

Range and Energy of Interaction at Infinite Dilution in Aqueous Solutions of Alcohols and Hydrocarbons

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Infinitely dilute hydrocarbon/water and alcohol/water systems were examined, with the objective to gather information about the size of the volume which is affected by the presence of a solute molecule and the interaction energy parameter between solute and solvent. First, an expression for the local composition at infinite dilution was obtained on the basis of the Kirkwood–Buff theory of solution. Second, equations for the activity coefficients at infinite dilution were derived using a modified Flory–Huggins equation for the excess free energy. In this modified expression, the molar fractions in the volume fractions were replaced by the local compositions provided by the first step. Finally, an additional expression for the local molar fraction was selected, which was coupled with that obtained on the basis of the Kirkwood–Buff approach. Experimental data regarding the activity coefficient at infinite dilution combined with the above equations allowed to obtain the values of the correlation volume (volume which is affected by a single solute molecule) and the interaction energy parameter between solute and solvent. The thickness of the layer of solvent influenced by the presence of a solute molecule was found to be equal to several molecular shells of water molecules (from 4 for propane to 7–8 for dodecane).

Introduction

The infinite dilution state is very suitable for the investigation of intermolecular interactions between solute and solvent molecules, because in that state a single solute molecule is completely surrounded by solvent molecules and thus information regarding the solute–solvent interaction in the absence of the solute–solute interactions can be obtained. This is particularly relevant for systems with complicated intermolecular interactions such as the aqueous systems.

To characterize the process of dissolution in water, Butler suggested that “the process of bringing a solute molecule into a solvent may be supposed to consist of two steps: (1) making a cavity in the solvent large enough to hold the solute molecule; (2) introducing the solute molecule into the cavity”.¹ In the calculation of the contribution of the second step to the enthalpy of hydration, Butler considered only the interactions between the solute molecule and the nearest-neighbor water molecules. He also assumed that the water molecules are distributed around a solute molecule as randomly as in its absence. Butler’s assumption of random distribution in solution was replaced by Frank and Evans² by a nonrandom distribution. The latter authors suggested that around a molecule of a nonpolar solute, there is a layer of more ordered water molecules (“iceberg”). The approach can account for the negative enthalpy and entropy of solution (see discussion for additional comments). No evaluation of the thickness of this layer was, however, provided. Nemethy and Scheraga³ extended their model for water to aqueous solutions of hydrocarbons, but considered that only a monolayer of solvent molecules is affected by a solute molecule. The aim of this paper is to evaluate the thickness of the layer of water, which is affected by a solute molecule. In addition,

information about the interaction energy parameter between the solute molecule and a solvent molecule will be obtained. In order to evaluate those quantities, expressions for the correlation volume (volume which is affected by a single solute molecule), the local compositions, and the activity coefficients at infinite dilution are needed, and they are presented below.

Theory and Formulas

1. Correlation Volume. We consider a molecule of species i and its surrounding correlation volume V_{cor}^i in which the composition and/or the structure differ from the bulk one. The total number of molecules i and j in this volume is given by the expressions

$$n_{ii} = \Delta n_{ii} + c_i V_{\text{cor}}^i \quad (1)$$

$$n_{ji} = \Delta n_{ji} + c_j V_{\text{cor}}^i \quad (2)$$

where Δn_{ii} and Δn_{ji} are excess (or deficit) number of molecules i and j around a central molecule i . Using the Kirkwood–Buff theory (KB)⁴ of solution and a suitable reference state for the excess quantities, Δn_{ii} and Δn_{ji} can be expressed as follows:⁵

