High-pressure investigations of solubility*

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Abstract: We have measured the solubilities of several inorganic and organic compounds at high pressures up to 400 MPa. For this purpose, care should be exercised in instrumentation. The results include solubility values for aqueous solutions of NaCl, NaCl·2H$_2$O, toluene, anthracene, phenanthrene, and amino acids (Gly, Ala, Val, Leu, and Ile). In addition, we determined the solubility of C$_{60}$ in *n*-hexane and toluene. The data for individual systems served to elucidate the mechanisms of dissolution. For example, the data for toluene, anthracene, and phenanthrene in water provided insight into hydrophobic hydration.

Keywords: solubility; hydrophobic hydration; clamp-type cells; fullerene solubility; high pressure.

INTRODUCTION

Solubility, one of the fundamental properties of a system with two or more components, is a function of both pressure and temperature. It is important to determine the domain where the system is stable without any phase separation or precipitation. High-pressure solubility recently has become relevant to such industrial fields as high-pressure crystallization [1] as a separation or purification process, and the high-pressure treatment of foods [2].

We have measured the high-pressure solubility of several compounds having typical and simple structures. In this review, we discuss our results and describe the technical issues pertinent to high-pressure solubility.

METHOD OF SOLUBILITY MEASUREMENT UNDER HIGH PRESSURE

Solubility measurements generally consist of 4 processes: (1) mixing or stirring of the solute and solvent; (2) holding a constant pressure and temperature for a long time; (3) separating the saturated solution from a mixture; and (4) measuring the concentration of the saturated solution. Until each operation has been mastered, the investigator should not attempt to measure the solubility. The same situation applies to high-pressure solubility determinations; furthermore, any such measurement under high pressure would face the additional restriction imposed by the extreme conditions at hand.

The following are the points of interest in high-pressure measurements:

1. *Mixing or stirring of the sample*: The mixing or equilibration times for our solutes range from one day to several weeks. Stirring with a screw, a magnetic stirrer, or a sonicator are the usual methods for mixing under atmospheric pressure. But they are not convenient for a high-pressure vessel that is completely closed, though in one case, a magnetic shaker was inserted into a pressure

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vessel [3] by means of a special technique. Fortunately, such a rigorous mixing is not always required in the solubility measurement. In most cases, shaking the mixture several times a day is enough to produce equilibration. Indeed, in the past, researchers have not stirred their solutions, but have waited for an equilibration to be reached by convection or by the diffusion of a solution in a heavy pressure vessel [4–7].

2. *Regulation of pressure and temperature*: There are two methods for regulating the temperature of the pressure vessel. The first is immersing the pressure vessel in a thermostatic water bath. The second is attaching a heat exchanger through which thermostatic water circulates to the pressure vessel. The former method is better in the accuracy of its temperature regulation, but is not applicable to a pressure vessel made of a corrosive material such as carbon steel.

    In our measurements, the pressure in the vessel was fixed at a constant value by completely sealing or closing the pressure vessel, or the whole high-pressure system. Using a pressure regulator in which the piston of a hydraulic pump often moves back and forth adversely affects accuracy in the high-pressure region. Therefore, the most important factor in experiments involving high-pressure solubility is understanding how to completely seal the vessel or whole system for a long time.

3. *Separation of the sample mixture*: The separation of the saturated solution from the solute particles with a filter seems convenient, but in fact, is not good, because fine particles can escape through it. We can avoid this difficulty with the filter by using a method that does not generate these smaller particles. Here, success mainly depends on the intensity of the mixing or stirring of the sample. In the case of the solubility of naphthalene in water or fullerene in hexane, mixing by a sonicator or a magnetic stirrer is too vigorous and results in fine particles which cannot be filtered. In such cases, a mild shaking, using a seesaw and a mixing ball, is better.

4. *Measuring the concentration of a saturated solution*: For this task, high-pressure solubility experiments have relied on two procedures. In the first, the concentration is measured in the pressure vessel at high pressures. In the second, it is measured at atmospheric pressure after the saturated solution has been removed from the pressure vessel. The former has the advantage of measuring the concentration with fewer operations, but the disadvantage that a calibration for estimating the concentration must be carried out at a high pressure, a situation which may cause a loss of accuracy. In the latter operation, the saturated solution has to be taken out from the pressure vessel before the concentration is measured. This removal must be performed with particular caution, and without disturbing the sample mixture at a high pressure. We have designed and used types of pressure vessels that work with both methods.

Considering the means to prevent the leaking of compression oil and to achieve a long equilibration time is important for the design of high-pressure equipment components for the solubility measurement; that is, the investigator must decide how to maintain the pressure securely and constantly for a long time. As the equipment consists of many fittings and parts, the pressure of the equipment cannot be regulated if even one of them has a problem. A high-quality control of the sealing technique for each fitting and part, and the maintenance of these parts and fittings—in other words, "quality control for high pressure"—is absolutely necessary.

