Effects of Pressure and Temperature on the Solubility of Alkylbenzenes in Water: Volumetric Property of Hydrophobic Hydration

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The solubility of toluene, ethylbenzene, and propylbenzene in water was measured over conditions of 0.10–400 MPa and 273.2–323.2 K. Solubility was found to initially increase with increasing pressure and then decrease from a maximum at around 100 or 200 MPa. On the other hand, the solubility–temperature curve at 0.10 MPa exhibited a minimum at around 290 K. The solubility minimum of toluene disappeared at high pressures. The overall solubility–pressure–temperature surface resembles a portion of a distorted hyperboloid. The partial molar volume of these solutes in water was estimated from the pressure coefficient of solubility using the compression of the solutes in the pure liquid state, a property that was also measured in the present study. Expansion coefficient and isothermal compressibility of partial molar volume of hydrophobic groups in water at atmospheric pressure are estimated from literature data. The expansion coefficient of partial molar volume was found to be significantly larger at atmospheric pressure than at high pressure. Partial molar volume in the low-temperature region was found to increase with increasing pressure and then to decrease at pressures over ca. 100 MPa, resulting in a maximum. However, the maximum was found to disappear in the high-temperature region, where the volume decreases regularly. This behavior can be ascribed to a unique property of pure water: the compressibility of water increases with decreasing temperature, or the expansion coefficient increases with increasing pressure in the range of pressure and temperature in the present study. Such a unique property seems to weaken or disappear in the water under hydrophobic hydration.

Introduction

Several interesting thermodynamic phenomena have been observed when a hydrophobic molecule is transferred from a nonpolar solvent to the water phase: The partial molar entropy and partial molar volume of the solute decrease in the transfer ($\Delta S < 0$ and $\Delta V < 0$, respectively), the heat capacity increases ($\Delta C_p > 0$), and the enthalpy at low temperature decreases ($\Delta H < 0$).[1,2] These phenomena have been attributed to the ordering of water molecules around the solute. Kauzmann[2] pointed out that the ordering of water molecules around a hydrophobic molecule plays an important role in controlling the stability of biological macromolecules such as proteins and further proposed the idea of a "hydrophobic bond". Many subsequent studies have been conducted on hydrophobic interaction and hydration.[3]

Kauzmann suggested that the negative volume change that accompanies hydrophobic hydration is a driving force in protein denaturation by pressure.[2] However it has subsequently been discovered that the volume change that accompanies the dissolution of liquid hydrocarbons in water becomes positive at high pressures of around a few hundred MPa. This change in sign corresponds to high-pressure stability of proteins.[4,5] Therefore, hydrophobic interaction seems not always to be important in protein denaturation. To make the situation clear, as Kauzman pointed it out,[6] it is important to extend the study to a broader range of pressures and temperatures though many studies have persisted in ambient conditions.[3,7]

Though the thermodynamic properties of the hydrophobic interaction can be related to the difference between the partial molar quantities of hydrocarbon or nonpolar solute in liquid hydrocarbon and water phases, the specifics of the interaction between the solute and water molecules in water phase have only been effectively investigated since Frank and Evans[1] proposed the "iceberg structure" of hydration water and hence directing attention to the properties and structure of hydrophobic hydration. Computer simulations such as molecular dynamics or Monte Carlo methods have recently proven to be a useful research method, with reports[8,9] of several findings that water molecules surround a solute molecule in an ordered form, which invokes an analogy to clathrate hydrate. Similar "iceberg" formation has been observed using neutron diffraction, where water molecules gather around the quasi-hydrophobic tetraalkyl-ammonium ion in water,[10] and the directions of the O–H bonds of water molecules around argon and methane solutes are parallel to the surface of the solute molecules.[11,12] Additionally, the dynamic properties of hydration water have been measured using dielectric[13,14] and NMR relaxation[14–17] methods. Hydration water has been observed to undergo slower motion than bulk water, which allows solute molecules of benzene[17] and methane[15] to rotate almost freely in the hydration shell.

The iceberg structure proposed by Frank and Evans[1] has been supported by these studies. However, the behavior of hydrophobic hydration at high pressures where pressure denaturation of protein occurs has not been clarified.[5,18–21] The fact that the density maximum of pure water at 277 K becomes less pronounced with increasing pressure[22] indicates that the structure of pure water is dependent on pressure. For this reason, the

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corresponding structure of hydrophobic hydration at high pressure is attractive.

Generally, hydrophobic compounds have a low solubility. Therefore, several previous studies of hydrophobic hydration have utilized quasi-hydrophobic solutes bound to an ionic or hydrophilic substituent, such as an OH group, to obtain sufficiently high concentrations for the analysis of hydrophobic hydration from neutron diffraction measurement[10] and others.[3] Solubility, on the other hand, is easily measured even for hydrocarbons that do not include any polar substituent. Furthermore, low solubility is advantageous because chemical potential, which is related to solubility, can be regarded as the ideal case of an infinitely diluted solution. In the previous study, the high-pressure solubility of liquid alkylbenzenes in water was measured at 298.2 K.[5] The solubility−pressure curves exhibit a maximum at around 100 MPa. Thermodynamically, this means that the sign of the volume change that accompanies dissolution changes from negative to positive. This is an origin of the controversy concerning the importance of hydrophobic hydration in protein denaturation.[2,6] On the other hand, the solubility−temperature curves for liquid alkylbenzenes at atmospheric pressure are known to exhibit a minimum at around room temperature.[23,24] These pressure and temperature dependencies of solubility imply that the solubility−pressure−temperature surface will be rather distorted. The solubility behavior of hydrophobic compounds in water is important in clarifying hydrophobic hydration, so solubility in regard to pressure and temperature is investigated.