$$\Delta n_{12} = -\frac{c_1 V_1 V_2 (1 - D)}{V} \quad (3)$$

$$\Delta n_{21} = -\frac{c_2 V_1 V_2 (1 - D)}{V} \quad (4)$$

and

$$\Delta n_{ii} = \frac{c_i x_j V_j^2 (1 - D)}{x_i V} \quad i \neq j \quad (5)$$

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where c_i is the overall molar concentration of species i in the mixture, x_i is the overall molar fraction of component i in solution, V is the molar volume of the solution, V_i and V_j are the partial molar volumes of components i and j , respectively, $D = (\partial \ln \gamma_i / \partial x_i)_{P,T} x_i + 1$, γ_i is the activity coefficient of component i , P is the pressure, and T is the absolute temperature. Because the local molar fractions are given by

$$x_{ii} = \frac{n_{ii}}{n_{ii} + n_{ji}} = \frac{\Delta n_{ii} + c_i V_{\text{cor}}^i}{\Delta n_{ii} + \Delta n_{ji} + (c_i + c_j) V_{\text{cor}}^i} \quad (6)$$

$$x_{ji} = \frac{n_{ji}}{n_{ii} + n_{ji}} = \frac{\Delta n_{ji} + c_j V_{\text{cor}}^j}{\Delta n_{ii} + \Delta n_{ji} + (c_i + c_j) V_{\text{cor}}^i} \quad (7)$$

one obtains

$$x_{ii} = \frac{x_j V_j^2 (1 - D) + x_i V_{\text{cor}}^i V D}{x_j V_j^2 (1 - D) - x_j V_i V_j (1 - D) + V_{\text{cor}}^i V D} \quad (8)$$

$$x_{ji} = \frac{-x_j V_i V_j (1 - D) + x_j V_{\text{cor}}^j V D}{x_j V_j^2 (1 - D) - x_j V_i V_j (1 - D) + V_{\text{cor}}^i V D} \quad (9)$$

where x_{ji} is the local molar fraction of component j in the vicinity of a central molecule i . Because for the dilute region one can consider that⁶ $(\partial \ln \gamma_i / \partial x_i)_{P,T}$ is independent of x_i , one can write that

$$D = K_i(P, T) x_i + 1 \quad (10)$$

where

$$K_i(P, T) = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{P, T, x_i \rightarrow 0}$$

For infinite dilution, eq 8 leads to

$$\lim_{x_i \rightarrow 0} \frac{x_{ii}}{x_i} = 1 - \frac{V_j^\infty K_i(P, T)}{V_{\text{cor}}^{i,0}} \quad (11)$$

where $V_j^\infty = \lim_{x_j \rightarrow 0} V_j$ is the partial molar volume of component j at infinite dilution and $V_{\text{cor}}^{i,0} = \lim_{x_i \rightarrow 0} V_{\text{cor}}^i$. One may note that $\lim_{x_i \rightarrow 0} (x_{ji}/x_i) > 1$ when $K_i(P, T) < 0$ (or $(\partial \ln \gamma_i / \partial x_i)_{P,T,x_i \rightarrow 0} < 0$). To calculate the correlation volume $V_{\text{cor}}^{i,0}$, hence the size of the region affected by a solute molecule, an additional expression for $\lim_{x_i \rightarrow 0} (x_{ji}/x_i)$ is needed. Such an expression, proposed in refs 7–9, will be used in what follows. Since that expression contains the interaction energy parameter between the solute and solvent molecules and this quantity is not known, an equation for the activity coefficients at infinite dilution will be also derived. This equation coupled with the two expressions for the local composition and experimental values for the activity coefficients at infinite dilution will allow to obtain both the correlation volume and the interaction energy parameter.

