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PHASE EQUILIBRIUM AND THERMODYNAMIC PROPERTIES IN MICROEMULSIONS

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Abstract

A calorimetric investigation was performed on the partition of *n*-pentanol in the external oil phase and in the interfacial layer of the water-in-oil microemulsion system sodium dodecyl-benzenesulfonate(DDBS)/*n*-pentanol/*n*-heptane/water. The results show that fine changes can be observed in the structure of the water-in-oil emulsion and microemulsion droplets, such as the *n*-pentanol/DDBS mole ratio increase in the interfacial layer; further, the alcohol/surfactant mole ratio α in the interfacial layer of the droplets, and also the standard thermodynamic functions of the alcohol transition from the external phase to the interfacial phase ($\Delta G^{o}_{e\rightarrow s}$, $\Delta H^{o}_{e\rightarrow s}$ and $\Delta S^{o}_{e\rightarrow s}$), can be derived from calorimetric data.

Keywords: calorimetry, *n*-pentanol, phase equilibrium, sodium dodecylbenzenesulfonate, thermodynamic function, water-in-oil microemulsion

Introduction

It is often necessary to add a medium chain length alcohol, used as a cosurfactant, to water, oil and surfactant to form a microemulsion. The behavior of four-component reversed micellar systems is more complex than that of three-component systems (such a well-studied system is sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/hydrocarbon/water). The adsorption densities of the surfactants and cosurfactants are essential quantities required for an understanding of microemulsions. The alcohol/surfactant mole ratio α in the water/oil interfacial layer seems to be a very important parameter which determines several physicochemical properties. In general, they are not well characterized.

A dilution method [1–6] has been used to determine the interfacial layer cosurfactant-to-surfactant ratio and the solubility of cosurfactant in oil, obtained from the intercept and the slope of a plot of added alcohol *vs*. oil required to reach the phase boundary. A dilution procedure was worked out to vary the concentra-

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tion of droplets without modification of their structure at a fixed water-to-surfactant mole ratio R.

Cazabat [7] indicated in 1983 that the droplet size will change when the disperse volume fraction $\varphi_d > 0.3$. According to the mass balance, the total number of moles of alcohol, n_a, can be written as

$$n_a = n_a^i + n_a^s + n_a^e \tag{1}$$

where superscripts i, s and e denote the internal phase, the interfacial phase (surfactant shell) and the external phase, respectively. Further, Birdi [4] assumed that the solubility of the alcohol in the external continuous phase (oil) is constant, and the distribution constant can be written as

$$k = n_a^s / n_o \tag{2}$$

where n_o is the number of moles of oil. Combining Eqs (1) and (2) and dividing by the number of moles of surfactant, n_s gives

$$\frac{n_a}{n_s} = \frac{n_a^i + n_a^s}{n_s} + k\frac{n_o}{n_s} \tag{3}$$

A plot of n_a/n_s *vs.* n_o/n_s would give a straight line with the slope S equal to k and the intercept I equal to $(n_a^i + n_a^s/n_s)$, and the standard Gibbs free energy $\Delta G^o_{e\to s}$ of alcohol transition from the external phase to the interfacial phase can then be estimated:

$$\Delta G^o_{e\to s} = -RT\ln\left(\frac{x_a^s}{x_a^e}\right) = -RT\ln\left[\frac{I(S+1)}{S(I+1)}\right] \tag{4}$$

where x_a^s and x_a^e represent the mole fraction of the alcohol in the interfacial phase and in the external phase, respectively. The experimental results of Birdi showed that a linear relationship exists for sodium dodecylsulfacte (SDS)/benzene/alcohol (C_5–C_9)/water systems and the standard Gibbs free energy of alcohol transition changes linearly with the number of carbon atoms in the alcohol (C_5–C_7) at 298 K:

$$\Delta G^o_{e\to s} = 1563 - 839.5\mathrm{N_c}(\mathrm{J\ mol^{-1}}) \tag{5}$$

Since the theory of Birdi was established, many authors [8–12] have proved experimentally that there is a linear relationship between n_a/n_s and n_o/n_s. Consequently, they believed that Birdi's assumption is correct. Further, it was presumed that the value of n_a/n_s is the mole ratio of alcohol to surfactant in the interfacial phase when n_o/n_s is extrapolated to zero, and the value was used to calculate structural parameters [12].

