Estimation of Surfactant Tail Transfer Free Energies from Polar Solvents to Micelle Core

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To predict the critical micelle concentration of surfactants on the basis of any thermodynamic model, it is necessary to know the magnitude of the transfer free energy of the surfactant tail from the solvent to a hydrocarbon liquid phase. This information is not available for almost all of the polar organic solvents in which micellization behavior has been examined in the past. In this paper, we use the experimental infinite dilution activity coefficient data for alkanes obtained in other polar solvents to empirically correlate the transfer free energy to the solvent characteristics (as represented by the dispersion, polar, and hydrogen-bonding components of the solubility parameter). On the basis of this correlation, we suggest how one can determine the free energies of transfer of the surfactant tail from polar solvents of interest to a hydrocarbon liquid, at any temperature.

Introduction

The solution behavior of surfactants in water has been extensively investigated in the literature. In general, one finds, in aqueous solutions, a well-defined critical micelle concentration (cmc) and the formation of micelles of sufficiently large aggregation numbers.[1] Some applications of surfactants involve the presence of polar organic solvents in addition to water. This has motivated a number of studies in recent years on the aggregation behavior of surfactants in polar organic solvents and in binary mixtures of water and organic solvents. These experimental studies using solvents such as ethylene glycol, formamide, glycerol, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, *N*-methylacetamide, formic acid, hydrazine, acetonitrile, methanol, ethanol, and dioxane have raised important questions concerning the occurrence or otherwise of a cmc and the formation of large aggregates versus small oligomers. These studies have been reviewed most recently in ref 2.

To examine the solution properties of surfactants from a theoretical point of view, it is necessary to know the standard state chemical potential difference between a surfactant molecule in the solvent and a surfactant molecule incorporated into the micelle.[1] One contribution to this standard chemical potential difference comes from the free energy change accompanying the transfer of the surfactant tail from the solvent to the hydrocarbon liquid-like interior of the micellar aggregate. This contribution has a dominant influence on the magnitude of the critical micelle concentration. For aqueous solutions, this free energy contribution can be readily estimated at any temperature using expressions developed in our earlier study of micellar solutions.[3] But similar information is not available for almost all of the polar solvents of interest mentioned above.

In principle, the transfer free energy can be estimated using theoretical models such as the scaled particle theory[4] or using semitheoretical group contribution procedures

such as UNIFAC or ASOG.[5] To apply the scaled particle theory, one needs a number of molecular constants for all the solvents of interest which are not readily available. Of particular concern are the magnitudes of the Lennard-Jones potential parameters for various solvents. The analysis of gas solubilities in many solvents shows[4] that the Lennard-Jones energy parameter that can provide accurate estimates of the gas solubilities is quite different from the energy parameter estimated from gas phase virial coefficients, viscosities, or liquid-state properties. Therefore, if the energy parameter for the solvents of interest to us can be estimated using experimental gas solubility data, we can exploit this method for the calculation of the transfer free energies.

Among the group contribution procedures, UNIFAC is probably the most widely used. The UNIFAC group parameters have been obtained from vapor-liquid equilibrium (VLE) data[5a] and also from liquid-liquid equilibrium (LLE) data.[5b] The LLE data employed for the determination of the LLE group parameters are available in book form in the DECHEMA Chemistry Data Series.[6] It is known that the UNIFAC VLE group parameters cannot be used to quantitatively predict the liquid-liquid equilibrium data.[5a] Further, even when the group parameters based on the LLE are used, the reliability of the calculated infinite dilution activity coefficient is generally poor. Indeed, the transfer free energies of hydrocarbons in water calculated using the UNIFAC LLE group parameters differ considerably from available experimental data. The reason lies in the type of data used for developing the LLE group parameters.[5b] If only the water-hydrocarbon binary LLE data are used, the resulting group parameters can accurately reproduce the solubility behavior. If, on the other hand, ternary LLE data are used (as is the case), such accuracy is lost. Large discrepancies result especially for the long chain hydrocarbons whose solubilities are quite small.

In this paper, we make use of the limited experimental data[7] on the finite dilution activity coefficient of hydrocarbons in polar solvents (including ethanol, phenol,

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(6) Sorensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection, DECHEMA Chemistry Data Series*; DECHEMA: Frankfurt, 1979; Vol. V, Parts 1-3 (also supplements to the volume).

