Aggregation of Hydrocarbons in Dilute Aqueous Solutions

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On the basis of the fluctuation theory of Kirkwood and Buff, the aggregation number of hydrocarbons in water at infinite dilution, defined on the basis of the radial distribution function, is related to the activity coefficient and partial molar volume of the solute. One concludes that the aggregation number should pass through a maximum with increasing temperature. The effect of pressure on aggregation in dilute solutions is also examined.

1. Introduction

The hydrophobic effect, which drives nonpolar solutes toward aggregation in aqueous solutions, plays a central role in many biological and chemical processes, such as formation of micelles and biological membranes. The study of such systems has attracted attention from both an experimental and a theoretical point of view.[1−3] A large number of experimental investigations have been carried out regarding the solubilities,[4−6] partial molar volumes,[7,8] activity coefficients at infinite dilution,[9,10] and vapor pressures and the osmotic second virial coefficients[11−15] of hydrocarbons in water. On the basis of vapor pressures studies, Tucker and co-workers obtained information about the dimerization of benzene and fluorobenzene in dilute aqueous solutions.[11−13] Numerous molecular dynamics calculations regarding the association of nonpolar substances (inert gases and hydrocarbons) in water[16−19] have been carried out as well. Watanade and Andersen[16] concluded that Kr does not aggregate in water, while more recent simulations indicated that benzene, methane, and ethane do aggregate in aqueous solutions.[17−19] Regarding the temperature dependence of the tendency to aggregate in aqueous solutions, the theoretical calculations of Pratt and Chandler[3] predicted that it should decrease with increasing temperature. Recent simulations[18,19] indicated, however, that the tendency to aggregate increases for methane, ethane, and benzene with increasing temperature.

The goal of this paper is to establish a relation between the degree of aggregation and thermodynamic properties, such as the activity coefficient and the partial molar volume of the solute. Then data from literature will be used to evaluate the aggregation number and its temperature dependence.

2. Aggregation in Infinitely Dilute Solutions

2.1. Theoretical Background. A widely used theory for describing the properties of strongly nonideal solutions, including aqueous solutions, is the fluctuation theory of Kirkwood and Buff.[20,21] In this theory, a key quantity is

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 \, dr \qquad (1)$$

where $g_{ij}(r)$ is the radial distribution function (RDF). G_{ij} has the dimension of volume, and $G_{ij} = G_{ji}$. A dimensionless quantity, called total correlation function integral (TCFI), is also widely used

$$H_{ij} = \rho G_{ij} = \rho \int_0^\infty h_{ij}(r) 4\pi r^2 \, dr \qquad (2)$$

where $h_{ij}(r) = g_{ij}(r) - 1$ is the total correlation function (TCF) and ρ is the density of the solution. The G_{ij}'s were evaluated for various systems,[21] and the osmotic second virial coefficient B_2, which is related to G_{22} via the expression $B_2 = -(1/2)G_{22}$, was determined from vapor pressure measurements.[14]

The quantity $\rho_j G_{ij}$ represents the average excess number of j molecules in the surrounding of an i molecule. In a binary solution with solute (2) at infinite dilution, one can write

$$N_{22} \equiv \rho_2^0 G_{22}^\infty = \rho_2^0 \lim_{x_2 \to 0} \int_0^\infty [g_{22}(r) - 1] 4\pi r^2 \, dr \qquad (3)$$

where ρ_2^0 is the density of the pure solute and x_2 is the molar fraction of the solute in the solution. N_{22} represents the total excess of solute molecules in the surrounding of a solute molecule as the solute concentration approaches zero and is considered here a measure of the aggregation number. Similarly, denoting by ρ_1^0 the density of the pure solvent, one can write

$$H_{12}^\infty = \rho_1^0 G_{22}^\infty = \rho_1^0 \lim_{x_2 \to 0} \int_0^\infty [g_{12}(r) - 1] 4\pi r^2 \, dr \qquad (4)$$

H_{12}^∞ represents the excess solvent (1) molecules in the surrounding of a solute molecule at extremely low concentrations of the solute. Throughout this paper, the volume V and G_{ij} are expressed in cm³/mol and ρ is expressed in mol/cm³ ($\rho = 1/V$).

Using the Kirkwood−Buff theory, it is possible to estimate the values of the G_{ij}'s from experimentally measurable quanti-

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ties. For a binary system, the main results of the theory are given by eqs 5–7.[20]

$$\frac{x_2}{RT}\left(\frac{\partial \mu_2}{\partial x_2}\right)_{P,T} = 1 - \frac{x_1 x_2 \Delta H_{12}}{1 + x_1 x_2 \Delta H_{12}} \tag{5}$$

$$\bar{V}_2 = \frac{1 + x_1(H_{11} - H_{12})}{\rho(1 + x_1 x_2 \Delta H_{12})} \tag{6}$$

$$\frac{1}{k_T RT} = \frac{1 + x_1 x_2 \Delta H_{12}}{\rho^{-1}(1 + x_1 H_{11} + x_2 H_{22} + x_1 x_2 \Delta H_{12})} \tag{7}$$

In these equations, x_1 and x_2 are the molar fractions of the solvent and solute, respectively, μ_2 is the chemical potential of the solute, T the temperature, P the pressure, R the gas constant, $\bar{V}_2$ the partial molar volume of the solute, $k_T = (\partial \ln \rho / \partial P)_T$ the isothermal compressibility of the solution, and ΔH_{12} is defined as

$$\Delta H_{12} = H_{11} + H_{22} - 2H_{12} = \rho(G_{11} + G_{22} - 2G_{12}) \tag{8}$$

