

CORRELATION OF SOLUBILITIES OF CARBON MONOXIDE, CARBON DIOXIDE, AND HYDROGEN IN PARAFFINS

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A lattice-gas model is used for calculating Henry's constants of binary mixtures of light gases in normal paraffins. The results, compared with experimental Henry's constants, have an error of around 10%. The paper shows the possibility of predicting gas solubility in normal paraffin using a binary parameter obtained in the process of correlating Henry's constants.

Introduction

Balbuena *et al.*³⁾ recently proposed a lattice-gas model for the solubility of solids in supercritical fluids. The model assumes that molecules are linear. It seems appropriate to test the model with mixtures that correspond to the linear molecules hypothesis. Normal paraffins could be considered linear molecules. In the literature there are available experimental data for the solubility of light gases in normal paraffin. Henry's constant for these systems is a thermodynamic variable for a state where a small molecule of gas is completely surrounded by the long chain hydrocarbon.

Calculations were carried out for Henry's constants of carbon monoxide, carbon dioxide and hydrogen in normal paraffins ranging from carbon twenty to carbon forty-four. A single binary parameter was chosen, denoting the interaction energy between segment *i* and segment *j* belonging respectively to the gas and normal paraffin molecules. Using the chosen parameter, calculations were performed to predict the solubility of carbon dioxide in dotriacontane and in a complex wax. In this work the results of all these calculations are presented

1. Method of Calculation

Henry's constant for solute 1 in solvent 2 is defined by

$$H_{1,2}^{Pr} = \lim_{x_1 \rightarrow 0} \frac{f_1}{x_1} \quad (1)$$

where *x* is the liquid-phase mole fraction and *f* is the fugacity. Superscript *Pr* indicates that Henry's constant is evaluated at some reference pressure taken in this work as the saturation pressure of solvent.

Using experimental data, graphs of $\ln(f/x)$ as a function of pressure at constant temperature were drawn. The fugacity was calculated from the equilibrium gas data. The intercept of the resulting straight line at the sat-

uration pressure of solvent determines an experimental Henry's constant as defined by Eq. (1)

The calculated Henry's constant was obtained by fitting the experimental gas fugacity to a calculated liquid fugacity using a lattice model³⁾. In the model the volume of the liquid phase is divided into *N* cells arranged in a lattice of coordination number *z*. Each cell of volume *V_o* can be occupied by a molecule, or by a segment of a molecule, or it can be empty. The number of cells occupied by a molecule *i* is *r_i*. The molecules interact through their segment surfaces only with their immediately adjacent neighbours. The interaction energy between segments *i* and *j* occupying nearest neighbour cells is *E_{ij}*. The number of contacts *N_{ij}* between different segments that are not part of the same molecule are quantities of significance in the model. The molecules are assumed to be linear. Using the quasichemical approximation, equations were obtained for the pressure and the chemical potential. The non-linear systems of equations were solved numerically. To simplify the calculations, the *N_{ij}* values were approximated by a Taylor series truncated after the second-degree term.

The pressure is given by³⁾

$$\frac{PV_o}{RT} = (1-z) \ln\left(\frac{N}{N_o}\right) + \frac{z}{2} \ln\left(\frac{Nz}{2N_{oo}}\right) \quad (2)$$

where subscript *o* indicates an empty cell or hole. Then *N_o* is the number of empty cells and *N_{oo}* is the number of contacts between two holes.

The chemical potential of component *i* is

$$\begin{aligned} -\frac{\mu_i}{RT} = & \ln(t_i) + (1-z)r_i \ln N_o - (1-zq_i) \ln N_i \\ & + \frac{z}{2} \left[r_i \ln\left(\frac{2N_{oo}}{z}\right) - q_i \ln\left(\frac{2N_{ii}}{z}\right) - \frac{E_{ii}q_i}{RT} \right] \\ & + zq_i \ln q_i \end{aligned} \quad (3)$$

where *t_i* is the molecular partition function and *zq_i* is the number of cells adjacent to molecule *i*. The interaction energy *E_{ij}* appears explicitly in Eq. (3). The interaction

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Table 1. Pure component parameters^{a)}

Component	r_i	E_{ij} (J mol ⁻¹)	Experimental Data
Carbon dioxide	5.87	-650	b)
Hydrogen	3.50	-405	c)
Carbon monoxide	4.83	-340	d)
Eicosane	63.01	-721 ^{e)}	f)
Tetracosane	75.21	-721 ^{e)}	f)
Octacosane	87.40	-721 ^{e)}	f)
Dotriacontane	99.60	-721 ^{e)}	f)
Hexatriacontane	111.79	-721 ^{e)}	f)
Tetratetracontane	136.17	-721 ^{e)}	f)

a) For all cases, $V_o = 5.418 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$

b) P-V-T data from reference [1]

c) P-V-T data assuming ideal gas behavior

d) P-V-T data from reference [5]

e) Value at $T = 373.25 \text{ K}$ using $E_{ij} = -469.86 - .67338T$

f) Vapor pressure data from reference [2]