Table 1. Hydrocarbon Transfer Free Energies for Polar Solvents at 25 °C and Solubility Parameters from Hoy's Tabulation[a]

solvent	$\left(\dfrac{\Delta\mu_A^\circ}{kT}\right)_{Tr}$		δ^d, (MPa)$^{1/2}$	δ^p, (MPa)$^{1/2}$	δ^h, (MPa)$^{1/2}$	$(\Delta\delta_{AS})^2$, MPa	R_{AS}^2, MPa
	$C_{12}H_{26}$	$C_{16}H_{34}$					
methyl ethyl ketone	−1.96	−2.29	14.1	9.3	9.5	180	135
						182	137
furfural	−4.64	−5.42	na	na	na	na	na
phenol	−3.69	−4.19	na	na	na	na	na
ethanol	−3.65	−4.36	12.6	11.2	20	536	336
						540	340
triethylene glycol	−6.59	−8.16	15	12.2	21.8	625	387
						626	388
diethylene glycol	−7.22	−8.89	12.4	12.3	23.3	706	434
						710	439
ethylene glycol	−10.4	−12.9	10.1	15.1	29.8	1148	704
						1156	712
water	−22	−27.7	12.2	22.8	40.4	2165	1349
						2170	1354

[a] na indicates parameters not available in the compilations. In the last two columns, the number listed above refers to dodecane while that listed below refers to hexadecane.

furfural, ethylene glycol, diethylene glycol, triethylene glycol, and methyl ethyl ketone) to generate an empirical correlation between the transfer free energy and the solvent properties. The Hildebrand−Scatchard solubility parameter is selected to represent the solvent characteristics. In the original formulation of the solubility parameter theory by Hildebrand,[8] the concept was applied to molecules in which the principal type of intermolecular interactions are of the dispersion type. Over the years, the solubility parameter concept has been applied[9] to systems where polar and hydrogen-bonding interactions are also present and where such interactions may even dominate the solution behavior. Although a rigorous theoretical foundation for extending the solubility parameter concept to such systems does not exist, the decomposition of the solubility parameter into dispersion, polar, and hydrogen-bonding components has played a very useful practical role in our qualitative or semiquantitative understanding of the solubility characteristics of many polymer systems. The simplicity of the solubility parameter concept has very much contributed to its widespread use. This provides the motivation for using the solubility parameter concept in developing a correlation for the surfactant tail transfer free energy in this paper.

Hydrocarbon Transfer Free Energy Data for Polar Solvents

Consider a hydrocarbon solute A at an infinitely dilute concentration X_A in a polar solvent S. The chemical potential μ_A of the solute can be represented by the two equivalent relations

$$\mu_A = \mu_A^\circ + kT \ln X_A$$

$$\mu_A = \mu_A^* + kT \ln(\gamma_A^\infty X_A) \tag{1}$$

where μ_A^* is the standard state of A defined as the pure solute phase of A while μ_A° is the standard state of A defined as the infinitely dilute solution condition in solvent S. The first equation represents an ideal dilute solution

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(8) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold Publishing Corporation: New York, 1950.

(9) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.

where the standard state chemical potential term μ_A° incorporates within it the nonideality of the solute−solvent interactions. In the second equation, because of the choice of the pure solute phase as the reference state, the nonideality of solute−solvent interactions are accounted for by the infinite dilution activity coefficient γ_A^∞. Consequently, one can write the following relation connecting the infinite dilution activity coefficient and the transfer free energy of the solute.

$$\ln \gamma_A^\infty = \frac{(\mu_A^\circ - \mu_A^*)}{kT} = -\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} \tag{2}$$

As mentioned before, estimates of the infinite dilution activity coefficient for alkanes in ethylene glycol, diethylene glycol, triethylene glycol, phenol, furfural, methyl ethyl ketone, and ethanol are available in the literature.[7] The estimates have their origin in phase equilibrium data for many binary mixtures. The phase equilibrium data have been reduced to activity coefficients at infinite dilution in the solvent and correlated to the number of carbon atoms in the alkanes. The correlations are associated with average and maximum percent deviations in γ_A^∞ of 11.5 and 37 for furfural (based on data for 4 alkanes), 5.1 and 19 for phenol (based on data for 6 alkanes), 4.8 and 15 for ethanol (based on data for 7 alkanes), 5.8 and 12 for triethylene glycol (based on data for 3 alkanes), 7.5 and 23 for diethylene glycol (based on data for 4 alkanes), 17 and 60 for ethylene glycol (based on data for 3 alkanes), and 4 and 15 for methyl ethyl ketone (based on data for 3 alkanes). Using the estimates for the infinite dilution activity coefficients, we have computed the transfer free energies for dodecane and hexadecane at 25 °C in the above solvents and the results are presented in Tables 1 and 2.