Clamp-type optical cell

Figure 1 illustrates our design for a clamp-type optical cell made of 17-4PH stainless steel [8]. This cell was used for experiments testing the solubility of toluene in water under high pressures [9]. The sample solution, a few drops of toluene and water, fills a space between a pair of optical windows (E) made of sapphire and allowing observation of the sample. The ball (F) in the sample space (G) is made of fluoride polymer and used for mixing the sample. Pressure is applied to this cell (see Fig. 2) by means of an oil press to push the piston (B). After the piston has been pushed into the cell cylinder (C), clamp

nut (A) is tightened. Then, the high pressure in the cell can be maintained while the cell is removed from the oil press. In our experiments, the cell was placed on a seesaw in a thermostatic water bath, and moved up and down for several days. Finally, it was taken out of the water bath and placed in the sample compartment of the spectrophotometer so that the absorption spectra of the sample solution in the cell could be measured. In the toluene in water case, since only a few drops of toluene were present, only the water phase could be observed in the cell.
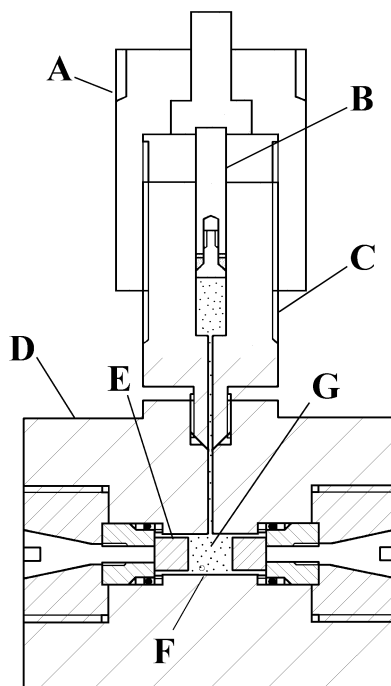

Fig. 1 Clamp-type optical cell [8]. A, clamp nut; B, piston; C, cylinder; D, main body; E, optical window; F, ball; G, sample space.

In such measurements of high-pressure solubility with an optical cell, the density of the solution should increase, the molar extinction coefficient of the solute should change, and the path length in the cell should rise with added pressure. These changes can be calibrated by measuring separately the absorption spectra of a dilute solution of toluene in water at high pressures [9]. As the absorbance of toluene in water was too high to measure, a clear cylindrical block replaced the stirring ball in the sample space (G) so that the path length might be reduced. Two types of pressure gauge were used for the oil press. One was a Bourdon-tube type (F in Fig. 2), and the other was a load cell (G in Fig. 2) with a main body made of phosphor bronze and specially machined by us to accept strain gauges. To estimate the pressure in the cell, we calibrated these pressure gauges by directly connecting a standard gauge to the optical cell at the window in advance.
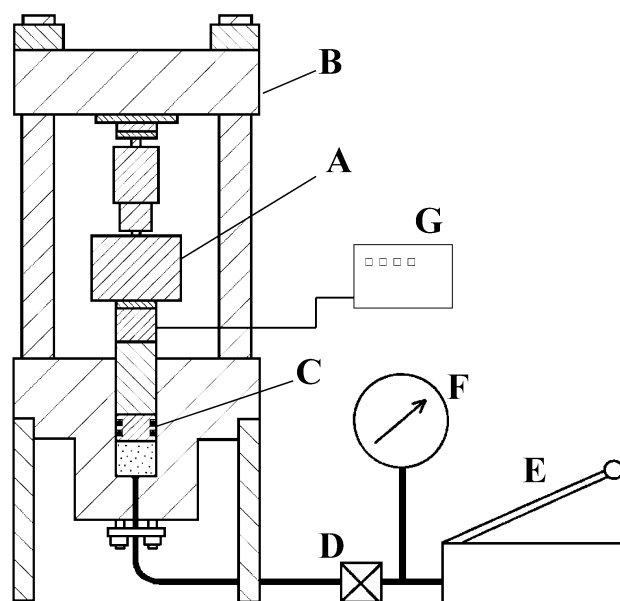
Fig. 2 System for pressing the clamp-type optical cell [8]. A, clamp-type optical cell; B, oil press; C, piston; D, valve; E, hydraulic pump; F, pressure gauge; G, load cell.

Cylindrical vessel with a valve

Figure 3 shows the pressure vessel for the preparation of a saturated solution of solid solutes under high pressure; e.g., sodium chloride or anthracene in water. The outer diameter of the main body (A) is 70 mm, and the inner bore is 15–18 mm. It is made of 17-4PH stainless steel and includes a valve (G) and an outlet tube (H). A jacket in which hot water circulates is attached to the outlet tube (H), and the valve block (G) is equipped with a similar mechanism for circulating hot water. An inner cell (B) made of poly(chlorotrifluoroethylene) plastic is connected to a plug (I). A glass filter, attached to the tip of the inner cell, separates the solid solute from the sample solution. The solvent and an excess quantity of a solid solute was placed in the inner cell fitted with a shaking ball (F) of poly(tetrafluoroethylene) plastic. The sample mixture and the hydraulic oil (kerosene) in the inner cell were separated by a piston [of poly(chlorotrifluoroethylene) plastic] with two fluoride o-rings. When we directly inserted such a piston into the pressure vessel without using the inner cell, a narrow gap would open between the piston and cylinder of the pressure vessel. Because the cylinder would expand, and pressure would compress the piston, compressive oil would contaminate the sample solution at pressures higher than 200 MPa. Thus, we used an inner cell as shown in Fig. 3. For sealing between the main body (A) and the plug (I), we used a fluoride o-ring and a back-up ring, which was made of annealed tough-pitch copper and designed by us with an accuracy of 0.01 mm; we exchanged these parts in each measurement. The valve cone (G) and other metal-to-metal sealing parts were often cut and polished, and some parts were exchanged for new ones. Such frequent maintenance for high-pressure sealing allows us to easily and safely hold a constant high pressure for a long time.

