J. Chem. Eng. Data 1986, 31, 175-180

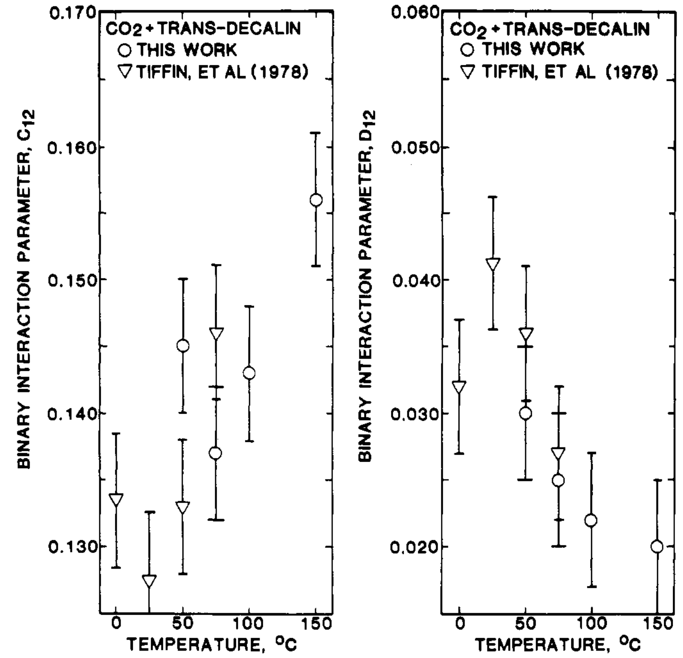

Figure 6. Soave interaction parameters for CO_2 + *trans*-Decalin.

P	bubble-point pressure
y	mole fraction
Δ	difference between calculated and experimental values

Registry No. CO_2, 124-38-9; C_6H_6, 71-43-2; *trans*-decalin, 493-02-7; cyclohexane, 110-82-7.

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Solubility of Gases in Liquids. 17. The Solubility of He, Ne, Ar, Kr, H_2, N_2, O_2, CO, CH_4, CF_4, and SF_6 in Tetrachloromethane at 283–318 K[†]

Toshihiro Tominaga,[‡] Rubin Battino,* Hemant K. Gorowara,[§] and Robert D. Dixon[§]
Department of Chemistry, Wright State University, Dayton, Ohio 45435

Emmerich Wilhelm*
Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria

The Ostwald coefficients $L_{2,1}(T,P)$ of He, Ne, Ar, Kr, H_2, N_2, O_2, CO, CH_4, CF_4, and SF_6 in tetrachloromethane have been determined at about atmospheric pressure, and from 283 to 318 K, by a modified Ben-Naim/Baer apparatus. Both pressure control and measurement of the volume of gas dissolved in a given amount of solvent were effected by a microprocessor. This improved, medium-precision design (about ±1%) combines easy handling with automated data retrieval, and is totally *mercury-free*. Test measurements for N_2, O_2, CO_2, and CH_4 dissolved in pure water showed excellent agreement with recent high-precision results. Henry coefficients $H_{2,1}(T,P_{s,1})$ are evaluated from the solubility data. Their variations with temperature yield the enthalpy changes upon solution $\Delta H_2{}^\circ$, which are compared with recent calorimetric measurements. Results obtained through application of scaled particle theory are also given.

Introduction

Tetrachloromethane (CCl_4) is a pseudospherical molecule of high symmetry with an average molecular polarizability and an effective hard-sphere diameter comparable to that of cyclohexane and benzene (*1–3*). As such, it plays a central role in assessing the performance of theories of pure liquids and liquid mixtures, as documented by the many measurements reported in the literature on thermodynamic quantities of mixtures containing tetrachloromethane (*4–6*). Of particular interest are those mixtures where the molecules are of substantially different size, since large size ratios will magnify existing deficiencies in the statistical-mechanical models (*7–9*). However, aside from Horiuti (*10*), who measured the solubility in tetrachloromethane of five of the gases reported on in this article, the literature contains few reliable gas solubility data for this solvent. Considering the importance of tetrachloromethane from both the theoretical and practical point of view, the paucity of solubility data is surprising. We suspect the reason for this is that most apparatuses used for gas solubility measurements contain mercury which is known to react with tetrachloromethane.