Introducing the activity coefficient γ_2 of the solute by the expression

$$\mu_2 = \mu_2^0(T) + RT \ln x_2 \gamma_2$$

where $\mu_2^0(T)$ is the standard chemical potential, eq 5 leads to

$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T} = -\frac{x_1 \Delta H_{12}}{1 + x_1 x_2 \Delta H_{12}} \tag{9}$$

As $x_2 \to 0$ ($x_1 \to 1$), eqs 6, 7, and 9 become, respectively

$$\rho_1^0 \bar{V}_2^\infty = 1 + H_{11}^0 - H_{12}^\infty \tag{10}$$

$$\rho_1^0 k_{T1} RT = 1 + H_{11}^0 \tag{11}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T}^\infty = -\Delta H_{12}^\infty = -\rho_1^0(G_{11}^0 + G_{22}^\infty - 2G_{12}^\infty) =$$
$$-(H_{11}^0 + H_{22}^\infty - 2H_{12}^\infty) \tag{12}$$

In eqs 10–12, the superscripts ∞ and 0 indicate a solute at infinite dilution and a pure component, respectively, and k_{T1} is the isothermal compressibility of the pure solvent. Denoting

$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T}^\infty \equiv -K_2 \tag{13}$$

eq 12 becomes

$$K_2 = \Delta H_{12}^\infty = H_{11}^0 + H_{22}^\infty - 2H_{12}^\infty \tag{14}$$

Combining eqs 3 and 4 with eqs 10, 11, and 14 yields

$$N_{22} = \frac{\rho_2^0}{\rho_1^0} H_{22}^\infty = \rho_2^0 k_{T1} RT + \frac{V_1^0}{V_2^0}(1 + K_2) - \frac{2\bar{V}_2^\infty}{V_2^0} \tag{15}$$

and

$$H_{12}^\infty = \rho_1^0 G_{12}^\infty = \rho_1^0(k_{T1} RT - \bar{V}_2^\infty) \tag{16}$$

where V_1^0 and V_2^0 are the molar volumes of the pure solvent and solute, respectively. Equations 15 and 16 allow one to estimate N_{22} and H_{12}^∞ from experimentally measurable quantities. Since at room temperature the isothermal compressibility of water is small, ($k_{T1} = 4.5 \times 10^{-5}$ bar^{-1} at 298.15 K[22]), the term $\rho_2^0 k_{T1} RT$ (=0.0125 for benzene, at 298.15 K) in eqs 15 and 16 is negligible near room temperature. Accordingly

$$N_{22} \approx \frac{V_1^0}{V_2^0}(1 + K_2) - \frac{2\bar{V}_2^\infty}{V_2^0} \tag{17}$$

and

$$H_{12}^\infty \approx -\rho_1^0 \bar{V}_2^\infty \tag{18}$$

Since in hydrocarbon + water systems, the partial molar volume of the solute is always positive,[7] eq 18 implies that the water molecules are excluded from the neighborhood of a solute molecule. The value of N_{22} is a result of the competition between two contributions. The first term stimulates the aggregation of the solute molecules because K_2 is always positive; the second term (always negative) stimulates the dispersion of the solute molecules.

Additional insight can be gained by using the direct correlation function (DCF) introduced by Ornstein and Zernike.[23] As shown in the Appendix, the following equation can be obtained

$$N_{22} = \frac{V_1^0}{V_2^0}\left(C_{22}^\infty + \frac{C_{12}^{\infty\,2}}{1 - C_{11}^0}\right) \tag{19}$$

and the direct correlation function integrals can be related to thermodynamic properties through the following equations:[24]

$$1 - C_{11}^0 = \frac{1}{\rho_1^0 k_{T1} RT} \tag{20}$$

$$1 - C_{12}^\infty = \frac{\bar{V}_2^\infty}{k_{T1} RT} \tag{21}$$

$$1 - C_{22}^\infty = \frac{\rho_1^0 (\bar{V}_2^\infty)^2}{k_{T1} RT} + \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T}^\infty \tag{22}$$

Using eqs 20–22 one can demonstrate that eqs 15 and 19 are equivalent. The first term in the right-hand side of eq 19 arises because of the solute molecules and, as shown below, is negative; the second term, which is always positive, arises because of both the solute and solvent molecules. Equation 19 shows that the solutes will aggregate if the solvent–solute contribution dominates.

2.2. Evaluation of K_2 and Calculation Results. From the above considerations, one can conclude that the molecular properties, N_{22}, H_{22}^∞, H_{12}^∞, C_{22}^∞, and C_{12}^∞ can be calculated in terms of $\bar{V}_2^\infty$, K_2, and the properties of the pure solute and water, V_2^0, V_1^0, and k_{T1}.

Some experimental results and estimation methods have been reported in the literature regarding the partial molar volumes of various solutes in water.[7,8] Moore et al.[7] determined the $\bar{V}_2^\infty$ of some hydrocarbons and gases in water at 298.15 K and proposed for relatively small molecules the empirical correlation

$$\bar{V}_2^\infty = 10.74 + 0.2683 V_{C2} \tag{23}$$

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TABLE 1: Comparison between Calculated and Determined Values for K_2[a]

	experimental			UNIQUAC		
system	$\ln \gamma_1^\infty$	$\ln \gamma_2^\infty$	K_2	τ_{12}	τ_{21}	K_2
benzene (2) + H_2O (1)	5.48	7.80	43.2 (298.15 K)	0.212 42	0.069 06	45.0 (298.15 K)
2-butanol + H_2O	1.53	3.57	12.0 (298.15 K)	0.712 21	0.411 8	19.2 (323.15 K)
pyridine + H_2O	0.788	3.37	30.0 (298.15 K)	0.117 97	2.623 55	40.4 (303.15 K)
piperidine + H_2O	1.10	1.89	14.0 (298.15 K)	2.019 24	0.189 34	14.2 (343.15 K)
tetrahydrofuran + H_2O	2.41	3.16	9.0 (298.15 K)	0.803 7	0.234 88	10.8 (308.15 K)