Figure 4 shows an entire high-pressure system. The pressure vessel (A) was fixed on a seesaw (F) in a water bath (J, 40 dm^3), and the seesaw was moved 2–3 times a minute for agitation of the solution. Hydraulic oil was pushed into the pressure vessel from a hydraulic pump (B) through a flexible stainless tube (E) with an outer diameter of 1.6 mm. The use of such a flexible tube permitted the pressure vessel connected to the tube to be shaken on the seesaw. Because the tube (E) was not immersed in a water bath, the pressure in the system consisting of the tube, the pressure vessel (A), and the closure valve (D) would have depended on the temperature of the room. However, that effect is negligibly small,
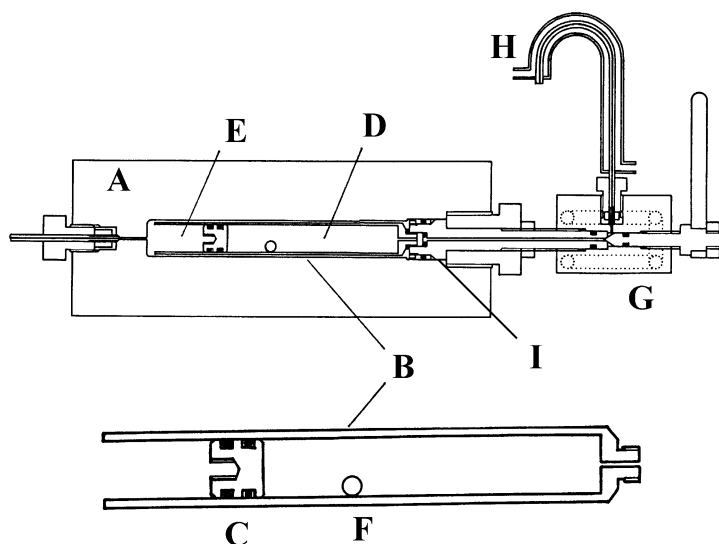
Fig. 3 Cylindrical pressure vessel with a valve and an inner cell [10]. A, main body; B, inner cell; C, piston; D, sample room; E, compression oil; F, ball; G, valve with a heating device; H, outlet tube with a heating jacket; I, plug.
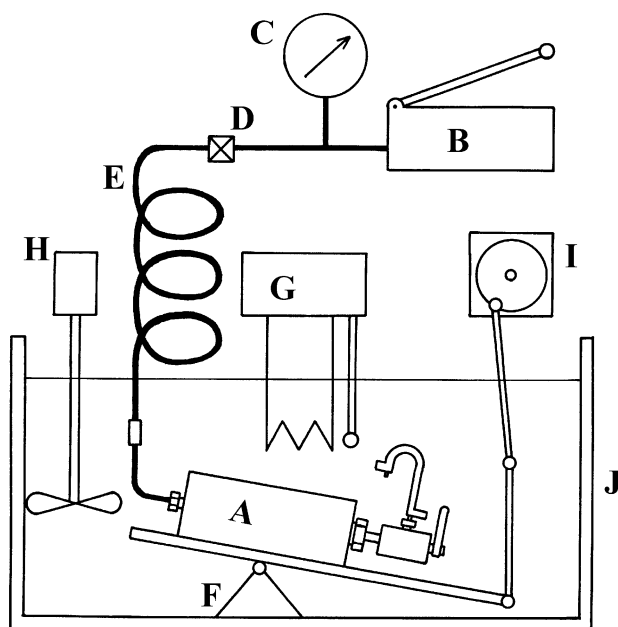

Fig. 4 Mixing equipment for the cylindrical pressure vessel with a thermostat [10]. A, pressure vessel; B, hydraulic pump; C, pressure gauge; D, valve; E, flexible tube; F, seesaw; G, thermoregulator; H, stirrer; I, motor with a reduction gear; J, water bath.

because the inner volume of the tube is only 1/50 of that of the pressure vessel. As the pressure in such a closed system decreased with the dissolution of the solute, we adjusted the pressure in the vessel several times until the system attained equilibrium. Using this process, we can conveniently recognize the equilibrium; pressure adjustments are no longer needed at the equilibrium state.

After stirring for several hours, the seesaw was stopped and the pressure vessel was allowed to stand for a while so that the particles of the solid solute in the inner cell could sink. Then, the sample solution was taken out drop by drop from the outlet by loosening the valve. Throughout this operation, the vessel (A) was held at a constant pressure by pushing hydraulic oil into the vessel from pump. The initial portion (2–3 cm^3) of the solution was discarded, and the subsequent part (7–9 cm^3) was collected. The sample, in the case of sodium chloride in water, was weighed before and after drying in an electric oven at around 440 K so that the concentration might be determined. For anthracene and phenanthrene in water, spectroscopic method was used. When the sample solution was removed from the pressure vessel, hot water was circulated around the valve (G) and outlet tube (H) in Fig. 3 to avoid any precipitation of the solute.