[†] Communicated in part at the 6th ISSSSI in Osaka, Japan, July 5–10, 1982.
[‡] On leave from Okayama University of Science, 1-1 Ridai-cho, Okayama 700, Japan.
[§] Department of Computer Science, Wright State University.

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In this work we report on the experimental determination, by a synthetic method, of the Ostwald coefficients $L_{2,1}(T,P)$ of 11 gases (He, Ne, Ar, Kr, H_2, N_2, O_2, CO, CH_4, CF_4, SF_6) dissolved in tetrachloromethane at about atmospheric pressure ($P = 10^5$ Pa) and from 283 to 318 K. The Ben-Naim/Baer design (*11*) was modified by incorporating a microprocessor for pressure control and measurement of gas volume. This improved apparatus is for medium-precision work with a reliability of about ±1%. Its assets are easy handling, relatively fast measurements (completion of one run, i.e., dissolution of one gas in the solvent at a given temperature usually takes less than 2 h), automated data retrieval, and total *absence of mercury*. The $L_{2,1}$'s are then converted to Henry coefficients $H_{2,1}(T,P_{s,1})$ by using the thermodynamically rigorous relations of Wilhelm (*12-15*). The variation of $H_{2,1}(T,P_{s,1})$ with temperature is accounted for by a power series in inverse temperature, T^{-1}, as suggested by Benson and Krause (*16*). The resulting enthalpy changes upon solution are compared with recent calorimetric measurements (*17*). Finally, the Henry coefficients are compared with predictions via a simple version of scaled particle theory (*1-3*, *18-20*).

Experimental Section

The tetrachloromethane used was Fisher "certified" grade, 99 mol % pure. It was distilled through a 1.2-m vacuum-jacketed packed column at a reflux ratio of 20 or better, and only the middle 80% was used. The solvent was stored in brown glass bottles and was protected from light as much as possible during experiments. Prior to actual measurements, tetrachloromethane was degassed by the method of Battino et al. (*21*), and transferred under its own vapor pressure into the apparatus.

All gases were used from the gas tanks as received. They were from Matheson and had the following minimum mole percentage purities: He, 99.995; Ne, 99.99; Ar, 99.995; Kr, 99.995; H_2, 99.99; N_2, 99.998; O_2, 99.99; CO, 99.8; CH_4, 99.97; CF_4, 99.7; SF_6, 99.8.

The solubility apparatus was housed in a large air thermostat. The temperature was controlled to better than ±0.1 K with a Yellow Springs Instrument Co. Model 72 proportional controller. Temperatures T are based on IPTS-68, and were determined wtih a Leeds and Northrup knife blade platinum resistance thermometer, which was calibrated with a triple-point-of-water cell and an NBS-certified benzoic acid cell.

As stated above, the basic design of the Ben-Naim/Baer apparatus (*11*) was used. Depending on the magnitude of the Ostwald coefficient, four mixing chambers with volumes v^L of approximately 26, 65, 380, or 1650 cm^3 can be attached. These chambers were calibrated with doubly distilled water and the respective volumes are known to better than ±0.01 cm^3. Gas volumes v^V were determined by having a Motorola microprocessor count the number of steps a stepping motor used to drive a close-fitting piston, with a Teflon seal backed up by O-rings, through a Fischer and Porter $^5/_8$ in. [=15.875 ± 0.008 mm] precision bore tube. The combination of tube diameter, the pitch of the drive screw, and the number of steps per revolution yields a volume change of about 0.0101 cm^3 per step. Thus, gas volumes can be determined to a few parts per thousand. Before dissolution begins the microprocessor is zeroed. From then on it automatically adjusts the piston to maintain the preselected pressure P constant. The pressure was determined with a Yellow Springs Instrument Co. Model 2014-27 pressure transducer (calibrated to ±0.2% by YSI) and was kept nulled to within 2 parts per thousand or better. A schematic diagram of the present improved apparatus is shown in Figure 1.