The results for water listed in the tables are obtained from the expressions for the transfer free energy of methyl and methylene groups developed in our earlier studies.[3] The transfer free energy for a methylene (CH_2) group as a function of temperature (expressed in K) can be written as

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,W} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056T \tag{3}$$

while for a methyl (CH_3) group, the transfer free energy is

Table 2. Hydrocarbon Transfer Free Energies for Polar Solvents at 25 °C and Solubility Parameters from Hansen's Tabulation[a]

solvent	$\left(\dfrac{\Delta\mu_A^o}{kT}\right)_{Tr}$		δ^d, (MPa)$^{1/2}$	δ^p, (MPa)$^{1/2}$	δ^h, (MPa)$^{1/2}$	$(\Delta\delta_{AS})^2$, MPa	R_{AS}^2, MPa
	$C_{12}H_{26}$	$C_{16}H_{34}$					
methyl ethyl ketone	−1.96	−2.29	16	9	5.1	107	94
						107	94
furfural	−4.64	−5.42	18.6	14.9	5.1	256	243
						253	240
phenol	−3.69	−4.19	18	5.9	14.9	262	151
						259	148
ethanol	−3.65	−4.36	15.8	8.8	19.4	454	266
						454	266
triethylene glycol	−6.59	−8.16	16	12.5	18.6	502	329
						502	329
diethylene glycol	−7.22	−8.89	16.2	14.7	20.5	637	426
						636	426
ethylene glycol	−10.4	−12.9	17	11	26	798	460
						797	459
water	−22	−27.7	15.6	16	42.3	2045	1151
						2046	1151

[a] na indicates parameters not available in the compilations. In the last two columns, the number listed above refers to dodecane while that listed below refers to hexadecane.

$$\left(\frac{\Delta\mu_A^o}{kT}\right)_{Tr,W} = 3.38 \ln T + \frac{4064}{T} - 44.13 + 0.02595T \tag{4}$$

The estimates for water have greater precision compared to the estimates for the other polar solvents.

Solubility Parameter of the Solvent and Its Decomposition

The solubility parameter δ of a molecule is defined by

$$\delta = \left(-\frac{U}{V}\right)^{1/2} = \left(-\frac{\Delta U_{vap}}{V}\right)^{1/2} = \left(-\frac{(\Delta H_{vap} - RT)}{V}\right)^{1/2} \tag{5}$$

where U is the molar internal energy (defined relative to the ideal vapor at the same temperature), ΔU_{vap} is the molar internal energy of vaporization, ΔH_{vap} is the molar enthalpy of vaporization, V is the molar volume, and R is the gas constant. Although the solubility parameter concept was pioneered by Hildebrand to characterize molecules which interact with one another mainly through dispersion type interactions, Hansen[10] proposed an extension of the Hildebrand method to interpret the behavior of nonpolar, polar, and hydrogen-bonding systems. In this approach, the cohesive energy U is divided into three components: dispersion interactions U^d, polar interactions U^p, and hydrogen-bonding interactions U^h. Correspondingly, the solubility parameter δ is also decomposed into a dispersion component δ^d, a polar component δ^p, and a hydrogen-bonding component, δ^h.

$$U = U^d + U^p + U^h, \quad (\delta)^2 = (\delta^d)^2 + (\delta^p)^2 + (\delta^h)^2 \tag{6}$$

The extension is empirical in origin but has played a useful role in explaining polymer−solvent miscibility behavior.

Two comprehensive tabulations of the dispersion, polar, and hydrogen-bonding components of the solubility parameters are available in the literature, developed respectively by Hansen (Chapter 8, Table 5 of ref 9) and Hoy (Chapter 7, Table 2 of ref 9). We have listed in Table 1 the solubility parameter components for various solvents based on Hoy's compilations and in Table 2 those based on Hansen's compilations. It may be observed that the