[a] The data for $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$ are from ref 10 and K_2 from ref 15. The values of τ_{12} and τ_{21} were obtained on the basis of eqs 25 and 26. The numbers in parentheses are the temperatures at which the values for K_2 were obtained.

where V_{C2} is the critical volume of the solute (in cm^3/mol). On the other hand, Kharakos[8] proposed the following semiempirical expression

$$\bar{V}_2^\infty = V_0 + k_{T1}RT \tag{24}$$

where V_0 is a characteristic volume, dependent on the structure of the solute molecule. For alkanes, $V_0 = 50.4 + 15.8(n_c - 2)$, where n_c is the number of carbons in the molecule. In this paper, eq 23 was used for hydrocarbons with $n_c < 7$, and eq 24 for the other compounds. In all cases, the estimated error was less than 10%.

For the pure liquid water, the isothermal compressibility k_{T1} and the molar volume V_1^0 were estimated using the equation proposed by Kell.[22] For pure solutes, the molar volume V_2^0 was estimated using the Hankinson−Brobst−Thomson method, which is recommended in the literature.[25] The errors regarding V_1^0 are less than 1%, and those regarding k_{T1} and V_2^0 less than 5%.

Numerous correlations have been proposed for the activity coefficient.[26] Among them, the Wilson,[27] NRTL,[28] UNIQUAC,[29] and Wang-Chao[30] equations have been most frequently used. The flexibility of these equations is a result of their adjustable parameters, two at least, which can be obtained by fitting the equilibrium experimental data. These equations can be used to calculate the quantity $K_2 = -(\partial \ln \gamma_2/\partial x_2)_{P,T}^\infty$. However, it should be noted that a satisfactory equation for the correlation of the activity coefficient may not provide a satisfactory estimation of the derivative involved in K_2.

In this paper, we adopted the UNIQUAC equation. From the expressions for the activity coefficients for solvent (1) and solute (2),[29] one finds

$$\ln \gamma_1^\infty = \ln\left(\frac{r_1}{r_2}\right) + \frac{z}{2}q_1 \ln\left(\frac{q_1 r_2}{q_2 r_1}\right) + l_1 - \frac{r_1}{r_2}l_2 + q_1(1 - \tau_{12} - \ln \tau_{21}) \tag{25}$$

$$\ln \gamma_2^\infty = \ln\left(\frac{r_2}{r_1}\right) + \frac{z}{2}q_2 \ln\left(\frac{q_2 r_1}{q_1 r_2}\right) + l_2 - \frac{r_2}{r_1}l_1 + q_2(1 - \tau_{21} - \ln \tau_{12}) \tag{26}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T}^\infty = 1 - \frac{r_2}{r_1} + \frac{z}{2}q_2\left(\frac{r_2}{r_1} - \frac{q_2}{q_1}\right) - \frac{r_2}{r_1}\left(l_2 - \frac{r_2}{r_1}l_1\right) + \frac{q_2^2}{q_1}\left(1 - \frac{2}{\tau_{12}} + \tau_{21}^2\right) \tag{27}$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1), \quad i = 1, 2 \tag{28}$$

In eqs 25−27, r_i and q_i ($i = 1, 2$) are the molecular volume and area parameters, respectively, which can be calculated from the van der Waals volume and area of the solute and solvent, as shown in refs 25 and 29. τ_{12} and τ_{21} are system-dependent parameters to be determined from experimental data, and z is the coordination number (10 in the present calculations).

The experimental data for the activity coefficients at the two extremes, $\ln \gamma_i^\infty = \lim_{x_j \to 0} \ln \gamma_i$ ($i = 1, 2$) together with eqs 25 and 26 are used to estimate the two parameters. Then eq 27 is employed to calculate the slope at infinite dilution. Experimental data regarding $\ln \gamma_i^\infty$ for various aqueous solutions are available in the literature.[9,10]

In Table 1, the values calculated for K_2 are compared to those determined experimentally.[15] The agreement is satisfactory.

Only few experimental data are available for $\ln \gamma_i^\infty$.[10] Therefore, it is not always possible to use eqs 25 and 26 to estimate the two parameters. The few experimental data available show, however, that the values of τ_{12} and τ_{21} are always less than 1 and $\tau_{12} \gg \tau_{21}$ for all hydrocarbon + water systems; therefore, the term τ_{21}^2 in eq 27 is negligible, and the following equation can be employed for K_2:

$$K_2 = -E_2 + \frac{q_2^2}{q_1}\frac{2}{\tau_{12}} \tag{29}$$

where

$$E_2 \equiv 1 - \frac{r_2}{r_1} + \frac{z}{2}q_2\left(\frac{r_2}{r_1} - \frac{q_2}{q_1}\right) - \frac{r_2}{r_1}\left(l_2 - \frac{r_2}{r_1}l_1\right) + \frac{q_2^2}{q_1} \tag{30}$$

Similarly, eq 26 can be simplified to

$$\ln \gamma_2^\infty = E_1 - q_2 \ln \tau_{12} \tag{31}$$

where

$$E_1 \equiv \ln\left(\frac{r_2}{r_1}\right) + \frac{z}{2}q_2 \ln\left(\frac{q_2 r_1}{q_1 r_2}\right) + l_2 - \frac{r_2}{r_1}l_1 + q_2 \tag{32}$$

Consequently, for the hydrocarbon + water systems, K_2 can be calculated on the basis of a single parameter, which can be obtained from the activity coefficient $\ln \gamma_2^\infty$. Combining eqs 29 and 31 yields

$$K_2 = \frac{2q_2^2}{q_1}(\gamma_2^\infty)^{(1/q_2)} \exp\left(-\frac{E_1}{q_2}\right) - E_2 \tag{33}$$

which, because q_1, q_2, E_1, and E_2 are constants for a given mixture, shows that the dependence of K_2 on temperature and pressure is due to the dependence of γ_2^∞ on those quantities.