This study investigates hydrophobic hydration by examining the solubilities of toluene, ethylbenzene, and propylbenzene in water over a wide range of pressures and temperatures: 0.10−400 MPa and 273.2−323.2 K, respectively. The compressions of pure liquid alkylbenzenes were also measured and used to estimate the partial molar volumes of the solutes in water at high pressure. The solubility of these alkylbenzenes in water is low, the mole fraction of toluene being ca. 10^{-4} and the mole fractions of ethylbenzene and propylbenzene being 10^{-5}. Hence the pressure and temperature coefficients of the solubility, x_S, can be expressed as[25]

$$(\partial \ln x_S/\partial p)_T = -\Delta V/RT \tag{1}$$

$$(\partial \ln x_S/\partial T)_p = \Delta H/RT^2 \tag{2}$$

respectively, where ΔV is the difference between the partial molar volume of alkylbenzene in saturated solution and the molar volume V^* of the pure solute. The former volume can be considered to be V^∞ of an infinitely diluted solution because of the low solubility of hydrocarbons in water. Therefore, ΔV can be expressed as

$$\Delta V = V^\infty - V^* \tag{3}$$

Experimental Section

High-pressure solubility was measured using a clamp-type optical cell designed by the authors.[4] A few drops of alkylbenzene and bulk water were placed in the cell and pressed and then shaken on a seesaw in a thermoregulated water bath for a few days. The absorption spectrum of the water phase in the prepared cell was then measured. The absorbance at absorption maximaum around 260 nm was converted to concentration using Lambert−Beer law as shown in the next section. The equilibration time of alkylbenzenes in water was examined by the same

method as previous studies.[4] The compression, k, of pure alkylbenzenes was measured using a piezometer of mercury-trapped type.[26] The definition is

$$k \equiv (V_0^* - V_p^*)/V_0^* \tag{4}$$

where V_0^* and V_p^* are the molar volumes of alkylbenzene at atmospheric and high pressures, respectively. Details of the high-pressure cell, method of measurement, and purification of reagents have been reported previously.[5]

Results and Discussion

A. Estimation of Solubility. By the Lambert−Beer law, the solubility, $x_S(T,p)$, of alkylbenzene in a mole fraction unit at pressure, p, and temperature, T, is related to the absorbance, $A_S(T,p)$, by

$$A_S(T,p) = \epsilon(T,p)l(T,p)x_S(T,p)/V_S(T,p) \tag{5}$$

where ϵ and V are the molar absorption coefficient of the solute and the molar volume of the solution, respectively, and l is the pass length of the cell. Subscript "S" denotes saturation. To examine the pressure and temperature dependences of ϵ, l, and V, the Lambert−Beer equation for an aqueous solution of alkylbenzene in an unsaturated concentration is introduced. It is written as

$$A_U(T,p) = \epsilon(T,p)l(T,p)x_U(T,p)/V_U(T,p) \tag{6}$$

where subscript "U" denotes unsaturated concentration. The molar volume of the solution can be assumed to be that of pure solvent, i.e., $V_S(T,p) = V_U(T,p) = V_W^*(T,p)$, where $V_W^*(T,p)$ is the molar volume of pure solvent. Then eqs 5 and 6 reduce to

$$A_S(T,p)/A_U(T,p) = x_S(T,p)/x_U(T,p) \tag{7}$$

In a similar way, at a standard temperature, T_0, and pressure, p_0,

$$A_S(T_0, p_0)/A_U(T_0, p_0) = x_S(T_0, p_0)/x_U(T_0, p_0) \tag{8}$$

The same unsaturated solution is used in eqs 7 and 8; then $x_U(T,p) = x_U(T_0,p_0)$, and

$$x_S(T,p) = x_S(T_0,p_0)[A_S(T,p)/A_S(T_0,p_0)]/[A_U(T_0,p_0)/A_U(T,p)] \tag{9}$$

Therefore the solubility at T and p can be estimated from the solubility at T_0 and p_0 and the absorbance ratios.

B. Solubility at Atmospheric Pressure. To estimate solubility using eq 9, the solubility at a standard pressure and temperature is required. Alkylbenzene solubility data at atmospheric pressure have been collected by Hefter.[27] Using that data and other recent measurements[24,28−30] which are not cited in Hefter's collection, average solubilities at 0.10 MPa and 298.2 K were recalculated to be 1.090×10^{-4} for toluene, 2.880×10^{-5} for ethylbenzene, and 8.23×10^{-6} for propylbenzene. These values are not significantly different from those of Hefter,[27] which are 1.04×10^{-4}, 2.87×10^{-5}, and 8.2×10^{-6}, respectively. The recalculated values are used for $x_S(T_0,p_0)$ in eq 9 to estimate the solubilities at other conditions, as listed in Table 1. The temperature dependence of solubility at atmospheric pressure has been compared with the data in Figure 1, which are normalized to 298.2 K. A solubility minimum is clearly seen for all alkylbenzenes, and the temperature at which