values of the solubility parameter and its components in the tabulations of Hansen are not the same as those in the tabulations of Hoy since they adopted different approaches to developing these estimates. It is essential to use either Hansen's or Hoy's estimates self-consistently, if reliable results are to be obtained, and the estimates from the two compilations should not be mixed with one another.
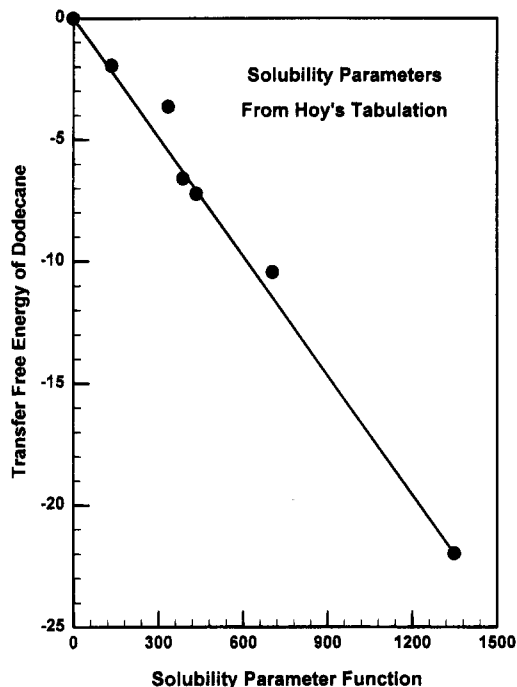
Correlation of the Transfer Free Energy with the Solubility Parameter

In the framework of the solubility parameter theory, the mutual interactions between component A and a solvent S are described by the interaction factor

$$(\Delta\delta_{AS})^2 = (\delta_A^d - \delta_S^d)^2 + (\delta_A^p - \delta_S^p)^2 + (\delta_A^h - \delta_S^h)^2$$

$$(\Delta\delta_{AS})^2 = (\delta_A^d - \delta_S^d)^2 + (\delta_S^p)^2 + (\delta_S^h)^2 \tag{7}$$

In the second expression in eq 7, we have incorporated the fact that the polar (δ_A^p) and hydrogen-bonding (δ_A^h) components of the solubility parameter for the hydrocarbon solute are zero. For polar solvents of interest to us, where polar and hydrogen-bonding interactions are important, the first term in eq 7 accounting for the dispersion interactions is often very small compared to the other terms. The calculated values of $(\Delta\delta_{AS})^2$, expressed in units of MPa, are listed in Tables 1 and 2 for both dodecane and decane, taking $\delta_A = \delta_A^d = 15.8$ MPa$^{1/2}$ for dodecane and $\delta_A = \delta_A^d = 16.4$ MPa$^{1/2}$ for hexadecane. One can see that $(\Delta\delta_{AS})^2$ is virtually independent of the hydrocarbon solute and is entirely determined by the solvent properties because of the relative insignificance of the dispersion term in eq 7.

We have correlated the transfer free energies against $(\Delta\delta_{AS})^2$ and find that the deviations between the correlated and experimental transfer free energies are not sufficiently small to allow the use of this correlation for predictive purposes. Therefore, we have examined the importance of the dispersion, polar, and hydrogen-bonding components individually with respect to their ability to correlate the transfer free energy data. We find that a slight modification of the interaction parameter $(\Delta\delta_{AS})^2$ by accounting for only half of the hydrogen-bonding contribution leads

(10) Hansen, C. M. *J. Paint Technol.* **1967**, *39*, 104, 505.

Figure 1. Correlation between the transfer free energy of dodecane (in units of kT) and the solubility parameter function R_{AS}^2 (in units of MPa). The solubility parameter components for the polar solvents have been obtained from Hoy's compilations and are summarized in Table 1.
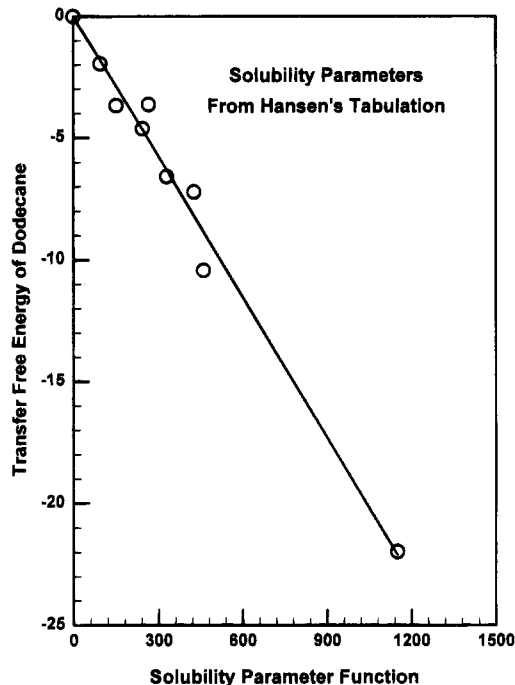
to a reasonable correlation. The modified interaction parameter denoted as R_{AS}^2 is