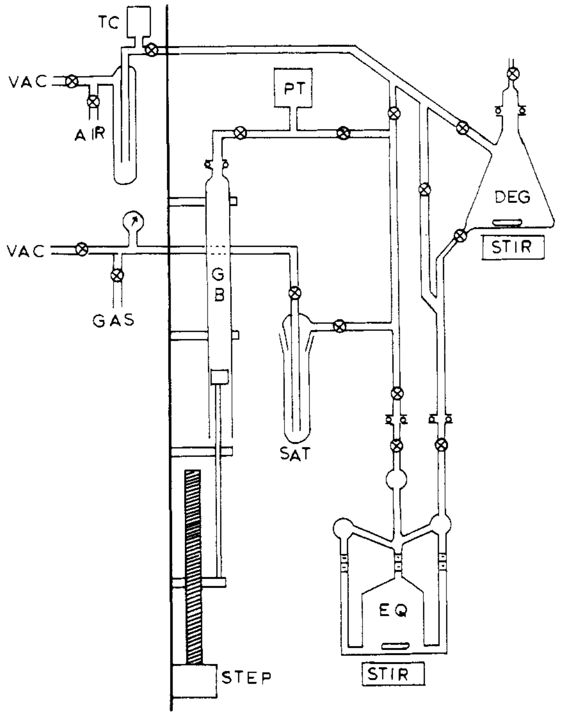

Figure 1. Schematic diagram of the Ben-Naim/Baer type apparatus for determining Ostwald coefficients of gases dissolved in liquids (synthetic method). TC is the thermocouple gauge; PT is the pressure transducer; DEG is the degassing flask; SAT is the saturation chamber; EQ is the equilibration vessel; STIR are the magnetic stirring motors; STEP is the stepping motor; and GB is the gas buret.

Data Reduction

The Ostwald coefficient is a frequently used measure of the solubility of a gas in a liquid. However, of the several definitions of the Ostwald coefficient introduced in the literature (*22*), the most appropriate one for the thermodynamically rigorous description of gas solubility is (*12-15*)

$$L_{2,1}(T,P) \equiv (\rho_2^{L}/\rho_2^{V})_{\text{equil}} \quad (1)$$

Here, $\rho_2^L \equiv n_2^L/v^L = x_2/V^L$ and $\rho_2^V \equiv n_2^V/v^V = y_2/V^V$ are the amount-of-substance concentrations at $\{T,P\}$ of the solute (gas) in the liquid-phase solution (indicated by a superscript L) and in the coexisting vapor-phase solution (indicated by a superscript V), respectively. With the appropriate superscripts, n_1 and n_2 denote the amount of solvent and solute in the two phases, x_2 is the mole fraction of gas in the liquid phase, y_2 is the mole fraction of gas in the vapor phase, and $V = v/(n_1 + n_2)$ is the corresponding molar volume. The link with the experimentally accessible quantities is established through

$$L_{2,1}(T,P) = v^V/v^L \quad (2)$$

where v^V is the volume determined through the microprocessor (see above), and v^L is the volume of the liquid solution *after* equilibrium is reached.

As indicated, $L_{2,1}(T,P)$ depends on temperature as well as on total pressure. However, for conditions well below the critical point of the solvent, the pressure dependence is usually very small and can be detected only by measurement techniques of the highest accuracy, that is to say by methods where the experimental error is, roughly, less than 0.1% (see ref *22-26*). Thus, given the limits of experimental precision attainable with this apparatus (see below), to an excellent approximation the Henry coefficient $H_{2,1}(T,P_{s,1})$ is given by (*13-15*)

$$H_{2,1}(T,P_{s,1}) = \frac{RT}{V^L L_{2,1}(T,P)} Z^V \phi_2^V \mathcal{P}_2^{-1} \quad (3)$$

where the Poynting term is

$$\mathcal{P}_2 \equiv \exp\left[\int_{P_{s,1}}^{P} (RT)^{-1} V_2^{L}\, dP\right]$$

$$\simeq \exp[(RT)^{-1} V_2^{\infty L}(P - P_{s,1})] \qquad (4)$$

Here, Z^V is the vapor-phase compressibility factor, ϕ_2^V is the vapor-phase fugacity coefficient of the solute, $P_{s,1}$ is the vapor pressure of pure solvent, and R is the gas constant. As concerns the liquid phase, V^L is the corresponding molar volume, V_2^L is the partial molar volume of dissolved gas at composition x_2, and $V_2^{\infty L}$ is the partial molar volume of the gas at infinite dilution.