In this cylindrical cell, pressure was measured with a precise, Bourdon-tube type gauge (C in Fig. 4) with an accuracy of ±1 MPa. It was connected to the hydraulic pump (B) and the pressure vessel (A). The pressure gauge was a Heise model (45 cm diameter, produced by Dresser Industries, with a full-scale reading of 700 MPa and a smallest division of 0.5 MPa). It was calibrated by the manufacturer with a standard free-piston-type pressure gauge with an accuracy of 0.01 % of full scale according to the American National Standards Institute methods NCSL Z540-1 and ISO-10012. Because of the long duration of the solubility measurements, we recalibrated the pressure gauge (C) with a new pressure gauge of the same type purchased from and calibrated by Dresser industries.

The temperature of the water bath was regulated within ±0.05 K by means of an on-off type regulator designed by us with a sensitivity better than 1 mK. A regulating heater with suitable power was selected, and a cooler unit was included in case of need. The temperature was measured with a three-wire platinum resistance thermometer.

INORGANIC COMPOUNDS IN WATER

Sodium chloride in water is a typical solute/solvent pair for solubility studies. The number of papers providing measurements of the solubility of this pair is over 100 [11]. Figure 5 shows the domains where measurements have been done at pressures higher than 3 MPa. In this figure, only four studies, numbers 2, 3, 4, and 5, have exceeded a pressure of 50 MPa, and the bulk of these studies are about 100 years old. In these experiments, several methods were used to obtain a saturated solution. Usually, the general method for experiments under atmospheric pressure, i.e., mixing the solid solute and solvent for a long time, was used at high pressures. For example, Cohen et al. [3] inserted a magnetically agitated shaker in a pressure vessel. Their arrangements were too structurally complex to be useful. Sill [14] shook an entire pressure vessel. Adams et al. [4] prepared a saturated solution by convection without any shaking. The maintenance of a constant pressure for a long time with such apparatus is not easy at pressures over 50 MPa. Therefore, after their studies, no further direct measurements were carried out at these high pressures. Alternatively, other authors have attempted to use the density of the solution to estimate high-pressure solubilities thermodynamically [19,20].

Several improvements in the design of pressure vessels and other high-pressure components, such as hydraulic pumps, pressure gauges, fittings, and so on, have been made in the 80 years since Adams et al. published their work [4]. Now, we can measure solubility under high pressure more reliably. Using the pressure vessel shown in Fig. 3, we have evaluated the solubility of sodium chloride in water as a function of pressure and temperature [18]; we present our results in Fig. 6. The low temperature region represents the solubility of NaCl·2H$_2$O in water. The standard deviations for both solutes are ca. 0.1 %, comparable with atmospheric pressure results.
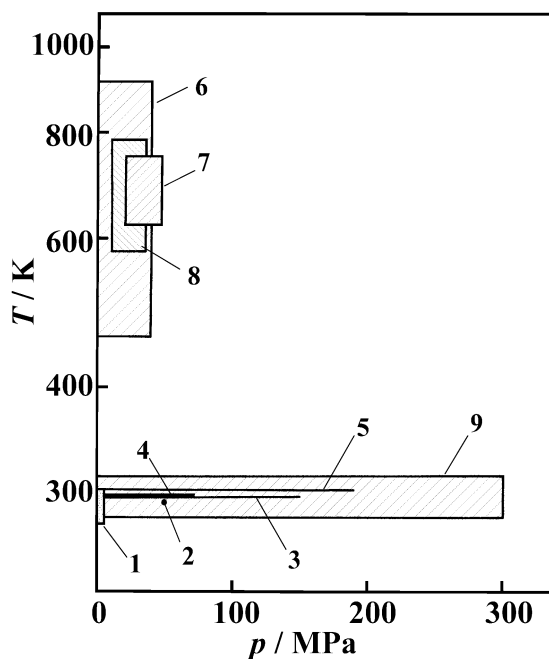
Fig. 5 Diagram of solubility data of sodium chloride in water ($p > 3$ MPa). 1, K. Möller (1862) [12]; 2, E. F. von Stackelberg (1896) [13]; 3, E. Cohen et al. (1910) [3]; 4, H. F. Sill (1916) [14]; 5, L. H. Adams, et al. (1931) [4]; 6, N. B. Keevil (1942) [15]; 7, A. Olander (1950) [16]; 8, J. L. Bischoff et al. (1986) [17]; 9. S. Sawamura et al. (2006) [18].
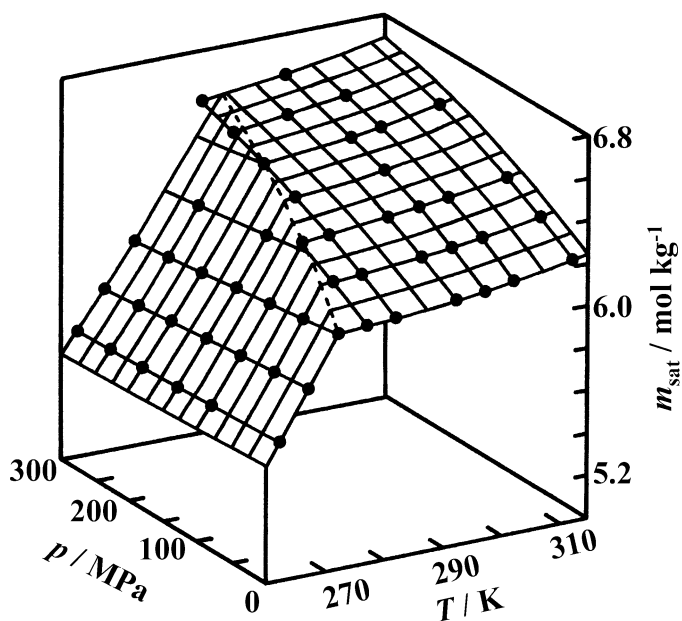

Fig. 6 Solubility of sodium chloride in water [18].