$$R_{AS}^2 = (\delta_A^d - \delta_S^d)^2 + (\delta_A^p - \delta_S^p)^2 + 0.5(\delta_A^h - \delta_S^h)^2$$
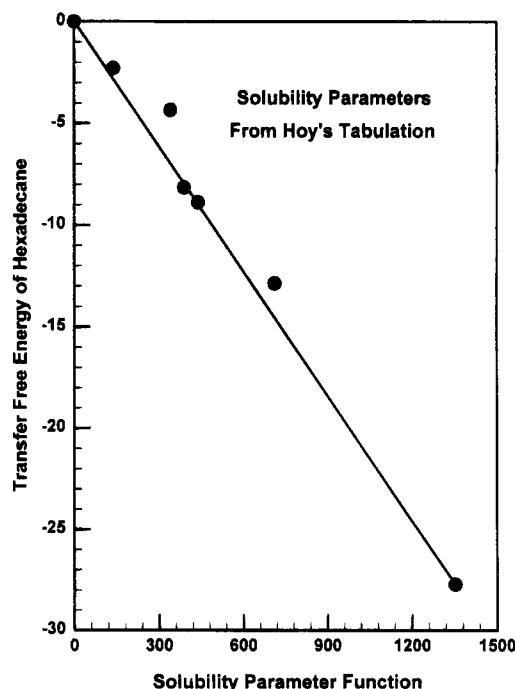
$$R_{AS}^2 = (\delta_A^d - \delta_S^d)^2 + (\delta_S^p)^2 + 0.5(\delta_S^h)^2 \qquad (8)$$

As before, the second relation in eq 8 incorporates the fact that the polar and hydrogen-bonding components of the solubility parameter for the hydrocarbon solute are zero. The calculated values of R_{AS}^2 are also listed in Tables 1 and 2 for both dodecane and hexadecane (expressed in units of MPa). As expected, R_{AS}^2 is virtually independent of the hydrocarbon solute and is entirely determined by the solvent properties. We have plotted the transfer free energy of dodecane and hexadecane against the interaction parameter R_{AS}^2 in Figures 1 and 2 for dodecane and Figures 3 and 4 for hexadecane. Figures 1 and 3 are based on Hoy's solubility parameter compilation while Figures 2 and 4 are based on Hansen's compilation.

Given the deviations in the estimated γ_A^∞ in the polar solvents and the relative precision of the transfer free energy data in water, we bias the correlation toward the water data by requiring the correlation line to pass through the water data. The correlations are reasonable, though there is appreciable deviation for some solvents (appreciable in relation to the precision of cmc measurements). The deviations are comparable to or smaller than the average deviations on γ_A^∞ specified in ref 7. We find that when Hoy's solubility parameters are used, the transfer free energies are given by the relations

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} = -0.0163\,R_{AS}^2 \quad \text{for dodecane}$$

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} = -0.02055\,R_{AS}^2 \quad \text{for hexadecane} \quad (9)$$

Figure 2. Correlation between the transfer free energy of dodecane (in units of kT) and the solubility parameter function R_{AS}^2 (in units of MPa). The solubility parameter components for the polar solvents have been obtained from Hansen's compilations and are summarized in Table 2.
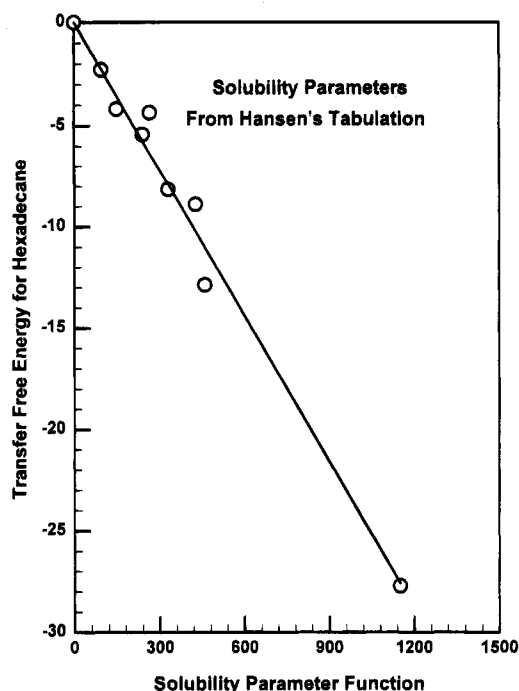

Figure 3. Correlation between the transfer free energy of hexadecane (in units of kT) and the solubility parameter function R_{AS}^2 (in units of MPa). The solubility parameter components for the polar solvents have been obtained from Hoy's compilations and are summarized in Table 1.

