Partial Molar Volumes of "Gases" at Infinite Dilution in Water at 298.15 K

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Precision density measurements on "gas-free" and "gas-saturated" water (at a total pressure of about 100 kPa and at 298.15 K) yield partial molar volumes at essentially infinite dilution (V_2^∞) of 20 fluids (about half of them supercritical) in liquid water. The experimental technique is based on vibrating-tube densimetry under flow conditions, the precision of which is in the range of a few parts per million. The results for the supercritical solutes can be correlated well with a corresponding states relation due to Brelvi and O'Connell, whereas a strictly empirical linear relation between V_2^∞ and $V_{c,2}$ (critical volume of solute) is valid for all solutes investigated.

Introduction

The partial molar volume of a fluid at infinite dilution in a liquid, V_2^∞, is an important thermodynamic quantity, yet experimental data are not plentiful. Besides other applications, it may be used to correct for the effect of pressure on Henry's constant of solute 2 dissolved in solvent 1 (Poynting correction)

$$H_{2,1}(P,T) = H_{2,1}(P_{\sigma,1},T)\exp\left[\int_{P_{\sigma,1}}^{P}(V_2^\infty/RT)\,\mathrm{d}P\right] \quad (1)$$

where $P_{\sigma,1}$ is the vapor pressure of pure solvent (*1*, *2*). For aqueous solutions it provides valuable information on hydrophobic interaction (*3*).

Partial molar volumes of gases in liquids have been obtained by various methods, such as by determining the pressure dependence of Henry's constants, by density measurements, and by dilatometric methods. Work prior to 1966 has been surveyed in ref *4* and was updated to some extent in 1975 (*5*) and 1978 (*6*). Here, we report on the determination of partial molar volumes of 20 fluids dissolved in liquid water at a total pressure of about 100 kPa at 298.15 K (at this temperature, about half of them are supercritical). For all practical purposes, data obtained under these conditions may be regarded as being identical with those at infinite dilution. The experimental technique is based on measuring the density of "gas-free" water and "gas-saturated" water with a vibrating-tube densimeter capable of parts-per-million precision (*7*, *8*).

Experimental Section and Results

The water used in the experiments was initially purified by reverse osmosis (house "distilled"), followed by continued cycling through research-grade ion exchangers. It had a resistivity greater than $5 \times 10^4\ \Omega$ m. All gases were from Matheson, with purities of 99 mol % or more. The nitrogen used for calibrating the densimeter was Matheson ultrahigh-purity quality, i.e., 99.999 mol % minimum purity.

Densities were measured with a vibrating-tube densimeter (from Sodev, Model O2D) operating under flow conditions (*9*, *10*). The instrument is based on the principle that the density d of a fluid contained in a U-shaped hollow oscillator is related to the natural vibration frequency of the tube; that is to say, for the density range of interest

$$d = a + b\tau^2 \quad (2)$$

Here, τ is the period of vibration, and a and b are temperature-dependent constants characteristic for a particular oscillator. The densimeter was shock-mounted and isolated from power line fluctuations and surges, and it was housed—together with auxiliary apparatus (see below)—in an air bath controlled to ±0.1 K. Upon entering the densimeter, the fluid was thermostated at the desired temperature by circulating water from a bath controlled to ±0.0005 K with a Tronac thermoregulator. The period of the filled tube was then measured with a high-resolution digital frequency meter (from Newport, Model 6130) whose output was fed directly into a printer. The stability of the meter was 1 part in 10^7, and, although it only showed 5 digits, we could read up to 10 digits by ranging. (Our system is inexpensive, and details of the wiring diagram are available upon request.) The meter was set to average 10^4 vibrational periods, and a total of 10 such successive readings were averaged manually. Two fluids of known density were used to calibrate the densimeter: nitrogen at atmospheric pressure and pure degassed water (*11*). After having determined the constant b, one may obtain density differences $\Delta d = d_i - d_1$ of any fluid i relative to pure water (d_1) from

$$\Delta d = b(\tau_i^2 - \tau_1^2) \quad (3)$$

The constancy of b was checked frequently and showed no significant drift over several weeks.