However, Eq. (2) shows the solubility of alcohol in oil rather than the distribution constant. Some alcohols are miscible in oil, such as *n*-pentanol in *n*-heptane, which can not be described in terms of solubility. Although the plot of n_a/n_s *vs.* n_o/n_s is a straight line, this does not prove that Birdi's method is correct; if not so, the distribution of alcohol between the external phase and the interfacial phase would obey a principle such that the alcohol saturates the external oil phase first, and then enters the interfacial phase. In other words, the external oil continuous phase is saturated with alcohol at any time. In reality, this is not the case.

SANS [13, 14], conductivity [1, 15], interfacial tension [5, 16], SAXS and QELS [1] have also been used to determine the partition constants for alcohols in microemulsions.

The enthalpy increment upon addition of pentanol to the various micellar solutions was considered to be the partial mole excess enthalpy of pentanol (relative to the pure liquid).

Increment calorimetric titration proved to be an effective method with which to study the partition constants [17, 18] and to observe the sphere-to-rod transition [19, 20] in aqueous solutions of ionic surfactant. However, the interfacial composition in water-in-oil microemulsions has not been investigated by calorimetry. Here, we report a calorimetric determination of the interfacial cosurfactant-to-surfactant mole ratio α in the system sodium dodecylbenzenesulfonate (DDBS)/water/*n*-heptane/*n*-pentanol. The standard Gibbs free energy of alcohol transition from the external phase to the interfacial phase is derived on the basis of rigorous physical chemistry methods from the phase equilibrium.

Theory

The distribution of the alcohol in the internal phase, the interfacial phase and the external phase depends on the chemical potentials of the alcohol in the three phases instead of on the solubility of the alcohol in them. The chemical potentials of the alcohol in the respective phases are

$$\mu_a^s = \mu_a^{so} + RT\ln a_a^s \tag{6}$$

$$\mu_a^e = \mu_a^{eo} + RT\ln a_a^e \tag{7}$$

where μ_a^{so} and μ_a^{eo} denote the chemical potentials of the alcohol under standard conditions, and a_a^s and a_a^e denote the activities of the alcohol in the surfactant shell and in the external phase.

When the distribution reaches phase equilibrium:

$$\mu_a^s = \mu_a^e \tag{8}$$

$$\Delta G^{o}_{e\rightarrow s(T)} = \mu_a^{so} - \mu_a^{eo} = -RT\ln k_{o(T)} \tag{9}$$

$$\text{with } k_{o(T)} = k_{o(\gamma)}k_{o(x)} \tag{10}$$

where x and γ are the mole fraction and activity coefficient of the alcohol; $k_{(T)}$ depends only on temperature, while $k_{(\gamma)}$ depends on both temperature and composition.

$$k_{o(x)} = \frac{x_a^s}{x_a^e} = \frac{n_a^s/(n_a^s + n_s^s)}{n_a^e/(n_a^e + n_o^e)} \tag{11}$$

From Eq. (11), we have

$$\frac{n_a^e}{n_o^e} = \frac{1}{k_{o(x)}(1 + n_s^s/n_a^s) - 1} \tag{12}$$

where n_o^e is the number of moles of oil in the external phase, while n_s^s is that of the surfactant in the interfacial phase.

When Eq. (12) is combined with Eq. (1), the result is

$$\frac{n_a}{n_s} = \frac{n_a^s}{n_s} + \left(\frac{n_a^i}{n_w^i}\right)\left(\frac{n_w^i}{n_s}\right) + \left(\frac{1}{k_{o(x)}(1 + n_s^s/n_a^s) - 1}\right)\left(\frac{n_o^e}{n_s}\right) \tag{13}$$

where n_w^i is the number of moles of water in the internal phase. Generally speaking, the surfactant in the interfacial phase, the water in the internal phase, and the hydrocarbon in the external phase are in an overall majority. We can assume that all of the water, surfactant and oil exist in the three respective phases: they are $n_w^i = n_w$, $n_s^s = n_s$, $n_o^e = n_o$; in addition, let $R = n_w/n_s$, $\alpha = n_a^s/n_s^s = n_a^s/n_s$. Thus, Eq. (13) becomes

$$\frac{n_a}{n_s} = \alpha + \left(\frac{n_a^i}{n_w}\right)R + \left(\frac{1}{k_{o(x)}(1 + 1/\alpha) - 1}\right)\left(\frac{n_o}{n_s}\right) \tag{14}$$