The pressure coefficient of the logarithm of the solubility of sodium chloride in water is thermodynamically related by eq. 1 to the volume change, ΔV°, accompanying dissolution [21]:

$$\theta_p \equiv (\partial \ln m_{sat}/\partial p)_T = -[\Delta V^\circ/(2RTf_\gamma)][A/(A - nm_{sat})] \qquad (1)$$

where A is the amount of substance of water molecule in 1 kg ($A = 55.51$ mol) and n is the number of molecules of water in the formula of the hydrate ($n = 2$ for NaCl·2H$_2$O). In addition,

$$f_\gamma \equiv 1 + (\partial \ln \gamma_\pm/\partial m)_{T,p} \qquad (2)$$

where $\gamma_\pm$ is the mean activity coefficient of the ion. As shown in eq. 3, the term ΔV° corresponds to the difference between the partial molar volume, V'_{sat}, of the solute (including that of 2 mole of water for NaCl·2H$_2$O) at a saturated concentration and the molar volume, V_C, of the solid solute.

$$\Delta V^\circ = V'_{sat} - V_C \qquad (3)$$

Using these three equations and the data for the V'_{sat}, V_C, and $\gamma_\pm$, θ_p can be estimated to be $(3.82 \pm 0.25) \times 10^{-4}$ MPa^{-1} for NaCl and $-(0.94 \pm 0.47) \times 10^{-4}$ MPa^{-1} for NaCl·2H$_2$O, respectively [18]. On the other hand, the experimental values of θ_p for NaCl and NaCl·2H$_2$O, evaluated from Fig. 6, are $(4.05 \pm 0.04) \times 10^{-4}$ MPa^{-1} at 0.10 MPa and 298.2 K and $-(0.74 \pm 0.05) \times 10^{-4}$ MPa^{-1} at 0.10 MPa and 273.2 K, respectively. The accuracy of the latter values is better than that of the former, though both values of θ_p coincide within the experimental error. Such a difference may be ascribed to a lower accuracy for the density of solution and solid solute (V'_{sat} and V_C). Similar situations have been observed in measurements of the high-pressure solubility of NH$_4$Cl [22], CsCl [10], and NaBr·2H$_2$O [23] in water. In the last case, even the signs calculated for θ_p differ from those of the direct measurement.

NONPOLAR ORGANIC COMPOUNDS IN WATER

In this section, we discuss the solubility of aromatic hydrocarbons in water. The solutes used comprise models for hydrophobic solutes. Figure 7 shows the solubility of toluene in water [9], which was measured with a clamp-type optical cell (Fig. 1). The solubility as a function of pressure and temperature exhibits an appreciably distorted surface; similar distortions were observed for the solubility of ethylbenzene and propylbenzene in water [9]. The isothermal solubility curves have a maximum at all temperatures, while the isobaric curves exhibit a minimum at atmospheric pressure, which diminishes at pressures approaching 400 MPa.

The pressure coefficient of the logarithm of solubility, x_S, is thermodynamically related to the volume change, ΔV°, accompanying the dissolution, as shown in eq. 4

$$[\frac{\partial \ln x_S}{\partial p}]_T = -\frac{\Delta V^\circ}{RT} \qquad (4)$$

where

$$\Delta V^\circ = V^\infty - V^* \qquad (5)$$

Though ΔV° should be equal to the difference between the partial molar volume, V'_{sat}, of the solute in saturation, and the molar volume of solute, V^*, in eq. 5, we take V'_{sat} to be equal to the partial molar volume of the solute at infinite dilution, V^∞, because the solubility of the solute is very low. In the case of toluene, where V^* is the molar volume of a liquid hydrophobic solute, the ΔV° of eq. 5 corresponds to a volume change for hydrophobic hydration. In the past, the sign of the volume change accompanying hydrophobic hydration has been believed to be negative at atmospheric pressure. However, using eqs. 4 and 5, we can show that the solubility maximum at each temperature means that the sign of ΔV° for hydrophobic hydration changes at this point, with increasing pressure, from negative to positive [9]. From a similar thermodynamic analysis for the minimum of the isobaric solubility
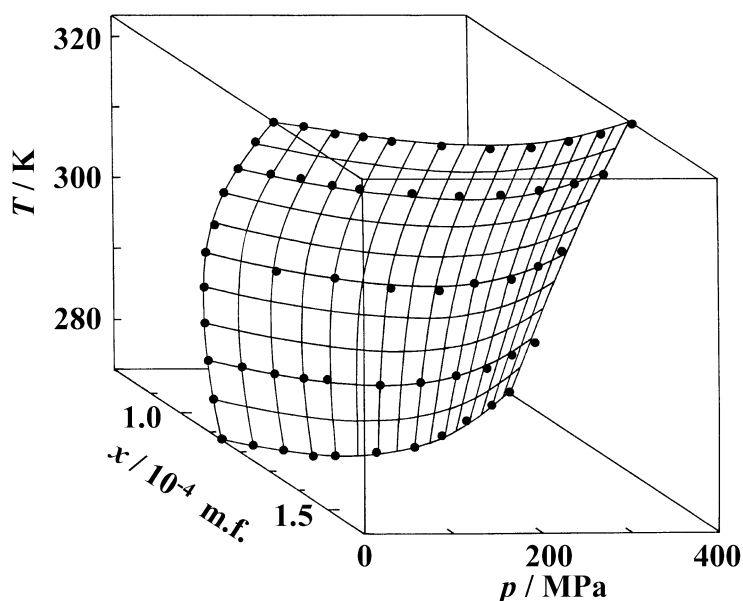
Fig. 7 Solubility of toluene in water [9,24].

