(1)}$	31.60246	-3.9871658	0.78109055	0.27564089	0.23236945	-1.684
$a^{(2)}$	-91.091705	5.3221259	0.32887296	-0.26691900	0.50280264	0.8393
$a^{(3)}$	87.313229	-2.0173053	0	0	0	0.6166
$b^{(0)}$	5.4596275	0.85156221	0.51562805	-0.18641436	1.0850499	0.4946
$b^{(1)}$	-6.8822815	-0.43356124	0.13875773	0.70192292	-0.83272574	-0.07109
$b^{(2)}$	3.5163760	0.18390608	-0.14895046	-0.17216026	0.26287190	0.01738
$b^{(3)}$	-0.79404039	-0.023563303	0	0	0	0
$b^{(4)}$	0.066921382	0	0	0	0	0
$c^{(0)}$	-3.2315364	0.0064893423	0.10154717	1.6055528	-0.0994264	61.089
$c^{(1)}$	39.383658	0.043762737	0.34050308	-8.8322325	0.64133174	-376.372
$c^{(2)}$	-171.10222	-0.071726863	-0.20892004	15.300526	-0.38075839	933.266
$c^{(3)}$	328.22313	0.034354091	0	-8.1621628	0	-1187.312
$c^{(4)}$	-234.60092	0	0	0	0	814.760
$c^{(5)}$	0	0	0	0	0	-283.650
$c^{(6)}$	0	0	0	0	0	38.268
T_c	125.95	151.0	304.2	190.65	305.4	647.3
v_c	90.07	75.2	94.0	99.16	148.0	57.1

in the low density region.

In order to apply Eq. (1) to binary mixtures, the following mixing rules are adopted.

$a_m = y_1^2 a_1 + y_2^2 a_2 + 2 y_1 y_2 (1 - k_{12}) (a_1 a_2)^{1/2}$ (6)

$b_m = y_1 b_1 + y_2 b_2$ (7)

$c_m = y_1^2 c_1 + y_2^2 c_2 + y_1 y_2 (1 - l_{12}) (c_1 + c_2)$ (8)

where k_{12} and l_{12} are the characteristic binary constants. The mixing rule for c_m is proposed here to make it applicable even though the values of parameters c_1 and c_2 are opposite in sign.

3. Thermodynamics of Water Solubility

The relation of vapor-liquid equilibrium for water is expressed by

$$\phi_2^V y_2 p = \gamma_2^L x_2 p_2^\circ \phi_2^{\circ V} \exp \left[\frac{v_2^{\circ L} (p - p_2^\circ)}{RT} \right]$$
 (9)

where p_2° and $v_2^{\circ L}$ are, respectively, the saturation vapor pressure and the saturated liquid molar volume of pure water at a given temperature. They can readily be calculated from the empirical equations of Prausnitz *et al.*¹³⁾. The solubility of any gas in liquid water is assumed to be negligible when compared to unity; *i.e.* $x_2=1$. Accordingly, the liquid phase activity coefficient of water γ_2^L can be taken to be unity without introducing an appreciable error. This assumption may not be suitable for the carbon dioxide-water system. However, this crude approximation is adopted for all gases to develop a practical estimating procedure which in many cases may be sufficiently accurate for engineering purposes. The fugacity coefficient ϕ_2^V can be derived as follows from Eqs. (1) and (6) to (8) according to the thermodynamic standard procedure.

$$\begin{aligned} \ln \phi_2^V = & \frac{4\xi - 3\xi^2}{(1 - \xi)^2} + \frac{b_2}{b_m} \left[\frac{4\xi - 2\xi^2}{(1 - \xi)^3} \right] + \frac{a_m}{RT(v^V + c_m)} \\ & + \frac{a_m + 2[y_1(1 - k_{12})(a_1 a_2)^{1/2} + y_2 a_2]}{c_m RT} \\ & \times \ln \left(\frac{v^V}{v^V + c_m} \right) \\ & - \frac{a_m [y_1(1 - l_{12})(c_1 + c_2) + 2y_2 c_2]}{RT} \\ & \times \left[\frac{1}{c_m^2} \ln \left(\frac{v^V}{v^V + c_m} \right) + \frac{1}{c_m(v^V + c_m)} \right] - \ln z \end{aligned}$$
 (10)

The fugacity coefficient of saturated vapor for pure water $\phi_2^{\circ V}$ can readily be obtained by letting $y_2=1$.