Volumetric Property of Hydrophobic Hydration

J. Phys. Chem. B, Vol. 105, No. 12, 2001 **2431**

TABLE 1: Solubilities of Alkylbenzenes in Water (mole fraction)

| p (MPa)	T (K)										
	273.2	278.2	283.2	288.2	293.2	298.2[a]	303.2	308.2	313.2	318.2	323.2
	Toluene (×10⁻⁴)										
0.1	1.140	1.111	1.090	1.080	1.080	1.090	1.121	1.151	1.201	1.251	1.322
25	1.180		1.130						1.232		1.353
50	1.211		1.161			1.180			1.261		1.383
75	1.232		1.191						1.292		1.403
100	1.232		1.201			1.228			1.312		1.424
150	1.221		1.221			1.267			1.332		1.453
200	1.191		1.211			1.280			1.342		1.464
250	1.130		1.180			1.267			1.332		1.464
300	1.059		1.140			1.225			1.312		1.433
350	0.988		1.090			1.163			1.282		1.393
400	0.917		1.029			1.082			1.242		1.342
	Ethylbenzene (×10⁻⁵)										
0.1	3.234	3.084	2.964	2.880	2.863	2.880	2.946	3.047	3.188	3.338	3.525
25	3.329					2.987			3.375		
50	3.488		3.283			3.214			3.508		3.804
75	3.563								3.609		
100	3.617		3.404			3.312			3.675		3.954
150	3.591		3.384			3.347			3.741		4.199
200	3.358		3.300			3.298			3.758		4.283
250	3.151		3.151			3.214			3.704		4.291
300	2.964		3.030			3.090			3.637		4.199
350	2.776		2.863			2.952			3.525		4.078
400	2.609		2.730			2.768			3.404		3.871
	Propylbenzene (×10⁻⁶)										
0.1	9.01	8.65	8.38	8.23	8.16	8.23	8.41	8.74	9.18	9.82	10.57
25						8.83			9.77		
50	9.67		9.35			9.17			10.19		11.48
75											
100	9.97		9.64			9.56			10.78		12.17
150	10.08		9.79			9.58			11.07		12.53
200	9.82		9.69			9.36			11.21		12.63
250	9.55		9.37			9.06			11.14		12.87
300	9.18		8.88			8.58			10.96		12.63
350	8.76		8.45			8.11			10.60		12.07
400	8.27		8.00			7.67			10.21		11.66

[a] Ref 5.
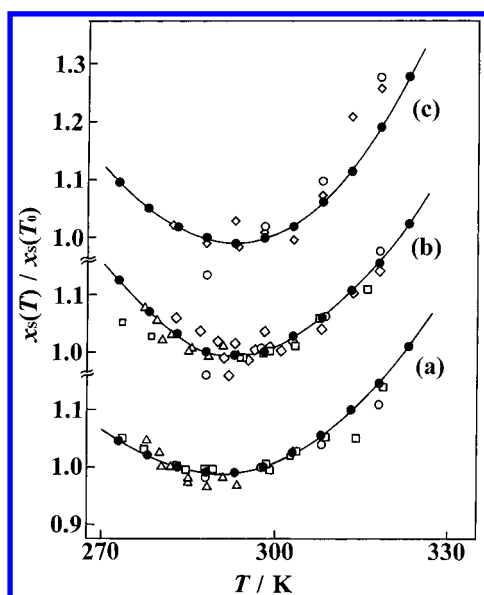
Figure 1. Temperature dependence of the solubility ratio, $x_S(T)/x_S(T_0)$, of alkylbenzenes in water at 0.10 MPa: (a) toluene, (b) ethylbenzene, (c) propylbenzene; ●, present work; ○, ref 31; △, ref 32; □, ref 23; ◇, ref 24. $T_0 = 298.2$ K.

the minimum occurs is dependent on the length of the alkyl groups: 290 K for toluene, 292 K for ethylbenzene, and 293 K for propylbenzene.