2. Activity Coefficient at Infinite Dilution. A procedure similar to that employed by Wilson¹⁰ will be used here to obtain an expression for the excess Gibbs energy. Wilson started from the Flory and Huggins expression^{11,12} for the excess free energy of athermal solutions, but expressed the volume fractions in terms of local molar fractions. We selected Wilson's approach from a number of approaches,¹³ because it provided a better description of phase equilibria and because the interactions that count the most are the local one, but started from the more

complete Flory–Huggins equation:

$$g^E = x_1 \ln \frac{\varphi_1}{x_1} + x_2 \ln \frac{\varphi_2}{x_2} + \chi \varphi_1 \varphi_2 \quad (12)$$

where φ_i are volume fractions and χ is the energetic parameter, given by

$$\chi = w/kT = z \frac{\Gamma_{12} - 0.5(\Gamma_{11} + \Gamma_{22})}{RT} \quad (13)$$

In eq 13, w is the interchange energy, k is the Boltzmann constant, R is the universal gas constant, Γ_{ij} is the energetic parameter for the interaction between molecules of species i and j and z is the coordination number.

We write for the volume fractions the expressions

$$\varphi_1 = \frac{V_1 x_{11}}{V_1 x_{11} + V_2 x_{21}} \quad (14)$$

$$\varphi_2 = \frac{V_2 x_{22}}{V_1 x_{12} + V_2 x_{22}} \quad (15)$$

which differ from those used by Wilson because they contain the partial molar volumes V_i instead of the molar volumes V_i^0 of the pure components. Eliminating the local molar fractions between eqs 8–9 and 14–15 yields

$$\varphi_1 = x_2 \frac{V_1 V_2^2}{V_{\text{cor}}^1 V^2} \left(\frac{1 - D}{D} \right) + \frac{x_1 V_1}{V} \quad (16)$$

$$\varphi_2 = x_1 \frac{V_2 V_1^2}{V_{\text{cor}}^2 V^2} \left(\frac{1 - D}{D} \right) + \frac{x_2 V_2}{V} \quad (17)$$

Assuming that $\chi = \chi(x_1)$, the activity coefficients are given by the expressions

$$\ln \gamma_1 = \ln \frac{\varphi_1}{x_1} + x_2 \left[x_1 \left(\frac{\partial \left(\ln \frac{\varphi_1}{x_1} \right)}{\partial x_1} \right) + x_2 \left(\frac{\partial \left(\ln \frac{\varphi_2}{x_2} \right)}{\partial x_1} \right) \right] + \chi \left[\varphi_1 \varphi_2 + x_2 \varphi_2 \frac{\partial \varphi_1}{\partial x_1} + x_2 \varphi_1 \frac{\partial \varphi_2}{\partial x_1} \right] + x_2 \varphi_1 \varphi_2 \frac{\partial \chi}{\partial x_1} \quad (18)$$

$$\ln \gamma_2 = \ln \frac{\varphi_2}{x_2} - x_1 \left[x_1 \left(\frac{\partial \left(\ln \frac{\varphi_1}{x_1} \right)}{\partial x_1} \right) + x_2 \left(\frac{\partial \left(\ln \frac{\varphi_2}{x_2} \right)}{\partial x_1} \right) \right] + \chi \left[\varphi_1 \varphi_2 - x_1 \varphi_2 \frac{\partial \varphi_1}{\partial x_1} - x_1 \varphi_1 \frac{\partial \varphi_2}{\partial x_1} \right] - x_1 \varphi_1 \varphi_2 \frac{\partial \chi}{\partial x_1} \quad (19)$$

Inserting eqs 16–17 into eqs 18–19, one obtains at infinite dilution, by assuming that the derivative of the correlation volume with respect to the molar fraction is negligible

$$\ln \gamma_1^\infty = \ln \left(\frac{-K_1(P, T) V_1^\infty}{V_{\text{cor}}^{1,0}} + \frac{V_1^\infty}{V_2^0} \right) + 1 - \frac{V_1^\infty}{V_2^0} + \frac{1}{V_2^0} \left(\frac{\partial V_2}{\partial x_1} \right)_{x_1=0} + \chi(x_1=0) \left(\frac{-K_1(P, T) V_1^\infty}{V_{\text{cor}}^{1,0}} + \frac{V_1^\infty}{V_2^0} \right) \quad (20)$$

$$\ln \gamma_2^\infty = \ln \left(\frac{-K_2(P,T)V_2^\infty}{V_{\text{cor}}^{2,0}} + \frac{V_2^\infty}{V_1^0} \right) + 1 - \frac{V_2^\infty}{V_1^0} + \frac{1}{V_1^0} \left(\frac{\partial V_1}{\partial x_2} \right)_{x_2=0} + \chi(x_2=0) \left(\frac{-K_2(P,T)V_2^\infty}{V_{\text{cor}}^{2,0}} + \frac{V_2^\infty}{V_1^0} \right) \quad (21)$$