The Wang−Chao equation,[30] which is considered one of the best equations for the excess Gibbs free energy,[31] was also

TABLE 2: Data for the Hydrocarbons Employed[a]

compound	r_2	q_2	V_2^0	$\bar{V}_2^\infty$	$\ln \gamma_2^\infty$	$\ln \gamma_1^\infty$	τ_{12}
propane	2.48	2.24	89.6	70.7	4.923	n.a	0.088 10
n-butane	3.15	2.78	101.4	76.6	9.99	n.a.	0.097 26
isobutane	3.15	2.77	105.6	81.3	9.86	n.a.	0.101 71
n-pentane	3.83	3.32	116.2	92.3	11.6	7.73	0.103 99
n-hexane	4.50	3.86	131.2	110.0	13.1	7.41	0.110 84
2,3-dimethylbutane	4.50	3.85	131.1	106.8	12.33	n.a	0.135 12
n-heptane	5.17	4.40	147.8	129.4	14.5	7.26	0.118 42
n-octane	5.84	4.93	163.1	145.2	16.1	7.12	0.119 22
n-decane	7.20	6.02	195.6	176.8	18.9	n.a.	0.129 15
n-dodecane	8.55	7.10	228.6	209.5	21.7	n.a.	0.135 41
cyclopentane	3.37	2.70	94.7	84.5	10.12	n.a.	0.107 57
cyclohexane	4.05	3.24	108.8	98.8	11.3	n.a.	0.129 33
cycloheptane	4.72	3.78	121.0	105.5	12.11	n.a.	0.160 52
benzene	3.19	2.40	89.8	82.5	7.80	5.48	0.227 61
toluene	3.87	2.93	106.6	97.7	9.2	n.a.	0.226 39
ethylbenzene	4.60	3.51	123.0	111.1	10.6	n.a.	0.229 56

[a] n.a. = not available. The volumes and activity coefficients are at 298.15 K. r_2, q_2, and V_2^0 were calculated according to the literature.[25,26] The data for $\bar{V}_2^\infty$ are from the literature.[7,8] The data for $\ln \gamma_2^\infty$ and $\ln \gamma_1^\infty$ are experimental.[9,10] The values of τ_{12} were calculated with eq 31.

TABLE 3: Data for Pure Water at 298.15 K[a]

r_1	q_1	V_1^0, cm^3/mol	k_{T1}, bar^{-1}	$k_{T1}RT$, cm^3/mol	$1 - C_{11}^0$
1.0	1.40	18.08	4.5×10^{-5}	1.122	16.05

[a] The values of r_1 and q_1 are from ref 34, and for V_1^0 and k_{T1} from ref 22.

employed for the estimation of K_2. In this case

$$\ln \gamma_1^\infty = \frac{z}{2}\left[\ln\left(\frac{V_2^0}{V_1^0 \Lambda_{12}}\right) + \frac{V_2^0 \Lambda_{21}}{V_1^0}\ln\left(\frac{V_1^0}{\Lambda_{21}V_2^0}\right)\right] - \ln \Lambda_{12} - \Lambda_{21} + 1 \quad (34)$$

$$\ln \gamma_2^\infty = \frac{z}{2}\left[\ln\left(\frac{V_1^0}{V_2^0 \Lambda_{21}}\right) + \frac{V_1^0 \Lambda_{12}}{V_2^0}\ln\left(\frac{V_2^0}{\Lambda_{12}V_1^0}\right)\right] - \ln \Lambda_{21} - \Lambda_{12} + 1 \quad (35)$$

$$\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T}^\infty = \frac{z}{2}\left[\frac{2V_1^0}{\Lambda_{21}V_2^0}\ln\left(\frac{\Lambda_{21}V_2^0}{V_1^0}\right) + 2\left(\frac{V_1^0\Lambda_{12}}{V_2^0}\right)^2\ln\left(\frac{\Lambda_{12}V_1^0}{V_2^0}\right)\right] - \frac{2}{\Lambda_{21}} + \Lambda_{12}^2 + 1 \quad (36)$$

where Λ_{12} and Λ_{21} are two adjustable parameters, which can be obtained from the values of $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$. Equation 36 was also used to estimate K_2, and the results were compared to the UNIQUAC equation, eq 27. In this case both Λ_{12} and Λ_{21} had to be evaluated.

Tables 2 and 3 list the data for the hydrocarbons and water, respectively, and Table 4 compares the values calculated for K_2 on the basis of eqs 27, 33, and 36 for five hydrocarbon +

water systems, for which $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$ have been determined experimentally.[10] One can conclude that there is excellent agreement between eqs 27 and 33 and that the Wang–Chao equation provides comparable results. Therefore, eq 33 will be used for estimating K_2 in the following calculations.