C. Solubility at High Pressure. The observed solubilities of alkylbenzenes are listed in Table 1 and are plotted as a function of both pressure and temperature in Figure 2. Solubility surfaces for all solutes are appreciably distorted. The isothermal solubility−pressure curve exhibits a maximum at around 100 or 200 MPa over all the applied temperatures. The position of the maximum can be seen to shift to higher pressures with increasing temperature. This inversion in the solubility curve represents a change in sign of the volume change that accompanies the dissolution changing from negative to positive at high pressures as indicated by eq 1. The volume change that accompanies hydrophobic hydration has been observed to be negative at atmospheric pressure and thought to be related to iceberg formation.[2,7] Scaled particle theory is a simple liquid theory that considers molecular size and the work required to create a space in a liquid in order to place a molecule. This theory has been used to semiquantitatively explain many thermodynamic properties of liquids and solutions.[33,34] The negative volume change in hydrophobic hydration at atmospheric pressure is ascribed to the small size of the solvent molecules of water as compared with general organic solvents, without the seed for any special structural explanation.[35] However, the positive change in volume at high pressure that has been observed in the present study cannot be explained by scaled particle theory because the situation of small size for water molecule remains the same at high pressures of 400 MPa. This suggests that specific molecular interaction is involved in hydrophobic hydration.
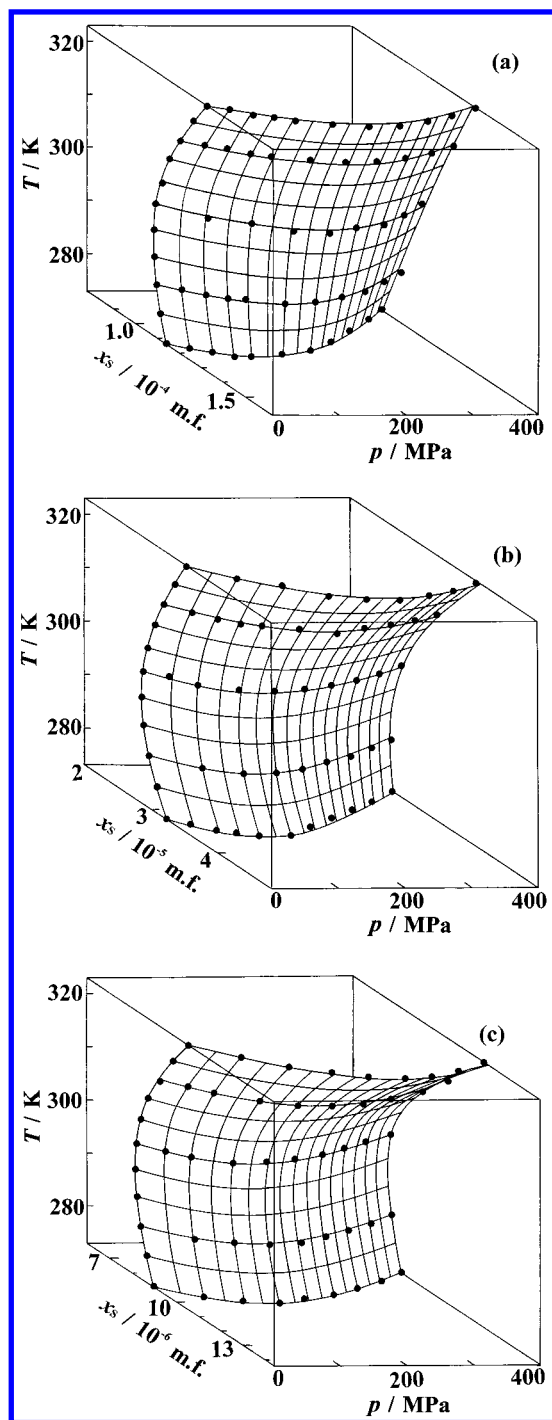
Figure 2. Solubility of alkylbenzenes in water as a function of pressure and temperature: (a) toluene, (b) ethylbenzene, (c) propylbenzene.

The isobaric solubility curves for toluene at atmospheric pressure in Figure 2 exhibit a minimum. However, the minimum disappears at 400 MPa. From eq 2, this is attributed to the fact that the enthalpy that accompanies dissolution of toluene at low temperature becomes less negative and eventually becomes positive with increasing pressure. This suggests that the icebergs around the solute are being weakened by pressure. Similar weakening is observed for ethylbenzene and propylbenzene, although these hydrocarbons retain the minima at high pressure. Similar solubility curves have been observed for the quasi-hydrophobic compound of 4-octanone in water over 278–353 K and 0.10–500 MPa by Kim.[36] A minimum was observed in the isobaric solubility–temperature curve at all pressures, and

a maximum was observed in the isothermal solubility–pressure curve at all temperatures.

The pressure coefficient of solubility is related to the difference between the partial molar volume of the solute in water and the molar volume of the solute, as shown in eqs 1 and 3. Therefore, it is possible to estimate the partial molar volume of alkylbenzenes in water using ΔV obtained from the slope of solubility in Figure 2 and V^* of the pure alkylbenzenes. The partial molar volume is usually estimated from a concentration dependence of the density of solution; however, estimation is not easy for a hydrophobic solute in water at atmospheric pressure because of low solubility, and it becomes even more difficult at high pressure. To resolve this problem, the compression of pure alkylbenzenes was measured in order to estimate partial molar volume at high pressure.

D. Compression of Alkylbenzenes. The compressions of alkylbenzenes are listed in Table 2. The compression of toluene was measured by Mopsik[37] at temperatures of 273.2 and 298.2 K and at pressures up to 200 MPa. Kashiwagi et al.[38] also made measurements at 273.2 and 323.2 K, up to 250 MPa. The present values differ from these values by less than ±0.05% in density. The compressions of ethylbenzene and propylbenzene are thought to be measured with similar precision. The data in Table 2 was fitted to Tait's equation:[39]

$$k = A \log[(B + p)/(B + 0.10)] \qquad (10)$$

The constants A and B are shown in Table 3. The compression at pressures exceeding 300 MPa was estimated by extrapolation using these parameters. The density, d_0, of the pure solutes at atmospheric pressure is also listed in Table 3, as cited from a data book.[40] The density of toluene as measured by Kashiwagi et al.,[38] Mopsik,[37] Skinner et al.,[41] and Gamboa et al.[42] agrees with the data in Table 3 within ±0.05% in the region of 273–323 K. V^* of alkylbenzenes at high pressure was estimated from the values in Table 3 using

$$V^* = M(1 - k)/d_0 \qquad (11)$$

where M is the molar mass of the solute.