For gas solubility measurements at such low pressures as in this work, the virial equation in pressure in the truncated form

$$Z^V = 1 + (RT)^{-1}P(y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}) \qquad (5)$$

is convenient for the description of real-gas behavior, whence

$$\phi_i^V = \exp[(RT)^{-1}P(B_{ii} + y_j^2\delta_{12})], \quad i, j = 1, 2; \ i \neq j \qquad (6)$$

B_{11} and B_{22} are the second virial coefficients of pure tetrachloromethane and gas, respectively, B_{12} is the second cross-coefficient and $\delta_{12} \equiv 2B_{12} - (B_{11} + B_{22})$.

At the same level of approximation, we obtain the vapor-phase mole fraction according to

$$y_2 = 1 - (1 - x_2)\frac{P_{s,1}}{P}\frac{\phi_{s,1}^*}{\phi_1^V}\mathcal{P}_1 \qquad (7)$$

$$\mathcal{P}_1 \simeq \exp[(RT)^{-1}V_{s,1}^{*L}(P - P_{s,1})] \qquad (8)$$

Here, $\phi_{s,1}^{*V}$ and ϕ_1^V represent the fugacity coefficients of pure solvent vapor at saturation conditions (indicated by the subscript s) and of the solvent in the vapor-phase solution, respectively, and $V_{s,1}^{*L}$ is the molar volume of pure liquid solvent. At the level of approximation indicated by eq 3, $x_2 = \phi_2^VP_2/[H_{2,1}(T,P_{s,1})\mathcal{P}_2]$, whence after substitution for $H_{2,1}(T,P_{s,1})$ according to eq 3 the liquid-phase mole fraction is given by

$$x_2 = \frac{P_2V^LL_{2,1}(T,P)}{RTZ^V} \qquad (9)$$

Here, $P_2 \equiv y_2P$ is the partial pressure of gas, and the molar volume of the liquid solution is obtained from the asymptotically valid expression

$$V^L \simeq x_1V_{s,1}^{*L} + x_2V_2^{\infty L} \qquad (10)$$

From eq 3–10 the compressibility factors, the fugacity coefficients, the mole fractions, and the Henry coefficients were calculated by a rapidly converging iteration procedure similar to that presented in ref *23*.

The vapor pressure of tetrachloromethane was calculated from the Antoine equation with parameters from ref 26. The volumetric properties of CCl_4 were taken from the work of Wood and Gray (*27*). The auxiliary quantities necessary for calculating $H_{2,1}(T,P_{s,1})$, that is to say the virial coefficients and $V_2^{\infty L}$, were either extracted from the literature (*10*, *28–34*) or estimated.

Virial Coefficients. For those systems where no experimental results are available, B_{12} was calculated by a generalized corresponding states correlation due to Tsonopoulos (*35*) and Pitzer and Curl (*36*). Reduced virial cross-coefficients at a reduced temperature $T_r \equiv T/T_{c,12}$ are thereby obtained from

$$\frac{B_{12}(T_r)P_{c,12}}{RT_{c,12}} = B^{(0)}(T_r) + \omega_{12}B^{(1)}(T_r) \qquad (11)$$

where $B^{(0)}(T_r)$ and $B^{(1)}(T_r)$ are universal functions of T_r^{-1}. The characteristic pseudocritical parameters $T_{c,12}$ and $P_{c,12}$ were correlated with the pure-component critical quantities $T_{c,i}$, $P_{c,i}$, and $V_{c,i}$, (i = 1, 2) through the conventional mixing rules

$$T_{c,12} = (1 - k_{12})(T_{c,1}T_{c,2})^{1/2} \qquad (12)$$

$$P_{c,12} = 4T_{c,12}(P_{c,1}V_{c,1}/T_{c,1} + P_{c,2}V_{c,2}/T_{c,2})(V_{c,1}^{1/3} + V_{c,2}^{1/3})^{-3} \qquad (13)$$

and ω_{12} is the arithmetic mean of the pure-component acentric factors

$$\omega_{12} = (\omega_1 + \omega_2)/2 \qquad (14)$$

The binary interaction parameters k_{12} (*37*, *38*) were estimated from a correlation k_{12} vs. $T_{c,2}$. This correlation is based on optimized k_{12} values obtained from all known experimental results on mixtures containing CCl_4. It yields k_{12} = 0.345 for CCl_4 + Ne, 0.155 for CCl_4 + CO, 0.130 for CCl_4 + O_2, 0.095 for CCl_4 + Kr, 0.086 for CCl_4 + CF_4, and 0.063 for CCl_4 + SF_6. The algebraic form of eq 10, in the pure-substance version, was also used to extrapolate experimental results on B_{11} (*28*, *29*) obtained at higher temperatures down to the range of interest for this work (see Figure 2).