A schematic diagram of the apparatus is shown in Figure 1. Both A and B are degassing flasks as described previously (*12*). After water is degassed in A, it flows by gravity into the evacuated vessel C with stopcocks 3–5 closed. Stopcock 2 is then closed and stopcock 5 opened to slightly pressurize the system via mercury (D). When stopcocks 4 and 6 are open, the degassed water can readily flow through the densimeter E. After water is degassed in B, it is saturated at atmospheric pressure with the gas of interest by slow bubbling via stopcock 9 through a fritted glass tube. During runs the degassed water and the gas-saturated water were alternated through the densimeter for measurement at least 3 times. The total pressure (about 100 kPa) was recorded to ±15 Pa by using a Fortin-type barometer (with all corrections applied). The temperature was measured with a platinum resistance thermometer to ±0.002 K. Stable values of τ were usually obtained after an equilibration time of about 300 s. We experienced few difficulties with outgassing during the actual measurements.

At the low pressures used in this work, the mole fraction solubilities x_2 of the investigated fluids in liquid water are very small; that is, with a few exceptions $x_2 < 10^{-4}$ (*13*). Thus, to a good approximation we may assume that the corresponding value of the partial molar volume is essentially the same as for infinite dilution, i.e., $V_2(x_2) \simeq V_2^\infty$, and hence may be obtained from the relation

$$V_2^\infty = d_1^{-1}d_s^{-1}[M_1(d_s - d_1)(1 - 1/x_2) + M_2 d_1] \quad (4)$$

Here, M_1 and M_2 are the molar masses of water and solute, respectively, d_1 is the density of pure degassed water, and d_s denotes the density of the solution. The mole fraction x_2 at the actual partial pressure of solute was calculated from the liter-

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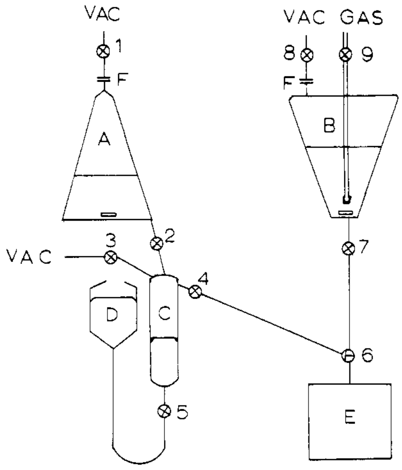

Figure 1. Schematic diagram of partial molar volume apparatus: (A) degassing vessel for pure water; (B) degassing vessel for water to be saturated with a gas; (C) pressurizing vessel; (D) mercury reservoir; (E) vibrating-tube densimeter; (F) O-ring joints. Stopcocks are indicated by ⊗ and numbered.

Table I. Partial Molar Volumes at Infinite Dilution in Water, V_2^∞, at 298.15 K

solute	no. of runs	$V_2^\infty/(\mathrm{cm^3\ mol^{-1}})$		
		exptl	lit.	ref
hydrogen	2	26.7 ± 0.2	25.2	*18*
nitrogen	3	35.7 ± 0.4	32.8	*19*
oxygen	3	33.2 ± 0.2	32.1	*20*
argon	3	32.6 ± 0.7	32.2	*20*
krypton	2	32.8 ± 0.1	31.3	*21*
carbon monoxide	2	37.3 ± 0.5	36.0	*22*
carbon dioxide	4	33.9 ± 0.4	34.8	*20*
methane	3	34.5 ± 0.5	37.4	*18*
ethane	3	52.9 ± 0.9	53.3	*18*
ethylene	3	51.3 ± 1.8		
acetylene	3	42.5 ± 0.6	40.0	*23*
propane	3	70.7 ± 1.4	66.6	*22*
propylene	1	56.7		
cyclopropane	2	54.3 ± 0.6		
n-butane	2	76.6 ± 0.1		
2-methylpropane	2	83.1 ± 1.0		
1-butene	1	62.3		
1,3-butadiene	1	68.3		
neopentane	3	100.5 ± 1.3		
methyl chloride	5	45.8 ± 0.6		

ature (*13*) by applying Henry's law.