curve at atmospheric pressure in Fig. 7, the heat capacity for hydrophobic hydration has been thought to be positive, a hypothesis suggesting the formation of an iceberg-like structure around the solute. However, the data in Fig. 7 indicate that this heat capacity diminishes at high pressures of 400 MPa.

The density, or V^*, of a pure liquid such as toluene at high pressures can be measured by the usual technique for high-pressure experiments [25]. Thus, using eq. 5 and our high-pressure solubility data, we can estimate the V^∞ of hydrophobic compounds in water as a function of pressure and temperature. These results are provided in Fig. 8. The V^∞ values reach a maximum in the low temperature region, and the sign of its compressibility is negative at lower pressures [9]. This negative compressibility means that the bulk water is more compressible than the hydration water in this region [24].

Figure 9 shows the solubility of anthracene and phenanthrene in water [26], measured with a cylindrical pressure vessel with a valve, as shown in Fig. 3. The logarithm of the solubility decreased linearly with increasing pressure. Equations 4 and 5, where the V^* for anthracene and phenanthrene is the molar volume of the solid solutes, not the liquid ones, indicate that the observed phenomena suggest that the partial molar volume is larger than the molar volume of the solid solute. Furthermore, the compressibilities of both volumes are similar, because ΔV^o does not depend on pressure. A similar linear reduction in the solubility was observed for naphthalene in water [27].

Using the ΔV^o estimated from the high-pressure solubility and the V^* of anthracene evaluated from X-ray data, we can estimate the V^∞ of anthracene in water to be 158.2 cm^3 mol^{-1} at atmospheric pressure. Though such a partial molar volume is usually estimated from the concentration dependence of the density of the solution, such a procedure is impossible for the cases of anthracene or phenanthrene in water because of their low solubility. Thus, high-pressure solubility provides the sole method of estimating this quantity.

The difference between the V^∞ of hydrocarbon in water and that in a nonpolar solvent corresponds to the volume change for hydrophobic hydration. This volume change is estimated to be –4.1 cm^3 mol^{-1} for benzene, –0.5 cm^3 mol^{-1} for naphthalene [27], and +1.4 cm^3 mol^{-1} for anthracene [26], respectively; to obtain these results, we used the V^∞ in water estimated from high-pressure solubility values and the partial molar volume of the solutes in a nonpolar solvent. Our findings indicate that the volume change for hydrophobic hydration increases with increasing molecular weight for a series

of hydrophobic solutes. This conclusion is contrary to the well-known attribution of a negative volume change to hydrophobic hydration, based on the fact that the volume change for hydrophobic hydration of the methylene group is –0.5 to 2 cm^3 mol^{-1} at atmospheric pressure [24]. Evidently, the volume change depends strongly on the structure of hydrophobic groups, such as whether they are aliphatic hydrocarbons or aromatics. Since Kauzmann proposed the existence of a "hydrophobic bond" in 1959, the volume change for hydrophobic hydration has been believed to be a negative value. Our new findings for the ΔV may occasion a reassessment of the topic of hydrophobic hydration.
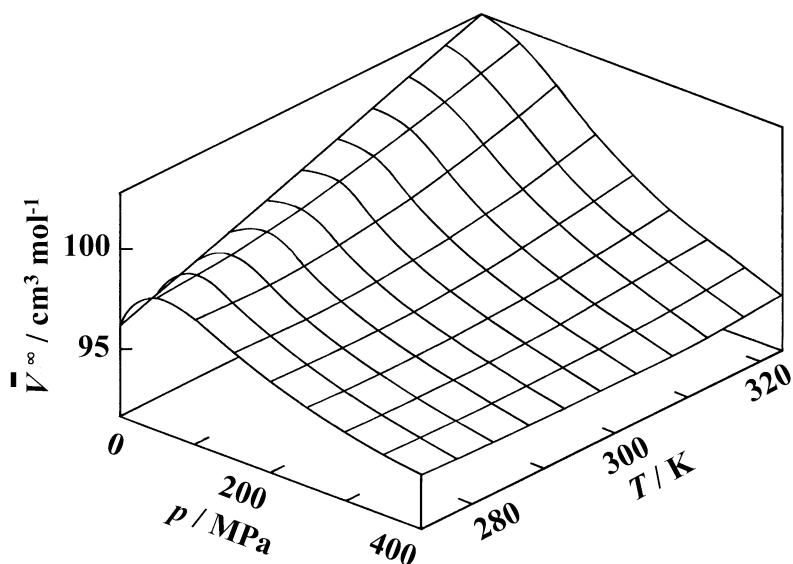