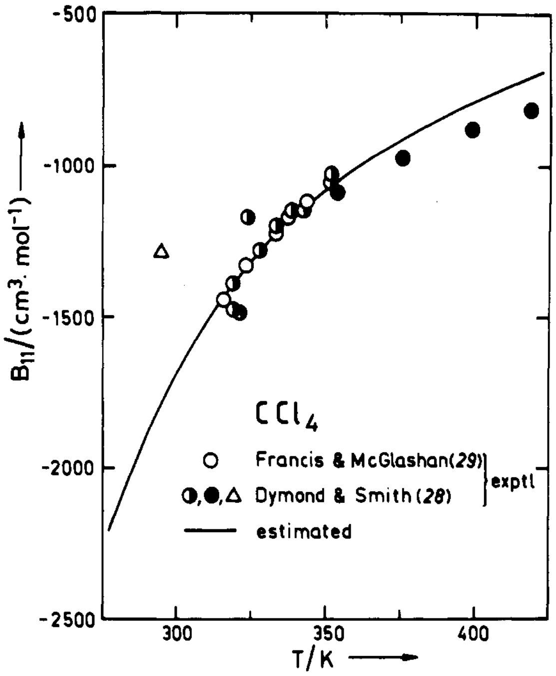

Figure 2. Second virial coefficient B_{11} of tetrachloromethane as a function of temperature T. Experimental results are indicated by ○, ◑, ● and △. The curve was calculated from a generalized corresponding states correlation of Tsonopoulos type (*35*) adjusted to be in accord with the measurements of Francis and McGlashan (*29*).

Partial Molar Volumes. Experimental partial molar volumes at infinite dilution have been reported (*32–34*) for all systems but three: for CCl_4 + He, + Ne, and + Kr. $V_2^{\infty L}$ at 298.15 K was estimated from an empirical linear relation (*39*)

$$V_2^{\infty L} = a + bV_{c,2} \qquad (15)$$

which was obtained through least-squares regression of the most reliable experimental data for 13 nonpolar (or slightly polar) gases dissolved in tetrachloromethane. Partial molar volumes calculated from eq 15, with a = 7.229 cm³·mol⁻¹ and b = 0.4591, agree with experimental results to within 10% in almost all cases (the standard deviation is 5.3 cm³·mol⁻¹) (see Figure 3). Any small temperature dependence of $V_2^{\infty L}$ was disregarded.

On the average, the imprecision of our measurements was found to be about ±1%. The inaccuracy is believed to be roughly of the same order, which estimate is corroborated by

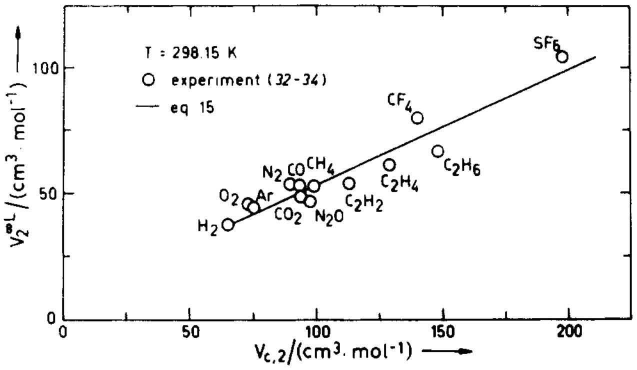

Figure 3. Correlation of partial molar volumes at infinite dilution $V_2^{\infty L}$ of 13 gases dissolved in liquid tetrachloromethane at 298.15 K with the corresponding molar critical volumes $V_{c,2}$ of the gases.

Table I. Ostwald Coefficients $L_{2,1}(T,P)$ of Nitrogen, Oxygen, Carbon Dioxide, and Methane Dissolved in Water at T = 308.15 K and $P = 10^5$ Pa: Comparison with Literature Values for $L_{2,1}^{\infty} = \lim_{\rho_2^L \to 0} L_{2,1}(T,P)$

gas	$L_{2,1}(T,P)$	σ^a	$L_{2,1}^{\infty}$
N_2	0.014 21	0.000 08	0.014 52 (*25*)
O_2	0.027 54	0.000 17	0.027 78 (*23*)
CO_2	0.658 2		0.665 9 (*40*)
CH_4	0.029 79	0.000 24	0.030 41 (*23*)

test measurements of $L_{2,1}(T,P)$ for N_2, O_2, CO_2, and CH_4 dissolved in pure water at 308.15 K and $P = 10^5$ Pa. These results are compared with some of the best literature values (*23*, *25*, *40*) in Table I.