Table I gives values for V_2^∞ at 298.15 K for 20 fluids dissolved in liquid water. We estimate the maximum imprecision of our results to be about ±1.5 cm^3 mol^{-1}, or about ±1.5–4%, which is supported by the average deviations for replicate measurements, also given in the table. Since, at temperatures far below the critical temperature of the solvent, Henry's constants of gases dissolved in organic liquids are roughly 1 order of magnitude smaller than those for gases in water, considerable improvement of precision is anticipated for such systems. A set of measurements on one system generally took 3–4 h.

Discussion

In Table I our results are compared with selected literature data. In general, agreement is satisfactory.

The partial molar volumes of gases at infinite dilution in liquids can be obtained from a correlation involving the reduced density of the solvent and the relative molecular sizes of the solute and the solvent (*14*). For the density of interest

$$V_2^\infty/\beta_{T,1}RT = 1 - C_{12}^\infty \qquad (5)$$

$$\ln\left[-C_{12}^\infty(V_1^*/V_2^*)^{0.62}\right] = -2.4467 + 2.12074\tilde{\rho}_1 \qquad (6)$$

Here, $\beta_{T,1}$ is the isothermal compressibility of the solvent, the reduced molar density $\tilde{\rho}_1 = \rho_1 V_1^* = V_1^*/V_1$, where V_1 is the molar volume of the solvent, and V_i^* values are reducing volumes. For the solutes, V_2^* was set equal to the molar critical volume $V_{c,2}$, and V_1^* for water was taken from Brelvi and O'Connell's work (*14*), i.e., $V_1^* = 46.4$ cm^3 mol^{-1}. C_{12}^∞ is the volume integral of the molecular direct correlation function between the two species. This correlation is shown in Figure 2 (solid curve). As already pointed out in ref *14*, it should not be used to describe the partial molar volume of liquids in liquids; that is to say, it should not be used at temperatures substantially below the critical temperature of the solute, $T_{c,2}$. This restriction is clearly shown by the graph: predictions of V_2^∞ are in general deteriorating for increasing values of $1 - T/T_{c,2}$.

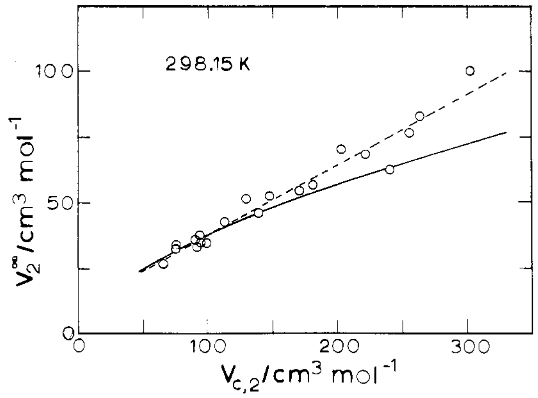

Figure 2. Correlations for partial molar volumes at infinite dilution in liquid water, V_2^∞, as function of the molar critical volume $V_{c,2}$ of the solute (T = 298.15 K). The solid curve was calculated with the aid of the Brelvi-O'Connell correlation, eq 5 and 6; the broken line represents eq 7. Experimental results for the 20 solutes investigated are indicated by circles.

On the other hand, our results are well represented by an empirical equation obtained by least-squares regression:

$$V_2^\infty/(\mathrm{cm^3\ mol^{-1}}) = 10.74 + 0.2683\ V_{c,2}/(\mathrm{cm^3\ mol^{-1}}) \qquad (7)$$

Partial molar volumes calculated from eq 7 agree with experimental volumes to within 10% in most cases. We note that, for small values of $V_{c,2}$, both correlations show asymptotically the same behavior.