Table 2. Interaction Parameters regressed from CO (1)-solvent (2) solubility data^{b)}

Solvent	T (K)	E_{12} (J mol ⁻¹)	AARD ^{a)} (%)
Eicosane	373.25	-357.8	15.44
Eicosane	473.45	-365.7	20.45
Eicosane	573.25	-344.1	21.86
Octacosane	373.45	-349.4	19.46
Octacosane	473.15	-349.6	16.21
Octacosane	573.45	-323.0	17.50
Hexatriacontane	373.15	-337.5	17.39
Hexatriacontane	473.05	-332.6	20.04
Hexatriacontane	572.95	-307.0	18.62

a) $AARD = [(1/M) \sum^M (|f_{CO}^{calc} - f_{CO}^{exp}| / f_{CO}^{exp})] 100$

b) For each solvent and each temperature the range of pressure is 1-5 MPa and at least five experimental points were fitted. Solubility data from reference [8]

energies E_{ij} and E_{ji} are also present in equations (3) and (2) in implicit form through the number of contacts (N_{ij}).

Knowing the chemical potential, the fugacity of component i is calculated with the following equation:

$$f_i = P^{ref} \exp \left\{ \frac{(\mu_i - \mu_i^{ref})}{RT} \right\} \quad (4)$$

where superscript ref indicates a reference state in which component i behaves as an ideal gas.

2. Results and Discussion

The model has three kinds of parameters: general, pure-component and binary parameters.

The values here adopted for the general parameter z and V_o are 10 and $5.418 \times 10^{-6} \text{ m}^3/\text{mol}$ respectively.

The pure-component parameters r_i and E_{ii} for each compound are shown in **Table 1**. The r_i and E_{ii} values for each gas were obtained by fitting P-V-T data. The number of cells occupied by the molecule i for the

normal paraffin was calculated by comparing the van der Waals volume of the molecule i with that of carbon dioxide. The volumes were calculated using Bondi's method⁴⁾. The energy parameter E_{ii} was calculated by fitting vapor pressure experimental data. For all the normal paraffins a single temperature-dependent segment energy parameter was used.

The binary parameter E_{ij} is the interaction energy between segments in molecule i and those in molecule j . The binary parameters for each gas-liquid system were calculated by fitting fugacity data. The experimental fugacity was calculated from equilibrium gas information. At gas-liquid equilibrium conditions the gas fugacity is equal to the liquid fugacity. The liquid fugacity was calculated using the experimental temperature, pressure and composition in the lattice model. The parameter E_{ij} was changed to minimize the difference between calculated and experimental fugacity. **Tables 2 to 4** present the values of E_{ij} for various gas-liquid systems. The average absolute relative deviation is also presented.

Table 2 shows the results of calculation for carbon monoxide in normal paraffin. The experimental fugacity was taken as the pure carbon monoxide gas fugacity, using data from reference 5.

Table 3 shows the results of calculation for carbon dioxide in normal paraffin. The experimental fugacity was obtained by the same approach as for carbon monoxide. Experimental data were collected from reference 1.

Table 4 presents the results of calculation for hydrogen. The ideal gas equation was used to obtain the experimental fugacity.

For each system of tables 2 to 4, Henry's constants were calculated using the binary parameters reported in those tables. **Table 5** shows the calculated Henry's constant, the experimental Henry's constant and the difference between them. The overall average relative deviation is -7.81%. The average relative deviation for all systems involving carbon monoxide is -9.29%, that for the carbon dioxide systems is -6.46% and that for the hydrogen systems is -8.59%.

The errors are in the range of dispersion of the experimental information. The calculated Henry's constant is always smaller than the experimental value. This fact is a consequence of the procedure used to calculate the constants. Fitting Henry's constants directly would make the difference less biased but not smaller.

There is a good linear correlation for each temperature between E_{ij} and the carbon number of the normal paraffin. On the contrary, the correlation between E_{ij} and temperature for each normal paraffin is not good. The difference between E_{ij} of different gases is very large. These facts suggest that, by choosing a value for the binary parameter E_{ij} obtained from a reduced set of systems, the model could be used to predict Henry's constants and solubilities of the same gas in a different set of normal paraffins. The only necessary datum for the calculation is r_i for the normal paraffin. The value of r_i can easily be estimated

Table 3. Interaction parameters regressed from CO₂
(1) solvent (2) solubility data^{b)}