On the basis of the experimental data for 31 aliphatic hydrocarbons and 40 aromatic hydrocarbons at 298.15 K reported in the literature,[9] we obtained the following empirical expression:

$$\ln \gamma_2^\infty = a + b(X^I - 1/X^I) + c(X^I)^n \quad (37)$$

where X^I is the first order connection index of the solute molecule, which reflects the size and structure of the molecule and can be calculated as indicated in ref 32. The values of the parameters a, b, c, and n are listed in Table 5. The average absolute deviation (AAD) of eq 37 for the aliphatic hydrocarbons is 5.38%, and for the aromatic ones is 2.23%.

Equations 33 and 37 allow one to calculate K_2 and then N_{22}. Table 6 lists the calculated results for 16 hydrocarbon + water systems, and Figure 1 presents the dependence of N_{22} on the number of carbon atoms of the hydrocarbon molecules. Table 6 and Figure 1 show that: (i) the hydrocarbon molecules aggregate even at infinite dilution, and the aggregation number increases as the molecular size increases; (ii) the aggregation of the cyclic hydrocarbons is weaker than that of the aliphatic ones. The aggregation of the aromatic hydrocarbons is weaker than that of the aliphatic and cyclic ones owing to their weak polarity.

2.3. Temperature Dependence of Aggregation. Regarding the temperature dependence of the tendency to aggregate of hydrocarbons in aqueous solutions, some inconsistencies can be noted in the literature.[3,13,15,18,19] Experimental observations[13,15] and computer simulations[18,19] found that with increas-

**TABLE 4: Comparison between K_2 Values Calculated with Eqs 27, 33, and 36[a]**

systems	UNIQUAC eq 27			Wang–Chao eq 36			eq 33	
	τ_{12}	τ_{21}	K_2	Λ_{21}	Λ_{12}	K_2	τ_{12}	K_2
benzene + H$_2$O	0.212 42	0.069 056	45.0	0.050 626	1.391 41	47.2	0.227 61	42.5
n-pentane + H$_2$O	0.102 91	0.010 438	152.0	0.035 105	2.017 80	119.2	0.103 99	150.4
n-hexane + H$_2$O	0.109 48	0.012 177	192.8	0.023 540	2.300 80	185.1	0.110 84	190.4
n-heptane + H$_2$O	0.116 93	0.012 629	234.1	0.016 235	2.530 88	269.0	0.118 42	231.0
n-octane + H$_2$O	0.117 66	0.013 198	291.9	0.011 740	2.744 40	374.8	0.119 22	288.1

[a] The values of τ_{12} and τ_{21} in eq 27 were obtained from eqs 25 and 26; the values of Λ_{21} and Λ_{12} in eq 36 were obtained from eqs 34 and 35.

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TABLE 5: Coefficients in Eq 37[a]

solute	a	b	c	n
aliphatic hydrocarbons	5.9413	2.8003	1.45×10^{-6}	24.55
aromatic hydrocarbons	6.5038	1.7342	-10.368	-2.991

[a] The data for γ_2^{∞} used in the correlation are at 298.15 K and from ref 9.
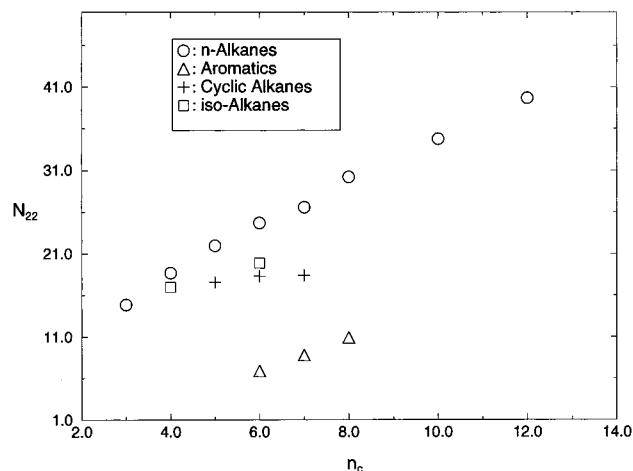
Figure 1. Plot of N_{22} against the number of carbons (n_c) of hydrocarbons at 298.15 K.

ing temperature the tendency to aggregate increases. Pratt and Chandler[3] predicted, however, that the tendency to aggregate always decreases with increasing temperature. In what follows an equation is derived to predict the temperature-dependence of aggregation.

From eq 17 one obtains

$$\left(\frac{\partial N_{22}}{\partial T}\right)_P = \left(\frac{\partial V_{12}^*}{\partial T}\right)_P (1 + K_2) + V_{12}^*\left(\frac{\partial K_2}{\partial T}\right)_P - 2\left(\frac{\partial V_2^*}{\partial T}\right)_P \quad (38)$$

where

$$V_{12}^* \equiv V_1^0/V_2^0, \quad V_2^* \equiv \bar{V}_2^{\infty}/V_2^0 \quad (39)$$

Thus the temperature dependence of N_{22} depends on the coefficients of thermal expansion of the pure solute and solvent and on the temperature dependence of K_2. Since V_{12}^* and V_2^* are volume ratios, their temperature dependencies are expected to be weak for not too large temperature changes. Therefore,

a reasonable approximation of eq 38 is

$$\left(\frac{\partial N_{22}}{\partial T}\right)_P \approx V_{12}^*\left(\frac{\partial K_2}{\partial T}\right)_P \quad (40)$$

The derivative $(\partial K_2/\partial T)_P$ can be obtained from eq 33, which leads to

$$\left(\frac{\partial K_2}{\partial T}\right)_P = (K_2 + E_2)\left(\frac{\partial \ln \gamma_2^{\infty}}{\partial T}\right)_P \quad (41)$$