Each of the above two equations contains two unknown, namely $V_{\text{cor}}^{i,0}$ and $\chi(x_i=0)$. The additional equation needed to calculate them can be obtained by equating eq 11 with another expression for the local compositions.

3. Local Composition. There have been many attempts to express the local composition in terms of the bulk composition and intermolecular interactions.^{7-10,13-17} While Guggenheim was the first to introduce the concept of local composition,¹⁷ this idea became extensively used after it was applied by Wilson to phase equilibria.¹⁰ A number of authors proposed various expressions for the local composition,^{7-10,14-17} among which we selected the following equations proposed in refs 7-9, because they were derived on the basis of some plausible theoretical considerations:

$$x_{ii} = \frac{x_i \exp\left(x_j \frac{\Delta}{RT}\right)}{x_j + x_i \exp\left(x_j \frac{\Delta}{RT}\right)} \quad (22)$$

$$x_{ji} = \frac{x_j}{x_j + x_i \exp\left(x_j \frac{\Delta}{RT}\right)} \quad (23)$$

where $\Delta = 2e_{12} - e_{11} - e_{22}$ and e_{ij} is the interaction energy parameter between species i and j . Equations 22 and 23 have been obtained by Lee et al.⁷ on the basis of Monte Carlo simulations for the nonrandom behavior of off-lattice square-well molecules, and derived theoretically by Aranovich and Donohue.⁸⁻⁹ The latter authors extended the Ono-Kondo lattice model for the density profile near a surface to the concentration profile around a solute molecule, by assuming that only the first shell has a composition different from that in the bulk. While approximate, their expression will be extended in this paper to the entire correlation volume. At infinite dilution, eq 22 becomes

$$\lim_{x_i \rightarrow 0} \frac{x_{ii}}{x_i} = \exp \left[\frac{2e_{12} - e_{11} - e_{22}}{RT} \right] \quad (24)$$

Data Sources and Numerical Calculations

The calculations were conducted for aqueous solutions of alcohols (methanol, ethanol, propanols, butanols, and *tert*-pentanol) and hydrocarbons (normal saturated aliphatic hydrocarbon from propane through dodecane, isobutane, cyclopentane, cyclohexane, cycloheptane, benzene, toluene).

The parameters Γ_{ii} (in eq 13) for pure substances can be identified with e_{ii} in eq 24 and evaluated from the heats of vaporization ΔH_{vap}^i using the expression

$$\Gamma_{ii} = e_{ii} = -\frac{2}{z}(\Delta H_{\text{vap}}^i - RT) \quad (25)$$

where ΔH_{vap}^i is the heat of vaporization of component i . The latter quantity was obtained from eq 26, which is based on the Antoine equation for the vapor pressure.¹⁸