Solvent	<i>T</i> (K)	<i>E</i> ₁₂ (J mol ⁻¹)	AARD ^{a)} (%)
Eicosane ^{c)}	373.45	-541.6	11.5
Eicosane ^{c)}	473.15	-551.1	10.5
Eicosane ^{c)}	573.35	-536.6	11.6
Tetracosane ^{d)}	373.15	-533.5	22.0
Tetracosane ^{d)}	473.15	-541.2	10.0
Tetracosane ^{d)}	573.15	-529.8	8.5
Octacosane ^{e)}	373.35	-532.5	10.6
Octacosane ^{e)}	473.45	-538.7	13.3
Octacosane ^{e)}	573.45	-525.0	18.6
Dotriacontane ^{d)}	373.15	-527.7	15.0
Dotriacontane ^{d)}	473.15	-532.3	17.8
Dotriacontane ^{d)}	573.15	-518.4	21.7
Hexatriacontane ^{f)}	373.15	-526.1	17.0
Hexatriacontane ^{g)}	373.20	-529.1	21.7
Tetratetracontane ^{g)}	373.20	-523.9	22.0

a) $AARD = [(1/M) \sum^M (|f_{CO_2}^{calc} - f_{CO_2}^{exp}| / f_{CO_2}^{exp})] \times 100$

b) For each solvent and each temperature the range of pressure is 1 to 5 MPa and at least five experimental points were fitted.

c) Solubility data from reference [7]

d) Solubility data from reference [11]

e) Solubility data from reference [9]

f) Solubility data from reference [10]

g) Solubility data from reference [6]

Table 4. Interaction Parameters regressed from H₂
(1) solvent (2) solubility data^{b)}

Solvent	<i>T</i> (K)	<i>E</i> ₁₂ (J mol ⁻¹)	AARD ^{a)} (%)
Eicosane	373.35	-178.3	12.64
Eicosane	473.55	-177.3	10.70
Eicosane	573.25	-123.6	16.91
Octacosane	373.25	-174.9	10.83
Octacosane	473.25	-144.6	15.48
Octacosane	573.15	-99.7	16.63
Hexatriacontane	373.15	-152.6	22.17
Hexatriacontane	473.05	-129.7	23.90
Hexatriacontane	573.15	-70.5	24.35

a) $AARD = [(1/M) \sum^M (|f_{H_2}^{calc} - f_{H_2}^{exp}| / f_{H_2}^{exp})] \times 100$

b) For each solvent and each temperature the range of pressure is 1 to 5 MPa and at least five experimental points were fitted.

Solubility data from reference [8]

by Bondi's method for van der Waals volume⁴⁾.

After looking at the *E*_{ij} values for the carbon dioxide-normal paraffin, the value of -530 J mol⁻¹ was chosen and solubility calculations for carbon dioxide in dotriacontane and in a complex wax were made. The wax was not included in the original fitting. **Figure 1** shows the results of the calculations at a temperature of 573.25 K. The agreement is very good for both solvents. Similar results were obtained at different temperatures and with a different gas.

Table 5. Comparison of calculated Henry's constant (*H*_{calc}) with experimental Henry's constant (*H*_{exp})^{a)}

System	<i>T</i> (K)	<i>H</i> _{calc} (MPa)	<i>H</i> _{exp} (MPa)	Dev ^{b)} (%)
Carbon monoxide-Eicosane	373.25	49.07	53.26	-7.87
Eicosane	473.45	38.68	43.16	-10.38
Eicosane	573.15	30.37	33.83	-10.23
Carbon monoxide-Octacosane	373.45	39.77	43.75	-9.10
Octacosane	473.15	32.75	35.76	-8.42
Octacosane	573.45	26.33	28.92	-8.95
Carbon monoxide-Hexatriacontane	373.15	35.39	38.81	-8.81
Hexatriacontane	473.05	29.27	32.54	-10.05
Hexatriacontane	572.95	23.29	25.83	-9.83
Carbon dioxide-Eicosane	373.45	10.87	11.50	-5.48
Eicosane	473.15	15.41	16.23	-5.05
Eicosane	573.35	17.09	18.11	-5.63
Carbon dioxide-Tetracosane	373.15	10.14	10.15	-0.10
Tetracosane	473.15	14.31	15.03	-4.79
Tetracosane	573.15	15.68	16.42	-4.51
Carbon dioxide-Octacosane	373.35	9.00	9.43	-4.56
Octacosane	473.45	12.83	13.79	-6.96
Octacosane	573.45	14.31	15.87	-9.83
Carbon dioxide-Dotriacontane	373.15	8.40	9.21	-8.79
Dotriacontane	473.15	12.00	13.18	-8.95
Dotriacontane	573.15	13.36	14.94	-10.57
Carbon dioxide-Hexatriacontane	373.15	7.69	8.48	-9.32
Hexatriacontane	373.20	7.49	8.05	-6.96
Carbon dioxide-Tetratetracontane	373.20	6.59	6.97	-5.45
Hydrogen-Eicosane	373.35	82.90	87.98	-5.77
Eicosane	473.55	51.43	54.27	-5.23
Eicosane	573.25	36.34	39.75	-8.58
Hydrogen-Octacosane	373.25	63.80	66.05	-3.41
Octacosane	473.25	45.01	48.84	-7.84
Octacosane	573.15	31.04	34.22	-9.29
Hydrogen-Hexatriacontane	373.15	58.06	65.65	-11.56
Hexatriacontane	473.05	38.69	44.48	-13.02
Hexatriacontane	573.15	27.70	31.70	-12.62