Results and Discussion

Experimental Ostwald coefficients $L_{2,1}(T,P)$ at $P = 10^5$ Pa and for 282.7 < T/K < 318.2 are given in Table II. These data were smoothed according to

$$\ln L_{2,1}(T,P) = \sum_{i=0} \ell_i (T/\mathrm{K})^{-i} \qquad (16)$$

and Table III contains the values of the coefficients ℓ_i. Henry coefficients $H_{2,1}(T,P_{s,1})$ were obtained as described above and smoothed analogously, with respect to temperature (*16*), via

$$\ln\,[H_{2,1}(T,P_{s,1})/\mathrm{Pa}] = \sum_{i=0} h_i (T/\mathrm{K})^{-i} \qquad (17)$$

The coefficients h_i have been included in Table III. The smoothed results at 298.15 K were used to estimate mole fraction solubilities corresponding to a partial gas pressure of P_2 = 101 325 Pa, which quantities are compared with literature values in Table IV. Agreement is satisfactory throughout, the only exception being Korosy's results (*42*) which are much too large.

Until very recently, measurements of $H_{2,1}(T,P_{s,1})$ over sufficiently large ranges of temperature were the only reliable source of information on enthalpy changes upon solution, ΔH_2°, of sparingly soluble gases in liquids. Specifically, it may be shown (*12*, *13*, *23*) that eq 16 yields

$$\Delta H_2^{\circ}/RT \equiv (H_2^{\infty L} - H_2^{\circ V})/RT$$
$$= \sum_{i=1} i h_i (T/\mathrm{K})^{-i} + \frac{V_2^{\infty L}}{R}\,\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} \qquad (18)$$

where $H_2^{\infty L}$ is the partial molar enthalpy of the solute at infinite dilution in the liquid solvent, and $H_2^{\circ V}$ is the molar enthalpy of pure solute in the ideal-gas reference state. The enthalpy changes so determined are also shown in Table IV and compared with results derived from solubility data given in the literature as well as with direct calorimetric results obtained via an isothermal displacement calorimeter (*17*). Considering the rather small temperature range covered by our solubility measurements (<35 K) in conjunction with the precision of the methods applied, the accord is reasonable.

Table II. Ostwald Coefficients $L_{2,1}(T,P)$ of 11 Gases Dissolved in Tetrachloromethane at 282.7 < T/K < 318.2 and $P = 10^5$ Pa, and Henry Coefficients $H_{2,1}(T,P_{s,1})$

T/K	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}(T,P_{s,1})$/Pa
	He	
282.71	0.02238	1102.3
282.75	0.02224	1109.4
282.76	0.02273	1085.5
298.14	0.02700	946.0
308.15	0.03113	837.9
308.15	0.03126	834.4
318.13	0.03413	779.5
	Ne	
298.14	0.04310	592.5
	Ar	
282.76	0.3235	76.01
282.76	0.3284	74.88
298.14	0.3399	74.86
308.15	0.3510	74.00
	Kr	
298.15	0.9490	26.74
	H_2	
282.71	0.06912	356.9
282.76	0.06782	363.7
298.15	0.07857	325.0
308.15	0.08482	307.3
308.15	0.08499	306.7
	N_2	
282.75	0.1473	167.0
298.14	0.1573	161.8
298.15	0.1604	158.7
308.15	0.1715	151.5
308.15	0.1735	149.8
308.15	0.1757	147.9
318.10	0.1781	148.7
	O_2	
298.14	0.2990	85.08
308.15	0.3156	82.27
310.11	0.3007	86.68
318.13	0.3029	87.35
	CO	
282.76	0.2064	119.1
282.76	0.2076	118.5
298.14	0.2184	116.5
308.14	0.2245	115.7
	CH_4	
282.71	0.7414	33.07
298.14	0.7060	35.95
308.15	0.7060	36.69
308.15	0.7122	36.37
308.15	0.7180	36.06
	CF_4	
298.14	0.2871	87.85
308.15	0.2946	87.41
308.15	0.3037	84.79
318.11	0.2980	88.06
	SF_6	
298.16	1.557	15.91