$$\Delta H_{\text{vap}}^i = \frac{RT^2 B_i}{C_i + T} \quad (26)$$

Equations 11, 13, 20, 21, 24-26 were employed to calculate $K_i(P,T)/V_{\text{cor}}^{i,0}$ and Γ_{ij} . The correlation volume was finally obtained by extracting $K_i(P,T) = (\partial \ln \gamma_i / \partial x_i)_{P,T,x_i \rightarrow 0}$ from vapor-liquid equilibrium data. The Antoine parameters B_i and C_i were taken from ref 18 and the activity coefficients at infinite dilution of the alcohols in water and water in alcohols from refs 19-22. The molar volume of alcohols was taken from ref 23, and the partial molar volumes at infinite dilution of alcohols in water and water in alcohol were taken from refs 23-27 and for *tert*-pentanol-water was calculated from the excess molar volume.²⁸ The values of $K_i(P,T)$ were extracted from vapor-liquid equilibria data^{20,21,29} in the dilute region. The values of γ_i^∞ , V_i^∞ , $K_i(P,T)$ used for the calculation of the correlation volume in hydrocarbon + water systems were taken from ref 30. The derivatives $(\partial V_k / \partial x_k)_{x_k=0}$ were estimated by $(V_k^0 - V_k^\infty)$ and were taken zero for all hydrocarbon/water systems. The coordination number was taken to be 4 for water and infinitely dilute aqueous solutions³¹ and 6 for alcohols and infinitely dilute alcohol solutions.³² All the data used in the calculations are listed in Tables 1-3. Throughout this paper, component 1 is an alcohol or a hydrocarbon and component 2 is water.

Results, Discussion, and Conclusion

The calculated correlation volumes and energetic parameters for the alcohol-water and hydrocarbon-water systems are listed in Tables 4 and 5. The calculated volumes are compared with the sizes of clusters in several alcohol/water systems determined by small-angle X-ray scattering or light scattering³³⁻³⁷ at low concentrations (Table 6). Table 6 shows that there is reasonable agreement between them and the calculated correlation volumes at infinite dilution.

For the systems investigated, the free energies, enthalpies and entropies of hydration are known.³⁸⁻⁴⁰ They exhibit linear dependencies on the number of carbon atoms for different homologous series.³⁸⁻⁴⁰ One may note that, for the systems investigated, ΔH_{hyd} is negative and much smaller in absolute value than $T\Delta S_{\text{hyd}}$, which is also negative. Frank and Evans² concluded that the decrease in entropy caused by the organization of the water molecules as an iceberg is responsible for the low solubility of hydrocarbons in water. In reality,⁴¹⁻⁴⁴ the change in entropy due to the ordering is compensated by the change in the enthalpy caused by the interactions between the hydrocarbon molecule and water, and the free energy associated with the formation of a cavity is mainly responsible for hydrophobic bonding.⁴¹⁻⁴⁴ Shinoda^{41,42} concluded that the formation of a cavity constitutes the main effect, while Ruckenstein^{43,44} has shown on the basis of a simple thermodynamic approach that while the formation of a cavity provides the largest contribution, the iceberg formation plays also a role. The emphasis in this paper is, however, only on the hydrophobic layer.

One can see from Tables 4 and 5 that the correlation volume at infinite dilution increases for both normal hydrocarbons and normal alcohols with the number of carbon atoms. A comparison between the two shows that they are several times larger for hydrocarbons than for the corresponding alcohols, but that the difference between them decreases as the number of carbon atoms increases (Figure 1).

The smaller values for alcohols are due to the presence of the hydroxyl group, which, because of its favorable interaction with the solvent, does not disturb, as much as the hydrocarbon

TABLE 1: Data Used for the Calculation of the Correlation Volumes of Alcohols at Infinite Dilution in Alcohol/Water Solutions

system	temp (K)	γ_1^∞	V_1^∞ (cm ³ /mol)	$-K_1(P,T)$
methanol–water	298.15	1.8	38.2	1.5
ethanol–water	298.15	4.0	55.1	4.5
1-propanol–water	303.15	16.3	70.7 ^a	11.5
2-propanol–water	298.15	8.3	71.8	6.5
1-butanol–water	323.15	78.7	86.37	31
2-butanol–water	323.15	35.5	87.72	23
<i>i</i> -butanol–water	323.15	58.1	87.63	28
<i>t</i> -butanol–water	323.15	19.2	89.2	18
<i>t</i> -pentanol–water	328.15	78.1	100.9 ^b	27

^a $T = 298.15$ K. ^b Calculated from excess volume data²⁸ at $T = 303.15$ K.