E. Thermal Expansion Coefficient of the Partial Molar Volume of Hydrophobic Solutes in Water at Atmospheric Pressure. To discuss the volumetric properties of hydrophobic hydration at high pressure, it is necessary to summarize the properties at atmospheric pressure. When the partial molar volumes, V^∞, of a series of aliphatic compounds such as alcohols $(H(CH_2)_nOH)$ in water are plotted against the number, n, of methylene groups $(-CH_2-)$, the volume increases linearly with increasing n. The linearity suggests that the methylene group $(-CH_2-)$ occupies an intrinsic volume (see Table 4). The values at several temperatures are plotted in Figure 3a, in which the volumes are normalized to 298.2 K. The relative volume of the methylene group increases linearly with increasing temperature. The expansion coefficient, α^∞ $[\equiv(\partial V^\infty/\partial T)_p/V^\infty]$, of partial molar volume is estimated from the slope of the relative volume as listed in Table 4. The partial molar volumes of benzene in water, as estimated from density measurements of the aqueous solution,[43,44,46] are also plotted in Figure 3b, and α^∞ obtained for benzene is tabulated in Table 4. The α^∞ of toluene ($n = 1$), ethylbenzene ($n = 2$), and propylbenzene ($n = 3$) in water were assumed to be as listed in Table 4 as determined from the expansion coefficients of the partial molar volumes of the methylene group and benzene on the assumption that their volume additivity is expressed by

Volumetric Property of Hydrophobic Hydration

J. Phys. Chem. B, Vol. 105, No. 12, 2001 **2433**

TABLE 2: Compression of Alkylbenzenes

p (MPa)	273.2	278.2	283.2	288.2	293.2	298.2	303.2	308.2	313.2	318.2	323.2
						Toluene					
50	0.0323	0.0333	0.0342	0.0353	0.0363	0.0374	0.0385	0.0396	0.0408	0.0420	0.0433
100	0.0562	0.0576	0.0591	0.0607	0.0622	0.0638	0.0655	0.0671	0.0689	0.0706	0.0724
150	0.0751	0.0769	0.0787	0.0805	0.0824	0.0843	0.0862	0.0882	0.0902	0.0923	0.0944
200	0.0908	0.0928	0.0948	0.0968	0.0989	0.1010	0.1031	0.1053	0.1075	0.1098	0.1121
250	0.1042	0.1063	0.1084	0.1105	0.1127	0.1150	0.1173	0.1196	0.1220	0.1244	0.1269
300	0.1159	0.1181	0.1203	0.1226	0.1249	0.1272	0.1296	0.1320	0.1345	0.1370	0.1396
						Ethylbenzene					
50	0.0304	0.0308	0.0312	0.0316	0.0319	0.0323	0.0327	0.0331	0.0335	0.0339	0.0343
100	0.0539	0.0546	0.0553	0.0560	0.0566	0.0573	0.0580	0.0586	0.0593	0.0600	0.0607
150	0.0731	0.0740	0.0749	0.0759	0.0768	0.0777	0.0786	0.0795	0.0804	0.0813	0.0822
200	0.0894	0.0905	0.0916	0.0926	0.0937	0.0948	0.0959	0.0970	0.0981	0.0992	0.1002
250	0.1034	0.1047	0.1059	0.1072	0.1084	0.1097	0.1109	0.1122	0.1134	0.1147	0.1159
300	0.1158	0.1171	0.1158	0.1199	0.1213	0.1227	0.1241	0.1255	0.1269	0.1283	0.1297
						Propylbenzene					
50	0.0313	0.0313	0.0314	0.0314	0.0315	0.0315	0.0316	0.0316	0.0317	0.0317	0.0318
100	0.0555	0.0556	0.0558	0.0559	0.0561	0.0562	0.0564	0.0565	0.0567	0.0568	0.0570
150	0.0751	0.0753	0.0756	0.0759	0.0762	0.0764	0.0767	0.0770	0.0773	0.0775	0.0778
200	0.0916	0.0920	0.0924	0.0928	0.0932	0.0936	0.0940	0.0944	0.0948	0.0952	0.0956
250	0.1058	0.1064	0.1069	0.1074	0.1079	0.1085	0.1090	0.1095	0.1101	0.1106	0.1111
300	0.1184	0.1190	0.1197	0.1203	0.1210	0.1216	0.1223	0.1229	0.1235	0.1242	0.1248

(with *T* (K) as header spanning columns 273.2 through 323.2)

TABLE 3: Density at 0.10 MPa and Tait Equation Parameter of Alkylbenzenes

	toluene			ethylbenzene			propylbenzene		
T (K)	d_0^a (g cm^{-3})	A	B (MPa)	d_0^a (g cm^{-3})	A	B (MPa)	d_0^a (g cm^{-3})	A	B (MPa)
273.2	0.8855	0.21135	118.23	0.8850	0.24109	148.22	0.8788	0.24119	142.96
278.2	0.8809	0.21076	113.77	0.8806	0.24282	147.13	0.8746	0.24558	145.96
283.2	0.8762	0.21038	109.68	0.8761	0.24497	146.43	0.8704	0.24871	147.72
288.2	0.8716	0.20925	105.06	0.8717	0.24709	145.68	0.8663	0.25246	150.13
293.2	0.8668	0.20921	101.48	0.8672	0.25054	146.22	0.8620	0.25566	151.92
298.2	0.8621	0.20868	97.59	0.8627	0.25300	145.79	0.8579	0.26028	155.06
303.2	0.8574	0.20836	93.99	0.8583	0.25515	145.15	0.8537	0.26356	156.88
308.2	0.8527	0.20838	90.78	0.8538	0.25827	145.33	0.8494	0.26749	159.38
313.2	0.8480	0.20799	87.28	0.8493	0.26043	144.71	0.8452	0.27038	160.83
318.2	0.8432	0.20793	84.16	0.8449	0.26290	144.32	0.8409	0.27571	164.51
323.2	0.8384	0.20785	81.08	0.8403	0.26512	143.83	0.8367	0.27830	165.73

[a] Ref 40.