Two other empirical correlations that we tried involve the molar volume of the gas at its normal boiling point, V_{bp}, and the van der Waals radius of the gas, V_{VDW}. For the former, eq 8 gives the least-squares fit (omitting neon and carbon dioxide) with an average deviation of ±7%. For the latter, eq 9 gives

$$V_2^\infty/(\mathrm{cm^3\ mol^{-1}}) = 10.77 + 0.7153 V_{bp}/(\mathrm{cm^3\ mol^{-1}}) \qquad (8)$$

the least-squares fit (omitting helium, krypton, carbon dioxide, 1-butene, and neopentane) with an average deviation of about ±10%

$$V_2^\infty/(\mathrm{cm^3\ mol^{-1}}) = 16.6 + 1.27\ V_{VDW}/(\mathrm{cm^3\ mol^{-1}}) \qquad (9)$$

Scaled particle theory may also be used to calculate V_2^∞, yielding results in fair accord with experiment. For details we refer to ref *15*, *16*, and *13*.

Hepler (*17*) has suggested that the pressure dependence of the partial molar heat capacity at infinite dilution, $(\partial C_{P,2}^\infty/\partial P)_T$, may serve as an indicator of structural changes in the solution relative to pure water. Since

$$(\partial C_{P,2}^\infty/\partial P)_T = -T(\partial^2 V_2^\infty/\partial T^2)_P \qquad (10)$$

measuring V_2^∞ over a sufficiently large temperature range might be a useful method to evaluate the "structure-making" or "structure-breaking" character of a solute. The rapidity of the present experimental method makes this approach appear attractive.

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The development and construction of the interface for the counter by Walter Babcock is gratefull acknowledged.

Literature Cited

(1) Prausnitz, J. M. "Molecular Thermodynamics of Fluid Phase Equilibria"; Prentice Hall: Englewood Cliffs, NJ, 1969.
(2) Rettich, T. R.; Handa, Y. P.; Battino, R.; Wilhelm, W. *J. Phys. Chem.* **1981**, *85*, 3230.
(3) Ben-Naim, A. "Water and Aqueous Solutions. Introduction to a Molecular Theory"; Plenum Press: New York, 1974.
(4) Battino, R.; Clever, H. L. *Chem. Rev.* **1966**, *66*, 395.
(5) Clever, H. L.; Battino, R. "Solutions and Solubilities"; Dack, M. R. J., Ed.; Wiley: New York, 1975; Vol. 8, Part 1, p 379.
(6) Long, P. L. Master's Thesis, Emory University, Atlanta, GA, 1978.
(7) Kratky, O.; Leopold, H.; Stabinger, H. *Z. Angew. Phys.* **1969**, *27*, 273.
(8) Picker, P.; Tremblay, E.; Jolicoeur, C. *J. Solution Chem.* **1974**, *3*, 377.
(9) Groller, J.-P. E.; Benson, G. C.; Picker, P. *J. Chem. Eng. Data* **1975**, *20*, 243.
(10) Wilhelm, E.; Groller, J.-P. E.; Karbalai Ghassemi, M. H. *Monatsh. Chem.* **1978**, *109*, 369.
(11) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(12) Battino, R.; Banzhof, M.; Bogan, M.; Wilhelm, E. *Anal. Chem.* **1971**, *43*, 806.
(13) Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219.
(14) Brelvi, S. W.; O'Connell, J. P. *AIChE J.* **1972**, *18*, 1239.
(15) Pierotti, R. A. *J. Phys. Chem.* **1965**, *69*, 281.
(16) Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717.
(17) Helper, L. G. *Can. J. Chem.* **1969**, *47*, 4613.
(18) Tiepel, E. W.; Gubbins, K. E. *J. Phys. Chem.* **1972**, *76*, 3044.
(19) Kobayashi, R.; Katz, D. L. *Ind. Eng. Chem.* **1953**, *45*, 440.
(20) Enns, T.; Scholander, P. F.; Bradstreet, E. D. *J. Phys. Chem.* **1965**, *69*, 369.
(21) Popov, G. A.; Drakin, S. I. *Zh. Vses. Khim. Obshchest.* **1972**, *17*, 696.
(22) Krichevsky, I. R.; Ilinskaya, A. A. *Acta Physicochim. URSS* **1945**, *20*, 327.
(23) Hiraoka, H. *Kogyo Kagaku Zasshi* **1959**, *62*, 921.