TABLE 2: Data Used for the Calculation of the Correlation Volumes of Water at Infinite Dilution in Alcohol/Water Solutions

system	temp (K)	γ_2^∞	V_2^∞ (cm ³ /mol)	$-K_2(P,T)$
methanol–water	298.15	1.5	14.48	0.5
ethanol–water	298.15	2.7	13.81	1.3
1-propanol–water	303.15	5.6	15.09 ^a	3.2
2-propanol–water	298.15	3.6	14.51	1.6
1-butanol–water	323.15	5.2	16.90 ^b	2.3
2-butanol–water	323.15	4.6	17.53 ^b	2.4
<i>i</i> -butanol–water	323.15	5.3	16.99 ^b	2.6
<i>t</i> -butanol–water	323.15	4.9	16.05 ^b	1.7
<i>t</i> -pentanol–water	328.15	3.43	14.7 ^b	2.0

^a $T = 298.15$ K. ^b $T = 318.15$ K.

TABLE 3: Data Used for the Calculation of the Correlation Volumes of Hydrocarbon at Infinite Dilution in Hydrocarbon/Water Solutions

system	temp (K)	$\ln \gamma_1^\infty$	V_1^∞ (cm ³ /mol)	$-K_1(P,T)$
propane–water	298.15	8.35 ^a	70.7	80.7
<i>n</i> -butane–water	298.15	9.99	76.6	112.6
isobutane–water	298.15	9.86	81.3	107.4
<i>n</i> -pentane–water	298.15	11.6	92.3	150.4
<i>n</i> -hexane–water	298.15	13.1	110.0	190.4
<i>n</i> -heptane–water	298.15	14.5	129.4	231.1
<i>n</i> -octane–water	298.15	16.1	145.2	288.1
<i>n</i> -decane–water	298.15	18.9	176.8	395.4
<i>n</i> -dodecane–water	298.15	21.7	209.5	523.5
cyclopentane–water	298.15	10.1	84.5	100.5
cyclohexane–water	298.15	11.3	98.8	120.2
cycloheptane–water	298.15	12.1	105.5	131.1
benzene–water	298.15	7.8	82.5	42.5
toluene–water	298.15	9.2	97.7	61.9

^a This value was taken from ref 19.

molecules do, the structure of water. Table 4 also reveals that the correlation volume is much larger when the alcohol is the solute. The larger value is due to the higher disturbance produced by the alcohol molecule in the structure of water solvent than that produced by a water molecule in the structure of alcohol solvent.

The correlation volume was not accounted in the Butler's scheme. Butler's scheme for dissolution in water¹ accounted only for the formation of a cavity, introduction of the solute molecule in that cavity, and its interactions with the nearest-neighbor water molecules. He assumed, however, that the water molecules are distributed around a solute molecule as randomly as in its absence. One more step should be added, namely, the formation of a "hydrophobic layer" of volume V_{cor}^1 around the cavity, in which the water molecules are reorganized and are no longer randomly distributed (Figure 2). While this layer is similar to that suggested by Frank and Evans in their "iceberg"

TABLE 4: Correlation Volumes and Intermolecular Interaction Energy Parameters in Alcohol/Water Systems at Infinite Dilution^a

system	temp (K)	$-\Gamma_{12}$ (J/mol)	$V_{\text{cor}}^{1,0}$ (cm ³ /mol)	$-\Gamma_{21}$ (J/mol)	$V_{\text{cor}}^{2,0}$ (cm ³ /mol)
methanol + water	298.15	16 750	270	17 000	80
ethanol + water	298.15	17 560	490	18 500	110
1-propanol + water	303.15	18 620	860	19 900	220
2-propanol + water	298.15	18 020	570	19 360	120
1-butanol + water	323.15	19 010	1900	20 240	180
2-butanol + water	323.15	18 070	1600	19 600	210
<i>i</i> -butanol + water	323.15	18 660	1800	19 940	210
<i>t</i> -butanol + water	323.15	17 600	1500	19 010	140
<i>t</i> -pentanol + water	328.15	17 960	1700	18 860	140

^a Component 1 is alcohol, component 2 is water and $V_{\text{cor}}^{i,0} = \lim_{x_i \rightarrow 0} V_{\text{cor}}^i$.