a) Sources of experimental data same as those of tables 2, 3, 4

b) $Dev = (H_{calc} - H_{exp}) / H_{exp} \times 100$

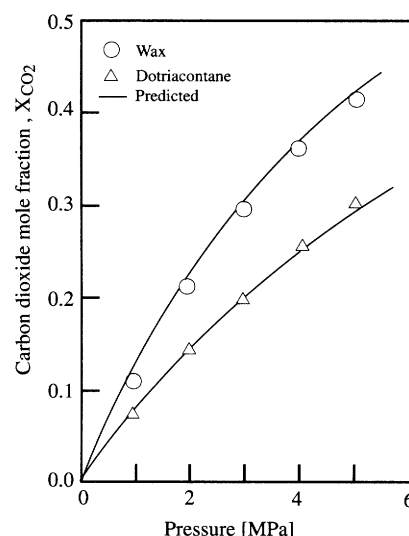


Fig. 1 Comparison of calculated solubilities of carbon dioxide in *n*-paraffins with experimental data at 573.25 K. Experimental data for dotriacontane according to reference [11]. Experimental data for wax according to reference [12].

Conclusions

For linear systems the lattice-gas model gives a fair correlation of the values of Henry's constant. On the other hand, the model gives a good prediction of the solubility of a light gas in normal paraffin solvent.

Research is under way to apply the model to non-linear systems.

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Nomenclature

$AARD$	= average absolute relative deviation	[-]
E_{ij}	= interaction energy between segments of molecules i and j	[J mol ⁻¹]
f	= fugacity	[Pa]
H	= Henry's constant	[Pa]
M	= number of experimental points	[-]
N	= total number of cells	[-]
N_j	= total number of molecules or holes	[-]
N_{ij}	= number of contact pairs between segments of molecules i and j	[-]
p	= pressure	[Pa]
q_i	= molecular surface area parameter	[-]
R	= universal gas constant	[J K ⁻¹ mol ⁻¹]
R_i	= number of cells occupied by molecule i	[-]
t_i	= molecular partition function	[-]
T	= temperature	[K]
V_o	= cell volume	[m ³ mol ⁻¹]
x	= liquid-phase mole fraction	[-]
z	= lattice coordination number	[-]
μ_i	= chemical potential of component i	[J mol ⁻¹]

<Superscripts>

$calc$	= calculated
exp	= experimental
P_r	= saturation pressure of solvent
ref	= reference state

<Subscripts>

o	= hole
1	= solute
2	= solvent
i	= component i
j	= component j
CO	= carbon monoxide
CO_2	= carbon dioxide
H	= hydrogen

Literature Cited

- 1) Angus, S., B. Armstrong, K.M. de Reuk: "IUPAC International thermodynamic tables of the fluid state: Carbon dioxide", Pergamon Press, Oxford (1976)
- 2) API: "Properties of hydrocarbons of high molecular weight", UMI, Ann Arbor (1989)
- 3) Balbuena P.B., E.A. Campanella and L.M. Gribaudo: *Fluid Phase Equilib.*, **62**, 225 (1991)
- 4) Bondi, A.: *J. Phys. Chem.*, **68**, 441 (1964)
- 5) Goodwin, R.D.: *J. Phys. Chem. Ref. Data*, **14**, 849 (1985)
- 6) Gassem, K.A.M. and R.L. Robinson: *J. Chem. Eng. Data*, **30**, 53 (1985)
- 7) Huang, S.H., H.M. Lin, F.N. Tsai and K.C. Chao: *J. Chem. Eng. Data*, **33**, 1445 (1988)
- 8) Huang, S.H., H.M. Lin, F.N. Tsai and K.C. Chao: *Ind. Eng. Chem. Res.*, **27**, 162 (1988)
- 9) Huang, S.H., H.N. Lin and K.C. Chao: *J. Chem. Eng. Data*, **33**, 143 (1988)
- 10) Tsai, F.N., S.H. Huang, H.M. Lin and K.C. Chao: *J. Chem. Eng. Data*, **32**, 467 (1987)
- 11) Tsai, F.N. and J.S. Yan: *J. Chem. Eng. Data*, **35**, 43 (1990)
- 12) Tsai, F.N., S.H. Huang, H.M. Lin and K.C. Chao: *Chem. Eng. J.*, **38**, 41 (1988)