Since[26]

$$\left(\frac{\partial \ln \gamma_2^{\infty}}{\partial T}\right)_P = -\frac{h_2^{E\infty}}{RT^2} \quad (42)$$

where $h_2^{E\infty}$ is the excess enthalpy of the solute at infinite dilution, combining eqs 40−42 yields

$$\left(\frac{\partial N_{22}}{\partial T}\right)_P \approx V_{12}^*(K_2 + E_2)\left(\frac{\partial \ln \gamma_2^{\infty}}{\partial T}\right)_P =$$
$$-V_{12}^*(K_2 + E_2)\frac{h_2^{E\infty}}{RT^2} \quad (43)$$

Since $-V_{12}^*(K_2 + E_2) < 0$, the sign of $(\partial N_{22}/\partial T)_P$ depends on the sign of $(\partial \ln \gamma_2^{\infty}/\partial T)_P$. When $h_2^{E\infty} < 0$, $(\partial \ln \gamma_2^{\infty}/\partial T)_P > 0$ and $(\partial N_{22}/\partial T)_P > 0$.

In the above expressions, no explicit dependence on temperature was assumed for the parameter τ_{12}. If one considers that

$$\tau_{12} = \exp\left(\frac{-\Delta u_{12}}{RT}\right) \quad (44)$$

as assumed in the UNIQUAC model,[29] then

$$\left(\frac{\partial \ln \gamma_2^{\infty}}{\partial T}\right)_P = -\frac{q_2 \Delta u_{12}}{RT^2} = \frac{q_2 \ln \tau_{12}}{T} \quad (45)$$

which combined with eq 43 yields

$$\left(\frac{\partial N_{22}}{\partial T}\right)_P = V_{12}^*(K_2 + E_2)\frac{q_2 \ln \tau_{12}}{T} \quad (46)$$

Since $\ln \tau_{12} < 0$ for all the systems considered here, eq 46 predicts that the aggregation of hydrocarbons in aqueous

TABLE 6: Calculated Results for C_{ij}^{∞}, H_{ij}^{∞}, and N_{22} of Hydrocarbons in Aqueous Solutions[a]

solute (2)	K_2	C_{12}^{∞}	C_{22}^{∞}	$C_{12}^{\infty 2}/(1 - C_{12}^0)$	H_{12}^{∞}	H_{22}^{∞}	B_2^{∞}, cm^3/mol	N_{22}
propane	80.7	-62.0	-164.8	238.7	-3.852	73.9	-668.1	14.9
n-butane	112.6	-67.3	-175.8	281.3	-4.178	105.2	-951.0	18.7
isobutane	107.4	-71.4	-217.6	316.6	-4.438	99.4	-898.6	17.0
n-pentane	150.4	-81.3	-268.8	410.5	-5.047	141.2	-1276.4	22.0
n-hexane	190.4	-97.0	-404.4	584.4	-6.026	179.3	-1620.8	24.7
2,3-dimethylbutane	155.3	-94.2	-406.3	551.2	-5.849	144.5	-1306.3	19.9
n-heptane	231.1	-114.3	-593.8	811.4	-7.100	217.8	-1968.9	26.6
n-octane	288.1	-128.4	-750.8	1024.0	-7.974	274.1	-2477.9	30.2
n-decane	395.4	-156.6	-1145	1522.7	-9.723	376.9	-3407.2	34.8
n-dodecane	523.5	-184.7	-1617	2118.2	-11.472	501.5	-4533.6	39.7
cyclopentane	100.5	-74.3	-250.7	342.8	-4.615	92.2	-833.5	17.6
cyclohexane	120.2	-87.1	-360.3	471.0	-5.407	110.3	-997.1	18.3
cycloheptane	131.1	-93.0	-416.3	537.0	-5.777	121.1	-1094.7	18.4
benzene	42.5	-72.6	-292.6	327.3	-4.504	34.4	-331.0	6.9
toluene	61.9	-86.1	-407.9	460.3	-5.346	52.1	-471.0	8.8
ethylbenzene	85.7	-98.0	-522.1	596.3	-6.087	74.4	-672.6	10.9

[a] All values are at 298.15 K, and the values of K_2 were calculated with eq 33.

solutions always decreases as the temperature increases. This conclusion is not always correct, and this is in agreement with the observation that the temperature dependence of the activity coefficient predicted by the UNIQUAC model is not always correct.[26]

A more suitable treatment should rely on the temperature dependence of the experimentally determined $\ln \gamma_2^\infty$, or $h_2^{E\infty}$. However, for only few systems are there data available for $\ln \gamma_2^\infty$ and solute fugacity at different temperatures.[10−15] From such data, one obtains for benzene + water $K_2 = 46.3$, 87.0, and 75.2 at 293.15, 308.15, and 313.15 K, respectively,[11,12] and $K_2 = 51$, 40, 43, 110 at 281.15, 288.15, 298.15, and 306.15 K, respectively.[15] From the first group of data for K_2 and eq 40, one can conclude that N_{22} passes through a maximum with increasing temperature, since K_2 also passes through one. Since at sufficiently high temperatures N_{22} is expected to decrease with increasing temperature, the second group of values, in which K_2 increases with temperature at relatively low temperatures, is also compatible with a maximum. From the vapor pressure measurements for the fluorobenzene + water system,[13] one can obtain $K_2 = 48.8$, 51.8, 63.4, and 82.2 at 288.15, 298.15, 308.15, and 318.15 K, respectively. For the same reason as for the latter set of data, these values are compatible with a maximum for N_{22} with respect to the temperature.