TABLE 4: Partial Molar Volume (V^∞) and Partial Molar Expansion Coefficient (α^∞) in Water at 298.2 K and 0.10 MPa

	V^∞ (cm^3 mol^{-1})	av	α^∞ (10^{-3} K^{-1})
-CH$_2$-	16.0 ± 0.3[a]		1.35 ± 0.1[a]
benzene	82.6,[b] 81.3,[c] 83.2[d]	82.4	1.03[a]
toluene	99, 98.6,[b] 97.7[c]		1.08[f]
ethylbenzene	115, 114.5[b]		1.12[f]
propylbenzene	131, 130.5[e]		1.15[f]

[a] Estimated from Figure 3. [b] Ref 43. [c] Ref 44. [d] Ref 45. [e] Estimated as (114.5 + 16.0) cm^3 mol^{-1}. [f] Estimated from eq 12.

$$\alpha^\infty \, (\mathrm{K}^{-1}) = (82.4 \times 1.03 + 16.0 \times 1.35n)/$$
$$(82.4 + 16.0n) \times 10^{-3} \quad (12)$$

This equation was used for the curves of toluene and ethylbenzene in Figure 3. It can be seen that the curves fit the observed data well. This suggests that α^∞ for propylbenzene as listed in Table 4 is an appropriate value, even though there has been no direct measurement.

F. Compressibility of the Partial Molar Volume of Hydrophobic Solutes in Water at Atmospheric Pressure. The adiabatic compressibility, κ_S^∞ [$\equiv -(\partial V^\infty/\partial p)_S/V^\infty$], of the partial molar volume has been estimated from sonic measurements for several organic compounds that have alkyl substituents in water. However, there are few measurements from which the isothermal compressibility, κ_T^∞ [$\equiv -(\partial V^\infty/\partial p)_T/V^\infty$], can be estimated.
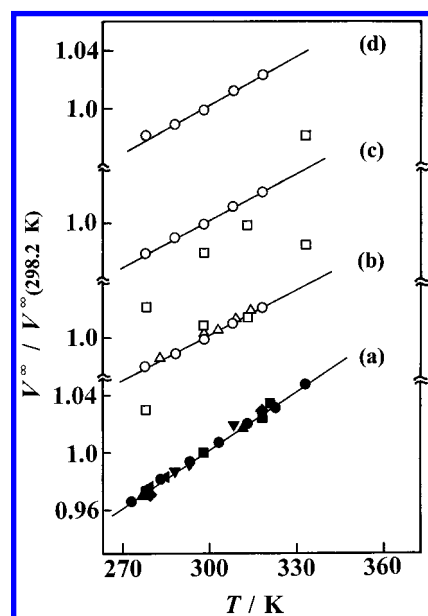

Figure 3. Temperature dependence of the partial molar volumes of methylene group (a), benzene (b), toluene (c), and ethylbenzene (d) in water at 0.10 MPa, normalized to the partial molar volume at 298.2 K: ●, H(CH$_2$)$_n$OH;[44,47−52] ▲, H(CH$_2$)$_n$COONa;[53] ■, H(CH$_2$)$_n$NH$_3$Cl;[53] ▼, H(CH$_2$)$_n$NH$_3$Br;[54] ◆, H(CH$_2$)$_n$O(CH$_2$)$_2$OH;[55] tilted ▲, HO(CH$_2$)$_n$OH;[50] ○, ref 43; □, ref 46; △, ref 44.

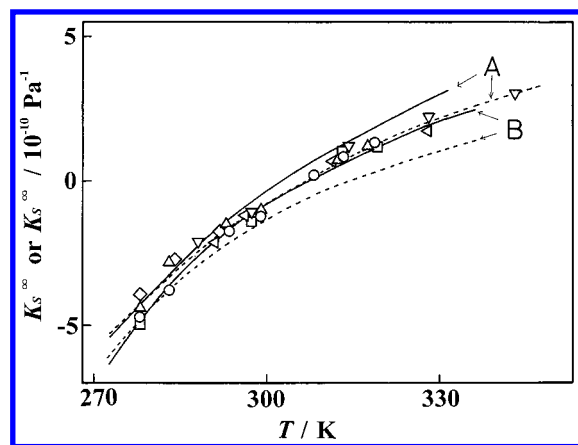**Figure 4.** Adiabatic (κ_S^∞) and isothermal (κ_T^∞) compressibilities of the partial molar volumes in water at 0.10 MPa: (A) methylene group, (B) phenyl group;[56,57] •••, κ_S^∞; —, κ_T^∞. Plots are κ_S^∞ for methylene groups: ○, H(CH$_2$)$_n$OH;[50,58−60] △, HO(CH$_2$)$_n$OH;[48,50,55] □, H(CH$_2$)$_n$-OC$_2$H$_4$OH;[55] ◇, H(CH$_2$)$_n$CH(OH)CH$_3$;[50] ▽, H(CH$_2$)$_n$CH(NH$_2$)CO-OH;[56,57,61] tilted △, H$_2$N(CH$_2$)$_n$COOH.[58]