TABLE 5: Correlation Volumes and Intermolecular Interaction Energy Parameters in Hydrocarbon/Water Systems at Infinite Dilution^a

system	temp (K)	$-\Gamma_{12}$ (J/mol)	$V_{\text{cor}}^{1,0}$ (cm ³ /mol)
propane–water	298.15	14 160	2900
<i>n</i> -butane–water	298.15	14 970	3760
isobutane–water	298.15	14 660	3710
<i>n</i> -pentane–water	298.15	15 710	5020
<i>n</i> -hexane–water	298.15	16 470	6350
<i>n</i> -heptane–water	298.15	17 240	8000
<i>n</i> -octane–water	298.15	18 090	9990
<i>n</i> -decane–water	298.15	19 930	13630
<i>n</i> -dodecane–water	298.15	21 950	18100
cyclopentane–water	298.15	16 120	2900
cyclohexane–water	298.15	16 810	3500
cycloheptane–water	298.15	17 750	3700
benzene–water	298.15	16 800	1440
toluene–water	298.15	17 510	2870

^a Component 1 is hydrocarbon, component 2 is water and $V_{\text{cor}}^{i,0} = \lim_{x_i \rightarrow 0} V_{\text{cor}}^i$.

TABLE 6: Comparison between the Radius of the Correlation Volume at Infinite Dilution of Alcohol in Alcohol/Water Systems and Size of Clusters at Small Concentration of Alcohol in These Systems Obtained by Different Physical Methods^a

system	radius ^b of correlation volume (Å)	radius of cluster obtained by different physical methods			ref
		radius (Å)	molar fraction, x_1	method	
1-propanol–water	7.0	7.3 ~4 ^c	0.05	LS	33
1-butanol–water	9.1	7.5	0.018	SAXS	35
2-butanol–water	8.6	8.2	0.041	SAXS	35
<i>i</i> -butanol–water	8.9	11.8	0.019	SAXS	35
<i>t</i> -butanol–water	8.4	~5 ^c	0.05	SAXS	36
		8.3	0.04	LS	37

^a LC = light scattering; SAXS = small-angle X-ray scattering. ^b The correlation volume is approximated as a sphere. ^c Data evaluated from the figures of the corresponding papers.

model,² the present approach provides also the size of the region of water affected by the presence of the solute.

The estimation of the thickness of the water layer affected by the presence of a solute molecule was made for two geometries: (1) the cavity containing the solute and the correlation volume have the shape of a sphere, (2) both have the shape of a cylinder. The results of the calculations are listed in Table 7, which shows that the water layer is formed of several molecular shells (between 4 and 8, Table 7). The correlation volumes for cyclic hydrocarbon are much lower than for aliphatic hydrocarbons, but, among the cyclic hydrocarbons, the

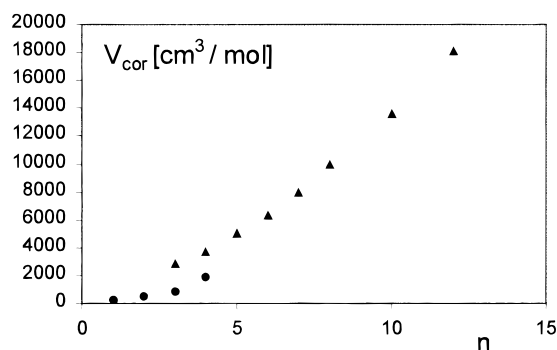


Figure 1. Dependence of correlation volume at infinite dilution on the number of hydrocarbon atoms n . Hydrocarbon in water (▲) and alcohol in water (●).