Another source for $\ln \gamma_2^\infty$ is from the data on Henry's law constant, H_2, reported in the literature.[4] From these data, γ_2^∞ can be calculated using the expression

$$\gamma_2^\infty = \frac{H_2}{p_2^s \varphi_2^s} \exp\left[-\frac{V_2^0(p_1^s - p_2^s)}{RT}\right] \qquad (47)$$

where p_1^s and p_2^s are the vapor pressures of the solvent (water) and solute, respectively, which are available in the literature,[25] and φ_2^s is the fugacity coefficient of the pure solute at saturation, which can be obtained using the method of Lyckman et al.[33]

Combining eqs 33 and 47, we calculated K_2, which, together with $\bar{V}_2^\infty$ given by eq 24 and k_{T1} given by the Kell equation,[22] allowed to estimate N_{22} from eq 15. The results for n-hexane + water and n-octane + water are plotted in Figures 2 and 3, respectively. One can see that the n-hexane + water system exhibits a maximum and that the n-octane + water system may exhibit a maximum at a temperature below those for which data are available.

3. Pressure Effects in the Dilute Solutions

As already pointed out in the literature,[11−15] the assumption of infinite dilution is not valid for some hydrocarbons, such as benzene, even for molar fractions of the order of 4×10^{-4}. For a dilute solution, the activity coefficient of the solute can be written as
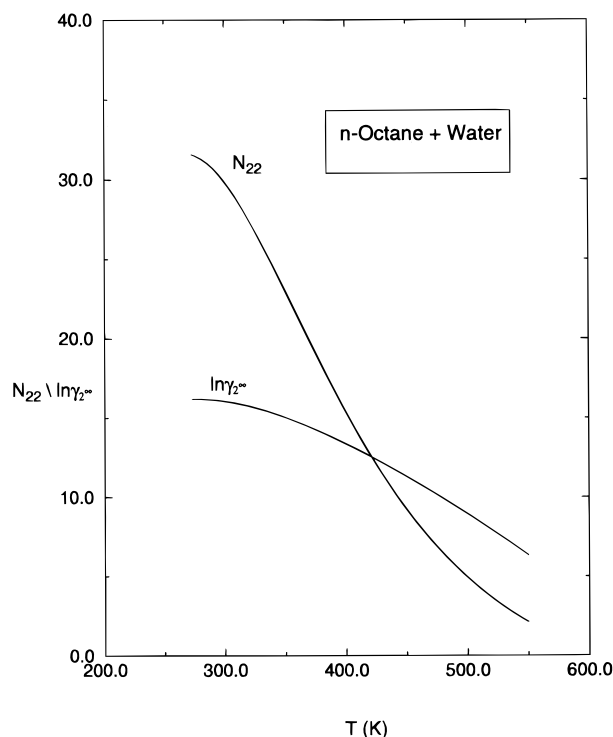
$$\gamma_2 = \gamma_2^\infty \exp(-K_2 x_2) \approx \gamma_2^\infty (1 - K_2 x_2) \qquad (48)$$

In this case, using an approach similar to that for the infinitely dilute solutions and assuming the molar volume of the mixture $V \approx V_1^0$, the partial molar volume $\bar{V}_2 \approx \bar{V}_2^\infty$, and the isothermal compressibility $k_T \approx k_{T1}$, one obtains

$$N_{22} = \rho_2^0 k_{T1} RT + \frac{V_1^0}{V_2^0}\left(1 + \frac{K_2}{1 - x_2 K_2}\right) - \frac{2\bar{V}_2^\infty}{V_2^0} \qquad (49)$$
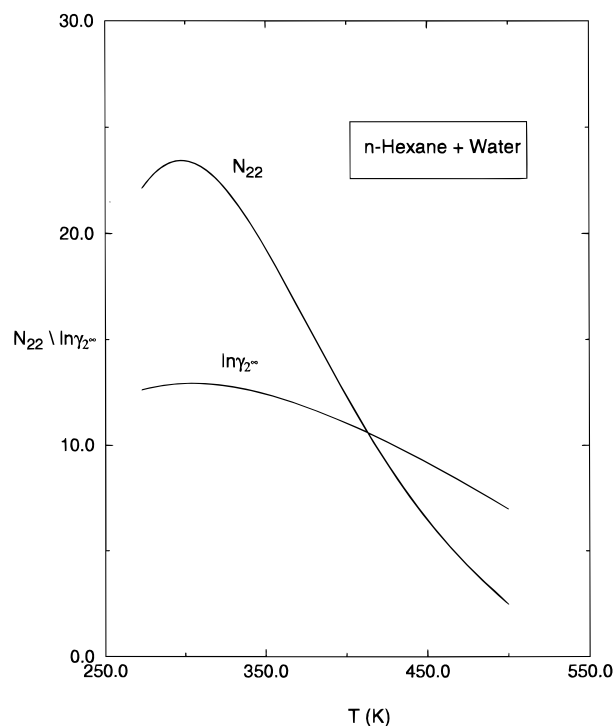
Figure 2. Temperature dependence of N_{22} and $\ln \gamma_2^\infty$ for the n-hexane + water system.

Figure 3. Temperature dependence of N_{22} and $\ln \gamma_2^\infty$ for the n-octane + water system.

Table 7 lists the concentration dependence of the activity coefficients for some systems at the normal pressure. One can see that only for cyclohexane and benzene the term $K_2 x_2$ contributes about 2%, but that for all other hydrocarbons this term is negligible. At high pressures this effect is likely to become more important.