Scaled particle theory has been used successfully for the prediction and correlation of Henry coefficients (*1–3*, *18–20*, *23–25*, *48*). The pertinent expression is

$$\ln\left[\frac{H_{2,1}(T,P_{s,1})V_{s,1}^{*L}}{RT}\right] = \frac{G_{\mathrm{cav}}}{RT} + \frac{G_{\mathrm{int}}}{RT} \qquad (19)$$

where G_{cav} is the partial molar Gibbs energy of cavity formation

Table III. Values of the Parameters ℓ_i of Eq 16 and h_i of Eq 17 and Smoothed Results for $L_{2,1}(T,P = 10^5$ Pa) and $H_{2,1}(T,P_{s,1})$ for 11 Gases Dissolved in Tetrachloromethane at 298.15 K

gas	$10\ell_0$	$10^{-2}\ell_1$	$L_{2,1}$-(298.15 K, 10^5 Pa)	h_0	$10^{-2}h_1$	$10^{-6}H_{2,1}$-(298.15 K, $P_{s,1}$)/Pa
He	0.6425	−10.9176	0.02739	17.6332	9.0054	932.7
Ne			0.04310			592.5
Ar	−2.3882	−2.4962	0.3409	17.9209	0.6180	74.64
Kr			0.9490			26.74
H_2	−0.6888	−7.3853	0.07840	17.7584	5.4952	325.7
N_2	−0.1478	−5.3929	0.1614	17.6984	3.5112	157.7
O_2	−10.1812	−0.5276	0.3027	18.6960	−1.3391	84.05
CO	−5.7915	−2.8150	0.2180	18.2607	0.9384	116.7
CH_4	−7.5847	1.2788	0.7192	18.4368	−3.1540	35.28
CF_4	−6.3181	−1.8057	0.2901	18.3069	−0.0778	86.95
SF_6			1.5570			15.91

Table IV. Comparison with Literature Values at 298.15 K: Mole Fraction Solubilities x_2 of Several Gases in Tetrachloromethane at a Partial Pressure P_2 = 101 325 Pa, and Enthalpies of Solution $\Delta H_2°$

	10^4x_2		$\Delta H_2°/(\text{kJ·mol}^{-1})$		
gas	this work	lit.	this work	lit. (solubility)	lit. (*17*) (calorimetry)
Ar	13.56	13.75 (*41*)	0.52	−0.09 (*41*)	−0.52
Kr	37.78	52.6 (*42*)			
H_2	3.11	3.29 (*10*); 3.20 (*43*)	4.57	5.25 (10); 5.71 (*43*)	
N_2	6.42	6.41 (*10*)	2.93	2.47 (*10*)	1.03
O_2	12.04	12.00 (*10*); 9.74 (*44*); 13.26 (*45*); 12.02 (*46*)	−1.10	0.01 (*10*)	
CO	8.67	8.65 (*10*)	0.79	1.38 (*10*)	
CH_4	28.64	28.56 (*10*)	−2.63	−2.91 (*10*)	−3.19
CF_4	11.59	11.84 (*47*)	−0.05	0.54 (*47*)	
SF_6	62.78	65.30 (*47*)		6.97 (*47*)	

Table V. Comparison of Experimental Values of Henry Coefficients for 11 Gases Dissolved in Tetrachloromethane at 298.15 K with Results from Scaled Particle Theory (SPT)

	$\ln[H_{2,1}(T,P_{s,1})/\text{Pa}]$			$\ln[H_{2,1}(T,P_{s,1})/\text{Pa}]$	
gas	exptl	SPT	gas	exptl	SPT
He	20.654	20.230	N_2	18.876	18.584
Ne	20.200	19.224	O_2	18.247	17.854
Ar	18.128	17.730	CO	18.575	18.272
Kr	17.102	17.124	CH_4	17.379	17.188
H_2	19.602	19.527	CF_4	18.246	18.290
			SF_6	16.582	16.637

and G_{int} is the partial molar Gibbs energy of interaction. Scaled particle theory provides a reasonable approximation of G_{cav} (*48*) in that it yields an asymptotic expansion in the radius of the cavity to be created, retaining terms up to the cubic. The interactional contribution G_{int} was, as usual, approximated by an effective Lennard-Jones term augmented by a term representing dipole–induced dipole interactions (*25*). Table V shows a comparison between experimental and calculated Henry coefficients. Considering the simplicity of the prediction method, the agreement is quite satisfactory.