The $-(\partial V^\infty/\partial p)_S$, which corresponds to κ_S^∞ times to V^∞, of a series of aliphatic compounds in water shows a linear relation to the number of methylene groups as well as the V^∞ does. It indicates the presence of an intrinsic value of $-(\partial V^\infty/\partial p)_S$, and hence κ_S^∞, for the methylene groups for a given temperature. The values are plotted in Figure 4 as a function of temperature. A similar curve for κ_S^∞ has been reported by Chalikian et al.[62] The κ_S^∞ for the phenyl group is also plotted in Figure 4, as estimated from the difference of $-(\partial V^\infty/\partial p)_S$ between phenylalanine and alanine in water.[56,57] It is worth noting that κ_S^∞ for both the methylene and phenyl groups is negative at low temperature; that is, the volume expands adiabatically with increasing pressure. To relate these adiabatic values to the high-pressure solubilities, κ_S^∞ should be translated to the isothermal condition. This can be achieved by using the following equation:[63]

$$\kappa_T^\infty = \kappa_S^\infty + \frac{TV_w\alpha_w}{C_{pw}}\left(2\alpha^\infty - \alpha_w\frac{V_wC_p^\infty}{V^\infty C_{pw}}\right) \qquad (13)$$

where V_w, α_w, and C_{pw} are the molar volume, expansion coefficient, and isobaric heat capacity of water, respectively. C_p^∞ is the partial molar isobaric heat capacity of a solute in an infinitely diluted aqueous solution. $C_p^\infty(-CH_2-)$ of the methylene group can be estimated from the C_p^∞ of a series of aliphatic compounds[46,64−69] as 88 ± 8 J mol^{-1} K^{-1}, independent of temperature between 273 and 333 K. The error of ca. 10% in $C_p^\infty(-CH_2-)$ is not significant in the estimation of κ_T^∞ because the contribution of this term to κ_T^∞ in eq 13 is small. The estimated values of κ_T^∞ are plotted as a solid line in Figure 4. It can be seen that κ_T^∞ does not differ significantly from κ_S^∞, with negative values at low temperature that increases to positive values with increasing temperature. The C_p^∞ per gram of the phenyl group is similar to that of the methylene group.[46,70] Therefore κ_T^∞ for the phenyl group is also temperature-dependent, similar to that of the methylene group.

G. Partial Molar Volumes of Alkylbenzenes in Water as a Function of Pressure and Temperature. The ΔV that accompanies the dissolution of alkylbenzenes in water and V^* for pure alkylbenzenes can be estimated from the slope of the isothermal solubility−pressure curve (Figure 2) and the parameters listed in Table 3 by using eq 11, respectively. These data are used to estimate V^∞ of alkylbenzenes in water at high
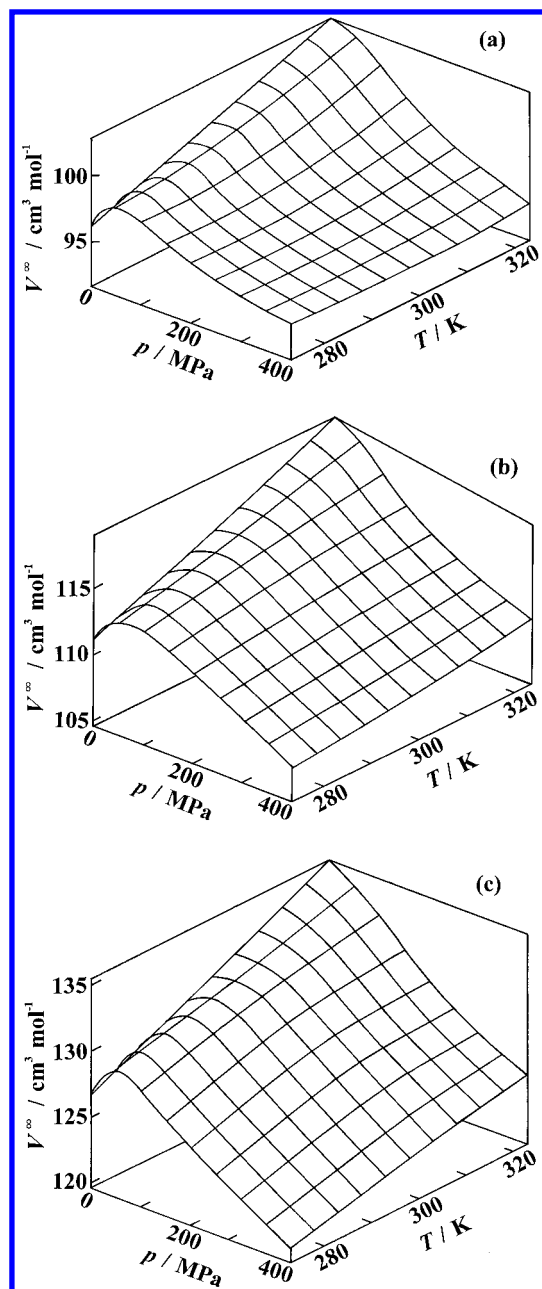