TABLE 7: Thickness of the Hydrophobic Layer (l) Covering an Aliphatic Hydrocarbon Molecule in Water at Infinite Dilution^a

n	l_1 (Å)	l_2 (Å)	N
3	7.4	7.9	~4
4	8.3	8.7	≥4
5	9.3	9.6	~5
6	10.1	10.4	≥5
7	11.0	11.2	~6
8	12.0	12.0	≥6
10	13.4	13.4	~7
12	14.9	14.7	≥7

^a n is the number of carbon atoms, l_1 is the thickness of the hydrophobic layer when the cavity and correlation volume are approximated as spheres and l_2 when they are approximated as cylinders, and N is the estimated number of water shells. This estimation was made on the basis of X-ray scattering data of cold water.³¹

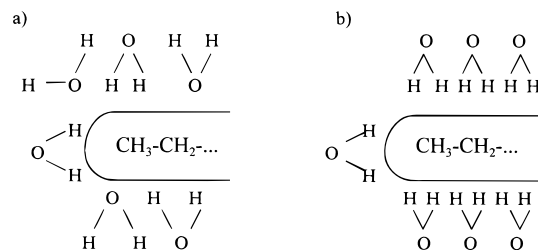


Figure 2. Schematic of a hydrocarbon molecule covered by water molecules at infinite dilution: (a) random distribution of water molecules around a hydrocarbon molecule; (b) water molecules with an ordered structure.

aromatic hydrocarbons have especially low correlation volumes (Table 5). These results should be attributed to the favorable interactions of the π electrons of the aromatic hydrocarbon with the surrounding water molecules. For this reason, the structure of water is less perturbed by the aromatic hydrocarbons than by the aliphatic ones.

Tables 4 and 5 also list the values of the energy interaction parameters Γ_{ij} for the alcohol/water and hydrocarbon/water systems. For the alcohol/water systems, the parameters were calculated for both dilute solutions of alcohol in water and dilute solutions of water in alcohol. For hydrocarbon/water systems, the calculations were carried out only for dilute solutions of hydrocarbon in water, because no experimental information could be found for the solutions of water in hydrocarbons. Figure 3 presents a plot of Γ_{12} versus the number of carbon atoms in molecules for normal alcohols and hydrocarbons.

Figure 3 and Tables 4 and 5 show that Γ_{12} increases when the number of carbon atoms increases and that Γ_{12} is greater for alcohols than for the corresponding hydrocarbons. This result

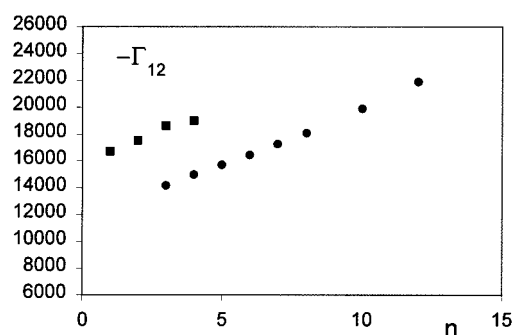


Figure 3. Energetic parameter Γ_{12} (J/mol) as a function of the number of carbon atoms in alcohol and hydrocarbon molecules (n): (■) alcohol/water systems; and (●) hydrocarbon/water systems.

is as expected, because the alcohol molecules have hydroxyl groups, which interact strongly with the water molecules. It is interesting to compare the value Γ_{ij} from both sides (when $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$) in the alcohol/water systems. The data listed in Table 4 show that Γ_{12} and Γ_{21} are different. This indicates that the interactions between alcohol and water are not the same in the two limiting cases and hence that the usual assumption that $\Gamma_{12} = \Gamma_{21}$ is not a good approximation. Of course, the present calculations involve a number of approximations and it is not yet clear how accurate is the above conclusion.

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