The pressure effect on the activity coefficient can be neglected in the present case.[26] However, since the solubility is strongly

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TABLE 7: Concentration Effect on the Activity Coefficient[a]

solute (2)	solubility (x_2)	x_2K_2
propane	2.73×10^{-5}	0.0022
n-butane	2.24×10^{-5}	0.0025
n-hexane	2.41×10^{-6}	0.00046
cyclohexane	2.10×10^{-4}	0.0252
n-octane	1.05×10^{-7}	0.00003
benzene	4.07×10^{-4}	0.0173
toluene	1.04×10^{-4}	0.0064
ethylbenzene	2.87×10^{-5}	0.0025

[a] The solubility data (at 298.15 K) are from the literature.[4,5] The values of K_2 are listed in Table 6.
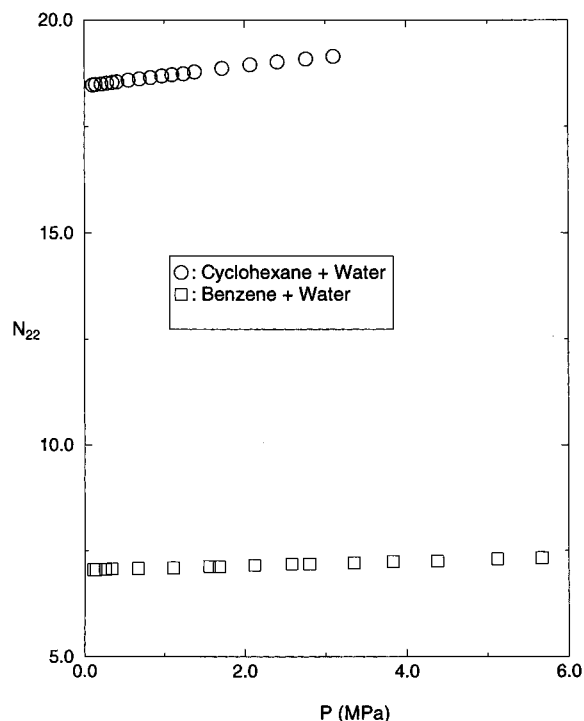
Figure 4. Pressure dependence of N_{22} for cyclohexane + water and benzene + water systems at 310.49 K.

dependent on pressure,[4,5] the term x_2K_2 may reach values of order of 0.1 or higher.

Figure 4 presents the pressure dependence of the aggregation of cyclohexane and benzene in aqueous solutions on ths basis of solubility data from literature.[5] Since the pressure change is not very large, V_1^0/V_2^0, $\bar{V}_2^\infty/V_2^0$, and K_2 have been treated as independent of pressure. For cyclohexane, the aggregation increases by more than 5% as the pressure increases from 0.1 to 3.0 MPa.

4. Conclusions

On the basis of the fluctuation theory of Kirkwood and Buff, an equation that relates the aggregation of solutes in infinitely dilute aqueous solutions to the slope of the solute activity coefficient and partial molar volume at infinite dilution is obtained. The aggregation of some hydrocarbons in aqueous solution was thus evaluated.

On the basis of the derived equations, one can conclude that the aggregation number passes through a maximum with increasing temperature and increases as the pressure increases.

Appendix

Ornstein and Zernike[23] suggested dividing the total correlation function into two parts, a direct part and indirect one; the direct

correlation function of a pair ij is defined as

$$c_{ij}(r_{12}) = h_{ij}(r_{12}) - \sum_k \rho_k \int c_{ik}(r_{13}) \, h_{jk}(r_{23}) \, dr_3 \quad \text{(A1)}$$

The direct correlation function integral (DCFI) given by

$$C_{ij} = \rho \int c_{ij}(r) \, d\bar{r} \quad \text{(A2)}$$

has the important characteristic that it is short ranged and has a finite value even at the critical point. In contrast, TCFI is long-ranged and diverges at the critical point. The DCFI and TCFI are related through the relations[24]

$$H_{11} = [(1 - x_2C_{22})/D - 1]/x_1 \quad \text{(A3)}$$

$$H_{12} = C_{12}/D \quad \text{(A4)}$$

$$H_{22} = [(1 - x_1C_{11})/D - 1]/x_2 \quad \text{(A5)}$$

where

$$D = (1 - x_1C_{11})(1 - x_2C_{22}) - x_1x_2C_{12}^2 \quad \text{(A6)}$$

Accordingly, the DCFIs can be related to thermodynamic properties by the following equations[24]

$$1 - C_{11} = \frac{\rho\bar{V}_1^2}{k_TRT} + x_2\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{P,T} \quad \text{(A7)}$$

$$1 - C_{12} = \frac{\rho\bar{V}_1\bar{V}_2}{k_TRT} - x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{P,T} \quad \text{(A8)}$$

$$1 - C_{22} = \frac{\rho\bar{V}_2^2}{k_TRT} + x_1\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T} \quad \text{(A9)}$$

where γ_1 and $\bar{V}_1$ are the activity coefficient and partial molar volume of the solvent, respectively. For $x_2 \to 0$ ($x_1 \to 1$), eqs A7−A9 lead to eqs 20−22 of the text, and eqs A3−A5 become

$$H_{11}^0 = \rho_1^0G_{11}^0 = \frac{C_{11}^0}{1 - C_{11}^0} \quad \text{(A10)}$$

$$H_{12}^\infty = \rho_1^0G_{12}^\infty = \frac{C_{12}^\infty}{1 - C_{11}^0} \quad \text{(A11)}$$

$$H_{22}^\infty = \rho_1^0G_{22}^\infty = C_{22}^\infty + \frac{C_{12}^{\infty\,2}}{1 - C_{11}^0} \quad \text{(A12)}$$

Finally, combining eqs 3 and A12, one obtains eq 19.

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