Glossary

a, b	constants of eq 15
$B^{(0)}$, $B^{(1)}$	Tsonopoulos functions (of reduced temperature T_r)
B_{ii}	second virial coefficient of pure i
B_{ij}	second virial cross-coefficient
G_{cav}	partial molar Gibbs energy of cavity formation
G_{int}	partial molar Gibbs energy of interaction
h_i	coefficients of smoothing function eq 17
$H_{2,1}$	Henry coefficient of solute 2 dissolved in solvent 1
$H_2^{\circ V}$	molar enthalpy of pure 2 in the ideal-gas reference state
$H_2^{\infty L}$	partial molar enthalpy of 2 at infinite dilution in 1 (liquid phase)
$\Delta H_2°$	$\equiv H_2^{\infty L} - H_2^{\circ V}$, enthalpy change upon solution
k_{12}	binary interaction parameter
ℓ_i	coefficients of smoothing function eq 16
$L_{2,1}$	Ostwald coefficient of solute 2 dissolved in solvent 1
n	amount of substance
p	pressure
P_2	$\equiv y_2P$, partial pressure of solute 2
$P_{s,1}$	vapor pressure of solvent 1
$\mathcal{P}$	Poynting correction
R	gas constant
T	thermodynamic temperature
v	experimentally determined volume
V^L	molar volume (of a solution)
$V_{s,1}^{*L}$	molar volume of pure liquid 1 (saturation)
V_2^L	partial molar volume of 2 (liquid phase)
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Z	compressibility factor

Greek Letters

δ_{12}	$\equiv 2B_{12} - (B_{11} + B_{22})$
ϕ_i	fugacity coefficient of component i
ω	acentric factor

Subscripts

c	critical (or pseudocritical) quantity
i	general index; frequently, i = 1 denotes the solvent and i = 2 the solute
ij	"binary" or "interaction" quantity
r	reduced quantity
s	saturation conditions

Superscripts

*	pure substance
°	ideal-gas reference state
∞	infinite dilution
L	liquid phase

V vapor phase

Registry No. CCl_4, 56-23-5; CO, 630-08-0; CH_4, 74-82-8; CF_4, 75-73-0; SF_6, 2551-62-4; H_2, 1333-74-0; N_2, 7727-37-9; O_2, 7782-44-7; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9.

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Vapor–Liquid Equilibrium for Quinoline/Methanol and Tetralin/Methanol Mixtures at Elevated Temperatures and Pressures

Suphat Watanasiri

School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma 73019

Mark C. Thies[†] **and Michael E. Paulaitis***

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Vapor and liquid equilibrium compositions have been measured for binary quinoline/methanol and tetralin/methanol mixtures at 248, 276, and 307 °C and over a range of pressures from approximately 1.5 MPa up to the critical pressure of each binary mixture. The mixture critical pressures are also determined by visual observation of critical opalescence.

Introduction

Experimental data are presented for quinoline/methanol and tetralin/methanol mixtures. These results are the latest in a series of measurements of vapor–liquid equilibrium compositions for binary mixtures of model coal-derived compounds with methanol at elevated temperatures and pressures. Such data are needed for the development of coal conversion processes, particularly those which would use dense fluids (such as methanol, water, or toluene) as extractive solvents.

The experimental technique that is used for measuring equilibrium compositions has been described previously (*1*, *2*). Compositions are obtained by direct sampling of the equilibrium phases, and a view cell allows direct observation of all phase behavior, including critical phenomena. The apparatus is rated for temperatures as high as 425 °C and pressures up to 30 MPa.

Previous measurements of fluid-phase equilibria for binary mixtures of quinoline and tetralin with dense fluids are relatively scarce. Chao and co-workers have used a similar experimental technique to measure vapor and liquid equilibrium compositions for binary mixtures of quinoline and tetralin with hydrogen, carbon dioxide, and methane (*3*–*8*). Measurements were made at temperatures up to 430 °C and pressures to 25 MPa. Schneider and co-workers (*9*) have used a synthetic experimental technique to determine phase boundaries and critical

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[†] Department of Chemical Engineering, Clemson University, Clemson, SC 29631.

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