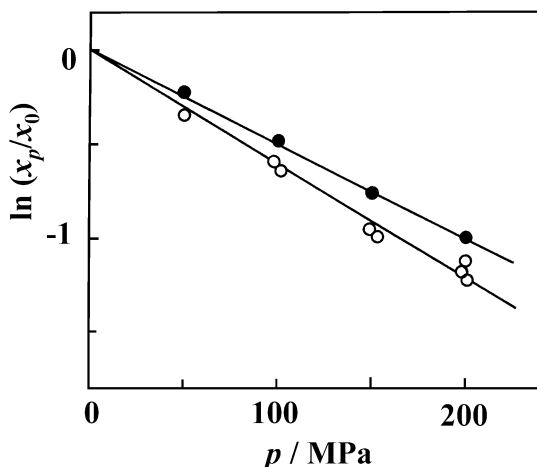**Fig. 8** Partial molar volume of toluene in water [9,24].

Fig. 9 Solubility of anthracene (○) and phenanthrene (●) in water at 298.15 K [26].

SOLUBILITY OF FULLERENE C$_{60}$

The high-pressure solubility of fullerene C$_{60}$ in hexane is presented in Fig. 10 [28]. This data was taken with a clamp-type optical cell, as shown in Fig. 1. The solubility steeply increases with increasing pressure. A similar pressure enhancement of the solubility of fullerene C$_{60}$ was observed in toluene at a low-pressure and high-temperature region, as demonstrated in Fig. 11. Another high-pressure and low-temperature region exists for the solubility of the solid solvate, C$_{60}$·2C$_7$H$_8$ [30]. However, it has been generally found that the solubility of nonpolar solids decreases with increasing pressure; e.g., the solubility of phenanthrene, tin tetraiodide, and hexachloroethane in hexane [29] shown in Fig. 10, and that of anthracene and phenanthrene in water [26] shown in Fig. 9. Equations 4 and 5 have provided a basis for understanding such reductions by pressure of the solubility of nonpolar solids, because the molar volume of a solid in which the solute molecules are ordered is lower than the partial molar volume of the solute in a solvent, where the solute molecule has space to move around. On the other hand, the enhancement of the solubility of fullerene C$_{60}$ in hexane with increasing pressure thermodynamically means that the solid solute is bulky compared with the solute in the solvent. The spherical molecule of fullerene C$_{60}$ has a face-centered cubic form in the solid phase. The solid C$_{60}$ has large spaces in which any molecule does not occupy, among the spherical molecules. When the solid C$_{60}$ is dissolved in hexane, the void volume decreases, because the small size of the solvent molecules allows them to fill the spaces around the solute molecules [28]. Overall, then, the present study of the high-pressure solubility of fullerene C$_{60}$ seems to tell us that recently discovered materials such as fullerene may generate new and previously unforeseen phenomena.
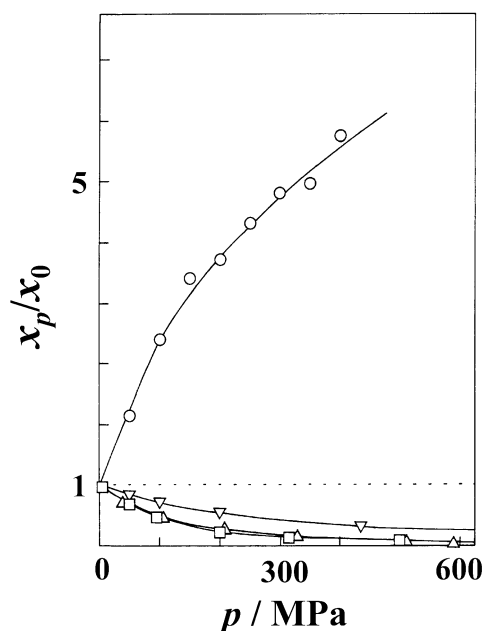

Fig. 10 Pressure dependence of the solubility for C$_{60}$ and several compounds in hexane at 298.2 K [28]. ○, fullerene C$_{60}$; ▽, phenanthrene [29]; □, SnI$_4$ [29]; △, C$_2$Cl$_6$ [29].
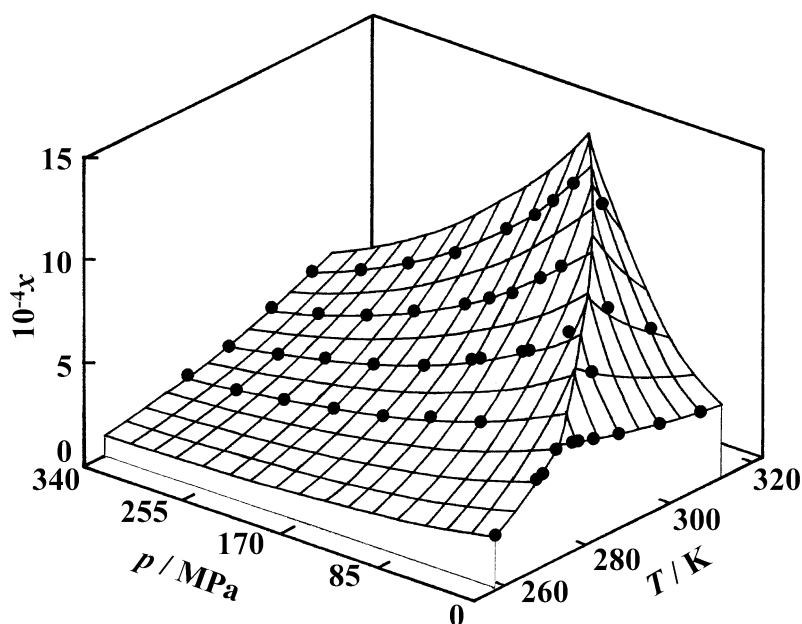
Fig. 11 Solubility of C_{60} in toluene.