4. Correlation of Water Solubility

The values of two characteristic binary constants k_{12} and l_{12} are necessary to calculate the water solubility expressed in mole fraction y_2 by use of Eq. (9). From Eqs. (1), (6) and (7) the second virial cross coefficient B_{12} can be derived as

Table 2 Characteristic Binary Constants (25-100°C)

Binary System (1)-(2)	k_{12}	l_{12}	Max. Press. (atm)	Error (%)*	
				Max.	Avg.
Nitrogen-Water	0.648	0.835	100	10.1	3.1
Argon-Water	0.687	1.079	92	12.1	1.6
Carbon Dioxide-Water	0.455	0.992	51	6.6	3.2
Methane-Water	0.657	1.040	92	3.0	1.3
Ethane-Water	0.638	1.056	36	3.4	1.8

* Error(%)=100 × | $y_2^{\text{exp}} - y_2^{\text{calc}}$ | / y_2^{exp} , Avg.= $\frac{1}{N} \sum_{i=1}^N$ (Error)_i;
N=No. of data points

$$B_{12} = \frac{1}{2} \left[(b_1 + b_2) - \frac{2(1 - k_{12})(a_1 a_2)^{1/2}}{RT} \right] \quad (11)$$

Therefore, the values of k_{12} can be estimated when experimental data for B_{12} are available. On the basis of the literature values^{14,15}, the values of k_{12} for nonpolar gas-water binary mixtures have been estimated. The values of l_{12} , on the other hand, have been determined here to give best fit to experimental y_2 . The values of k_{12} and l_{12} thus obtained are presented in **Table 2**. The procedure used for calculating y_2 is shown in **Fig. 1**. Typical representations for comparison between calculated and experimental solubilities of water in compressed gases are illustrated in **Figs. 2** to **4**. As shown in these figures, a good agreement is shown for wide ranges of temperatures and pressures.

Fig. 1 Calculation Procedure for Water Solubility in Compressed Gases

Fig. 2 Solubilities of Water in Compressed Methane

Fig. 3 Solubilities of Water in Compressed Ethane

Fig. 4 Solubilities of Water in Compressed Carbon Dioxide

5. Conclusion

The perturbed-hard-sphere equation of state has been found to be successful to correlate the solubility of water in compressed gases such as nitrogen, argon, carbon dioxide, methane, and ethane in the range from 25° to 100°C and up to 100 atm. In order to obtain a good correlation, two characteristic binary constants are required for the mixing rules for a_m and c_m .

Nomenclature

- a, b, c = coefficients in Eq. (1)
- $a^{(i)}, b^{(i)}, c^{(i)}$ = coefficients in Eqs. (3)–(5)
- B_{12} = second virial cross coefficient (cm³/mol)
- k_{12} = characteristic binary constant (—)
- l_{12} = characteristic binary constant (—)
- p = total pressure (atm)
- p_2° = saturation vapor pressure of pure water (atm)
- R = gas constant (cm³·atm/mol·K)
- T = absolute temperature (K)
- v = molar volume (cm³/mol)
- x = liquid phase mole fraction (—)
- y_1 = vapor phase mole fraction of nonpolar gas (—)

y_2 =vapor phase mole fraction of water (=water solubility in compressed gas)	(—)
z =compressibility factor ($=pv/RT$)	(—)
γ =activity coefficient	(—)
ξ =reduced density ($=b/4v$)	(—)
ϕ =fugacity coefficient	(—)

Superscripts

L =liquid phase
V =vapor phase
$\circ$ =pure state

Subscripts

c =critical property
m =mixture
r =reduced property ($T_r = T/T_c$)
1=nonpolar gas
2=water

References

- De Santis, R., Breedveld, G. J. F., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Dev.*, **13**, 374 (1974).
- De Santis, R., Marrelli, L., *Canadian J. Chem. Eng.*, **55**, 712 (1977).
- Carnahan, N. F., Starling, K. E., *J. Chem. Phys.*, **51**, 635 (1969).
- Luks, K. D., Kohn, J. P., Banchemo, J. T., *Ind. Eng. Chem. Process Des. Dev.*, **18**, 564 (1979).
- Heidemann, R. A., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Dev.*, **16**, 375 (1977).
- Nishida, N., Ohba, M., Arai, Y., *Fluid Phase Equilibria*, **4**, 303 (1980).
- Nakamura, R., Breedveld, G. J. F., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Dev.*, **15**, 557 (1976).
- Canjar, L. N., Manning, F. S., "Thermodynamic Properties and Reduced Correlation for Gases", (1967), Gulf Publ. Co., Houston Texas.
- Din, F., "Thermodynamic Functions of Gases", Vol. 1, 2, (1956), Butterworths Scient. Publ., London.
- Douslin, D. R., Harrison, R. H., Moore, R. T., McCullough, J. P., *J. Chem. Eng. Data*, **9**, 358 (1964).
- Douslin, D. R., Harrison, R. H., *J. Chem. Thermodynamics*, **5**, 491 (1973).
- Dymond, J. H., Smith, E. B., "The Virial Coefficients of Gases", (1969), Clarendon Press, Oxford.
- Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", (1967), Prentice-Hall Inc., Englewood Cliffs, N. J.
- Coan, C. R., King, A. D. Jr., *J. Am. Chem. Soc.*, **93**, 1857 (1971).
- Rigby, M., Prausnitz, J. M., *J. Phys. Chem.*, **72**, 330 (1968).