When Hansen's solubility parameters are used, the transfer free energies are given by the relations

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} = -0.0191\,R_{AS}^2 \quad \text{for dodecane}$$

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} = -0.02409\,R_{AS}^2 \quad \text{for hexadecane} \quad (10)$$

Figure 4. Correlation between the transfer free energy of hexadecane (in units of kT) and the solubility parameter function R_{AS}^2 (in units of MPa). The solubility parameter components for the polar solvents have been obtained from Hansen's compilations and are summarized in Table 2.

Purely statistical correlations without introducing the bias toward the water data give slopes of -0.0159 and -0.0197 in eq 9 and slopes of -0.0192 and -0.024 in eq 10.

The transfer free energy of dodecane is made up of contributions from 2 methyl and 10 methylene groups while that of hexadecane is made up of contributions from 2 methyl and 14 methylene groups. Therefore, from the transfer free energies of dodecane and hexadecane, the methyl and methylene group contributions can be calculated and, thus, the transfer free energy of a surfactant tail can be estimated.

Temperature Dependence of the Transfer Free Energy

The correlating equations (9 and 10) have been obtained at 25 °C. But the nature of the correlations also suggests a simple method for determining the transfer free energies at temperatures other than 25 °C. As mentioned before, the slopes of the correlating lines are determined by the transfer free energy in water and the interaction parameter R_{AW}^2 (subscript W denoting water as the solvent). Indeed, the correlating equations (9 and 10) can be rewritten as

$$\left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,S} = \left(\frac{\Delta\mu_A^\circ}{kT}\right)_{Tr,W}\frac{R_{AS}^2}{R_{AW}^2} \tag{11}$$

It is known that while the solubility parameters have a

Table 3. Interaction Parameter R_{AS}^2 (MPa) for Polar Solvents Based on Hoy's and Hansen's Compilations[a]

solvent	R_{AS}^2 (MPa)	
	from Hoy	from Hansen
formamide	772	869
	781	868
glycerol	na	578
		577
dimethylformamide	na	254
		253
dimethylacetamide	na	185
		184
dimethyl sulfoxide	na	328
		325
formic acid	na	282
		284
acetonitrile	346	343
	353	344
methanol	475	401
	480	402

[a] na indicates that parameters are not available in the compilations. The number listed above corresponding to each solvent refers to dodecane while the number listed below refers to hexadecane. As discussed in the text, the interaction parameters for the two solutes are practically independent of the hydrocarbon solute.

temperature dependence, the difference between the solubility parameters of two molecules can be assumed to be temperature independent. This is a common approach used in solution thermodynamics, and it results in satisfactory interpretation of solution properties. Therefore, R_{AS}^2 and R_{AW}^2 appearing in eq 11 can be considered as temperature independent. Consequently, if we know the transfer free energy of the surfactant tail in water at any temperature, then we can use eq 11 to calculate the transfer free energy in any polar solvent of interest at that temperature. For convenient reference, the interaction parameter R_{AS}^2 needed for such calculations (for various solvents in which surfactant aggregation behavior has been studied) are provided in Table 3 based on both Hansen's and Hoy's solubility parameter compilations.

Conclusions

An empirical correlation is developed to facilitate the estimation of the surfactant tail transfer free energy from a polar solvent to a hydrocarbon liquid. The estimation procedure can be summarized as follows: (i) Identify the solubility parameter values for the solvent of interest either from Hoy's or Hansen's compilations. (ii) Calculate the interaction parameter R_{AS}^2 for the solvent of interest using eq 8 if it is not listed in Tables 1–3. The interaction parameter R_{AW}^2 for water is listed in Tables 1 and 2. (iii) Calculate the transfer free energy of the surfactant tail in water at the temperature of interest on the basis of the temperature-dependent methyl and methylene group contributions given in eqs 3 and 4. (iv) Introduce the interaction parameter R_{AS}^2 for the solvent and the transfer free energy of the surfactant tail at the temperature of interest in water in eq 11 and calculate the transfer free energy of the surfactant tail in the polar solvent at the same temperature.