Figure 5. Partial molar volumes of alkylbenzenes in water as a function of pressure and temperature: (a) toluene, (b) ethylbenzene, (c) propylbenzene.

pressure by using eq 3. The results are plotted as a function of pressure and temperature in Figure 5. V^∞ and α^∞, as listed in Table 4, and κ_T^∞, as shown in Figure 4, are used to complete the curves around atmospheric pressure because the pressure coefficient of the solubility curve cannot be precisely estimated at the low-pressure (0.10 MPa) end of the curve. The surfaces obtained for V^∞ (Figure 5) are appreciably distorted. Chalikian et al.[61] showed that κ_T^∞ is negative for hydrophobic groups in water at low temperatures and at atmospheric pressure from measurements of adiabatic compressibility. This negative values mean an expansion of the partial molar volume with increasing pressure. In a previous paper,[5] a similar increase in V^∞ with pressure was observed for alkylbenzenes in water at 298.2 K up to ca. 100 MPa, followed by a volume decrease in the high-pressure region over ca. 100 MPa. The present study shows that the maximum exhibited by pressure dependence of V^∞ is remarkable in the low-temperature region, whereas V^∞ steadily

decreases with increasing pressure in the high-temperature region and does not exhibit a maximum.

The α^∞ of hydrophobic compounds in water at atmospheric pressure listed in Table 4 do not appear to differ from the expansion coefficients of general organic solvents: $(1 -2) \times 10^{-3}$ K^{-1}.[40] This seems a negative factor for the possibility that hydration structures such as icebergs form around a hydrophobic solute because such structures contain hydrogen bonds between water molecules that are thought to be highly temperature-dependent, resulting in a large value of α^∞.[43] However, the V^∞ of alkylbenzene in water has been surveyed over a wide range of pressures and temperatures, as shown in Figure 5, and it can be seen that the α^∞ at atmospheric pressure is undoubtedly larger than that at high pressure.

Scaled particle theory,[33,34] as described in section C, cannot explain the pressure dependence of ΔV that accompanies hydrophobic hydration because of the simplicity of the theory.[35] The expansion of V^∞ by pressure, as shown in Figure 5, also cannot be explained because the theory states that an increase in the packing density of water due to compression causes compression of V^∞. Therefore, the contribution of other factors needs to be considered in order to understand the volumetric properties of hydrophobic hydration at high pressure.

Though negative compression is not generally possible for ordinary solids, liquids, and gases, the situation is different for partial molar volume because molecular interaction between the solute and solvent occurs. Partial molar volume can be assumed to consist of two components: (1) the space in which water molecules are excluded to accommodate a solute molecule and (2) the volume change due to the rearrangement of water molecules in the hydration domain.[5] This is expressed by

$$V^\infty = V_{ex} + N(V_h - V_b) \qquad (14)$$

where V_{ex} is the exclusion volume due to component (1), V_b is the molar volumes of pure (bulk) water, and N is the number of water molecules in the domain of hydrophobic hydration around a solute molecule, in which the water has another molar volume of V_h. The second component of partial molar volume is represented by $N(V_h - V_b)$. The volumes of V_{ex}, V_h, and V_b should decrease with increasing pressure according to thermodynamic principles. N cannot contribute to any expansion of V^∞ with increasing pressure based on Le Chatelier's principle when we consider an equilibrium between hydration and bulk water. Hence, by eq 14, only the reduction of V_b due to pressure can contribute to the negative compressibility of V^∞. Therefore the increase of V^∞ with increasing pressure up to ca. 100 MPa at 298.2 K was ascribed to the reduction of V_b in the previous study.[5] This means that bulk water is more compressible than hydrating water. The present results shown in Figure 5 suggest that the reduction of V_b becomes significant at low temperature. This can be attributed to the fact that, contrary to other solvents, the compressibility of bulk water becomes large with decreasing temperature in the temperature range 273.2−323.2 K[22] and the property steeply diminishes with increasing pressure up to 400 MPa. The large expansion coefficient of V^∞ at atmospheric pressure shown in Figure 5 may be also due to the same unique property of bulk water: it is more expansible at higher pressures, which is an alternative expression to that it is more compressible at lower temperatures. Such an unique property of water has been thought to be based on bulky liquid structure consisting of a hydrogen-bonding network such as ice I.[71] The structure is easily broken by pressure and temperature. Then, water becomes less compressible with increasing temperature and more expansible with increasing pressure. Such property of (bulk) water

appears in the pressure and temperature dependences of V^∞ shown in Figure 5.

Conclusions

In this study, alkylbenzenes are used as a model compound to research the volumetric property of hydrophobic hydration under high pressure. The $p-T$ surface of their partial molar volume is appreciably distorted. This observation is reasonable, attributable to the unique property of water: Water becomes less compressible with increasing temperature. This consideration means that the unique property is weaken or disappears in the water under hydrophobic hydration. If not, the $p-T$ surface would flatten out because pressure and temperature dependences of V_b and V_h in eq 14 are compensating each other. Distortion of the surface in Figure 5 seems to show a difference of the property between bulk and hydrating water.

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