要 旨

無極性加圧気体に対する水の溶解度の相関

宮原 弘法*, 鈴田 聡*, 荒井 康彦*

加圧気体中の平衡水分含有量に関する知見は、石油化学関連プロセスにおける設計および運転にとって、きわめて重要である。一例をあげると、水分量がある程度以上になると加圧ガスとの間に気体水和物（ガスハイドレート）を形成し、安定した供給や輸送が困難となることが知られている。一方、極性の著しく強い水分子と無極性の不活性気体や低級炭化水素気体からなる混合物の特性を良好に表現する状態方程式の開発の観点からも、興味を集めている^{1), 2), 4), 5)}。

温度 T 、全圧 p における加圧気体中の水分量をモル分率 y_2 で表現すると、熱力学関係式より次式で与えられる。

$$y_2 = \frac{\gamma_2^L x_2 p_2^\circ \phi_2^{\circ V}}{\phi_2^V p} \exp \left[\frac{v_2^{\circ L} (p - p_2^\circ)}{RT} \right]$$

ここで温度 T における純水の飽和液体モル体積 $v_2^{\circ L}$ および飽和蒸気圧 p_2° は、広く用いられている実験式¹³⁾により求めることができる。いま水相に対する気体の溶解度が無視できるとすれば、水相における水のモル分率 x_2 を 1 と近似でき、活量係数 γ_2^L も 1 とおくことができる。この仮定は、溶解度の比較的大きい二酸化炭素については厳密なものとはいえないが、 y_2 が満足に相関できたので、計算上の簡便さから、すべての気体について $x_2=1$ 、 $\gamma_2^L=1$ の仮定を用いた。したがって、気相中の水のフガシチー係数 ϕ_2^V および純水の気相フガシチー係数 $\phi_2^{\circ V}$ が与えられると y_2 すなわち水分量が計算できる。フガシチー係数は、適当な状態方程式より導出できるが、こ

では前報⁶⁾における次式を採用した。

$$\frac{pv}{RT} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} - \frac{a}{RT(v + c)}$$

ここで、 $\xi = b/(4v)$ であり、3 個のパラメーター a 、 b 、 c を含む剛体球流体³⁾を基準にした摂動型状態方程式である。この型の状態方程式は、Nakamura ら⁷⁾の提案によるものであるが、著者らの研究⁶⁾により水蒸気の p - v - T および第 2、第 3 ビリアル係数を満足に表現し得ることが示されている。本研究では、前報⁶⁾と同様に p - v - T データ^{8)~11)}およびビリアル係数データ¹²⁾を用い、窒素、アルゴン、二酸化炭素、メタンおよびエタンのパラメーター a 、 b 、 c を温度の関数として決定し、Table 1 に示した。状態方程式を気体混合物に適用するためには、パラメーターの混合則が必要とされる（本文中、Eqs. (6)~(8) 参照）。パラメーター a 、 b については通常用いられているものを採用したが、 c については成分間で符号が異なる場合もあり、新たな混合則を用いた。フガシチー係数 ϕ_2^V および $\phi_2^{\circ V}$ を求めることにより（本文中、Eq. (10) 参照）水分量が算出されるが、必要とされる 2 個の 2 成分系特性因子のうちパラメーター a に含まれるものは交差第 2 ビリアル係数データ^{14), 15)}より決定した。パラメーター c に含まれるものは、 y_2 の計算値が実測値と最もよく合うように試行によって決定し、それぞれ Table 2 に示した。加圧気体に対する水の溶解度の計算手順を Fig. 1 に示し、計算値と実測値の比較を Figs. 2~4 に示すが、両者の一致は満足すべきものであり、工学的計算法として有用と思われる。

Keywords

Compressed nonpolar gas, Lower hydrocarbon, Solubility, Water

* 九州大学工学部化学機械工学科 (812 福岡市東区箱崎 6-10-1)