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Propylene Carbonate Cryoscopy

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The melting point and the molal melting point depression constant of propylene carbonate have been determined to be –54.53 ± 0.05 °C and 4.38 ± 0.18 °C m^{-1}, respectively. This melting point differs substantially from the most widely quoted value.

Introduction

The literature reports five estimates of the melting or freezing point of propylene carbonate (PC, 4-methyl-2-dioxolone) ranging from –41 to –73 °C (**1**–**5**), a surprisingly large range for such a value. The most widely quoted value of –49.2 °C (*1*) refers to the freezing point of PC as manufactured, which is ca. 98% pure. This value, which is derived from visual detection of the formation of a solid phase on cooling (*6*), may well reflect an artifact. As manufactured, PC commonly contains a few tenths of a percent of water, and the phase diagram of the PC–water system indicates that for such composition a solid–liquid phase transition occurs a few degrees above the melting point of pure PC (*4*). This suggests that visual detection for the formation of a solid phase on cooling the impure PC may be misconstrued as an indication of the true freezing point, leading to too high an estimate of the freezing point. In addition to this uncertainty in the melting point, the melting point depression constant of PC is unknown. We report here carefully measured values of the melting point and the molal melting point depression constant of highly purified PC.

Experimental Section

After purification by vacuum distillation (*7*), PC contained less than 1 ppm water, which was the only impurity detectable by gas chromatography. All preparative work was performed in a drybox with a moisture content of less than 1 ppm.

The apparatus for determination of the melting point was similar to that described by Anderson (*8*). The temperature probe was a glass-shielded thermistor (Omega No. 44004), whose resistance was monitored with a digital ohmmeter (Data Precision No. 1450) whose calibration is traceable to an NBS standard. The resistance of the Omega thermistor, which was ca. 200 kΩ at –55 °C, could be determined to within 0.3 kΩ, which corresponds to a temperature uncertainty of ±0.02 °C. This thermistor was calibrated over the range of interest against a reference thermistor (Thermometrics No. P85AA392N) which had been calibrated by the manufacturer and whose calibration is certified to be accurate to within ±0.05 °C. A Dewar flask of chloroform maintained at –41 ± 2 °C by a refrigerated immersion coil served as a warming bath.

All cryoscopic measurements were performed under a blanket of dry nitrogen with mechanical stirring. The sample was cooled initially with liquid nitrogen, and, when the temperature dropped below –55 °C, the stirring was interrupted momentarily and several drops of solid–liquid PC seed crystal slurry were added to the supercooled liquid. After the quantity of solid phase had become sufficient that the stirrer action became sluggish, the liquid-nitrogen cooling bath was replaced by the chloroform warming bath. Temperature–time data were then recorded for ca. 1 h during which period the solid phase melted completely and the temperature rose to ca. –46 °C.

Results and Discussion

Initial attempts to measure the freezing point of PC gave poorly reproducible results, a problem which we attribute to the high viscosity of PC just above its freezing point. This reduces the effectiveness of stirring and causes low crystallization velocities, and it may be a principal cause of the well-known tendency of PC to supercool. Because determination of the melting point is not subject to the problem of supercooling and can be performed under conditions which ensure a close approach to equilibrium, it proved to be much more precise.

Temperature–time plots for the melting of PC, such as that shown in Figure 1, were analyzed by the graphical and mathematical method of Taylor and Rossini (*9*) to determine the

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