POLAR ORGANIC SOLIDS IN WATER

As a comparison with the high-pressure solubility measurements of nonpolar solids such as anthracene, the solubility of amino acids, typical polar organic solids, in water was determined with a pressure vessel with a valve, as shown in Fig. 3. The results are shown in Fig. 12 [31]. That of sodium L-glutamate dihydrate, a famous seasoning, in water was also assessed [32], though not dealt with here. This figure demonstrates that the amino acid solubilities at atmospheric pressure decrease in the order of glycine (Gly), L-alanine (Ala), L-valine (Val), and L-leucine (Leu) or L-isoleucine (Leu), that is, with increases in the number of methylene or methyl substituents. However, no systematic change was observed for their high-pressure solubilities. The only common phenomenon for these amino acids is that the solubility-pressure curve is convex, a feature contrary to the linear reduction with increasing pressure of the logarithm of the solubility of nonpolar solids such as anthracene, etc. Based on eqs. 4 and 5, we suggest that these findings mean that the partial molar volumes of these amino acids in water are less compressible than the molar volumes of the solids. Such an interpretation is acceptable because the partial molar compressibility of amino acids in water, as well as that of electrolytes, is known to be negative [33,34]. The break point around 200 MPa for Leu in Fig. 12 is ascribed to a transition in the solid phase [35].
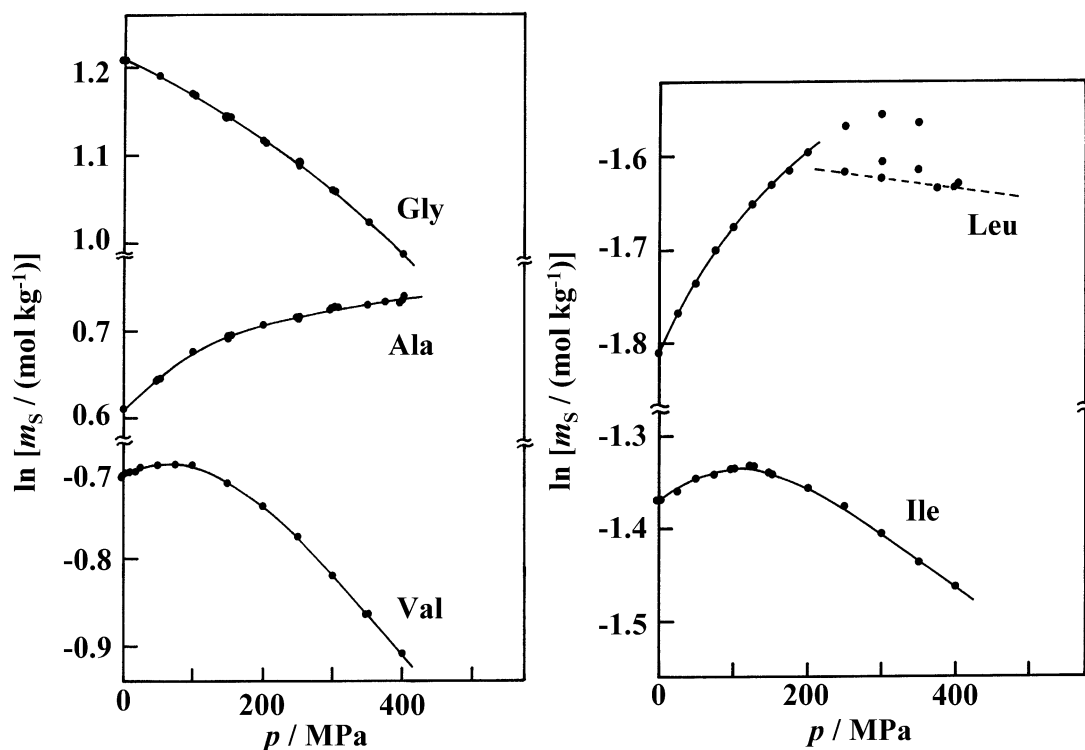
Fig. 12 Solubility of amino acids in water at 298.15 K [31].

CONCLUSION

Both high-pressure solubilities and solubilities at atmospheric pressure have been measured for more than 100 years. Improved accuracy in high-pressure measurements has accompanied technological progress in the sealing of pressure vessels and generating and regulating pressure in high-pressure systems. As a result, high-pressure solubility values become useful as a map for showing the domain where two or more components are stably present in a system free of phase separation or precipitation. Furthermore, such results enable us to estimate properties such as the partial molar volume of hydrophobic compounds in water, which can never be evaluated by any other method. Thus, high-pressure solubility measurements may provide a means to open up new scientific territory. To do so, the high-quality control of high-pressure techniques will be increasingly important.

ACKNOWLEDGMENT

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