where n_a^i/n_w is the ratio of the number of solubilized moles of alcohol (mole/mole) in the interfacial phase. It is reasonable to take n_a^i/n_w as zero for the systems containing medium chain alcohols [21]. Equation (14) shows that the plot n_a/n_s *vs.* n_o/n_s is a straight line if $k_{o(x)}$ and α remain constant at a water content R remaining unchanged at the experimental temperature. The slope S and intercept I are

$$S = \frac{1}{k_{o(x)}(1 + 1/\alpha) - 1} \tag{15}$$

$$I = \alpha + \left(\frac{n_a^i}{n_w}\right)R \approx \alpha \tag{16}$$

which means that the slope S is constant if the mole ratio α of alcohol to surfactant in the interfacial phase is independent of the water content R, whereas the intercept I is approximately equal to α only when the value of n_a^i/n_w is so small that it can be neglected.

From Eq. (15), we have

$$\Delta G^o_{e\to s(T,P)} = \Delta G^o_{e\to s(T)} + RT\ln k_{o(\gamma)}$$

$$= -RT\ln k_{o(x)} = -RT\ln\left[\frac{\alpha(S+1)}{S(\alpha+1)}\right] \tag{17}$$

which is equivalent to Eq. (4) for the systems containing medium and long chain alcohols.

Experimental

Materials

DDBS (>95%) was obtained from Japan, *n*-pentanol (>95%) from BDH Chemicals, and *n*-heptane (>98.0%) from the Beijing Jinxing Chemical Plant. All chemicals were used without further purification. The water was distilled two times.

Instrument and methods

Calorimetric measurements were performed on a Tronac model 450 isoperibol titration calorimeter with the bath at 25.000±0.001°C. 35.00 ml *n*-heptane, 2.00 ml water and 0.8853 g (1.4057, 1.9919 and 2.8500 g) DDBS were put into the 50 ml Dewar reaction cell to form the emulsion. When thermal equilibrium was reached, the lower electric power supply was used to heat the reaction cell up to 5000 μV, which can reduce the experimental error as it is an endothermic titration. Small successive increments of 0.050 ml *n*-pentanol were then titrated into the Dewar from a 5 ml Gilmont micrometer burette controlled by a computer; a 2 min delay was allowed for thermal equilibrium between two successive deliveries.

The heat of solution of *n*-pentanol was calculated by multiplying the effective heat capacity and the temperature displacement by a small correction for the difference in temperature between the solution and the bath.

$$\Delta H_{\mathrm{meas,i}} = E_i(U_f - U_i) + (C_{p,a}/k)(U_i - U_o) \tag{18}$$

$$\text{with } E_i = E_b + (E_e - E_b)i/n, \tag{19}$$

$$C_{p,a} = \overline{C}_{p,a}\rho_a V_a/M_a \tag{20}$$

where U_o, U_i and U_r are the response voltages at the temperatures of the water bath, before and after each titration, k is a conversion coefficient of thermal resistance, $C_{p,a}$ and $\bar{C}_{p,a}$ are the heat capacity and molar heat capacity of pure *n*-pentanol, and E_i, E_b and E_e are the apparent heat capacities of the solution at the **i**-th, the beginning and the end titrating points, including the agitator, the thermal resistance and the teflon tube. n denotes the total number of titration points, ρ_a, M_a and V_a denote the density, molar weight and volume increment of *n*-pentanol, respectively. E_b and E_e are calibrated three times in the beginning and end titration:

$$Q_{cali} = E_b(U_f - U_i)_{cali,b} = E_e(U_f - U_i)_{cali,e} \tag{21}$$

The increment enthalpies of solution are divided by the number of moles of *n*-pentanol added in each delivery. These enthalphy values have been shown to be close to the partial molar excess enthalpy of *n*-pentanol (ΔH_a) at the average concentrations of *n*-pentanol before and after each delivery.

Results and discussion

The partial molar enthalpies of *n*-pentanol (ΔH_a) as a function of the mole ratio of *n*-pentanol to DDBS, n_a/n_s, are shown in Fig. 1, and the plots of n_a/n_s *vs.* n_o/n_s are shown in Fig. 2. We found that all curves yield positive values and apparently the same pattern. Six periods appear along each successive titration. The titration points jump up and down first (not shown in Fig. 1).

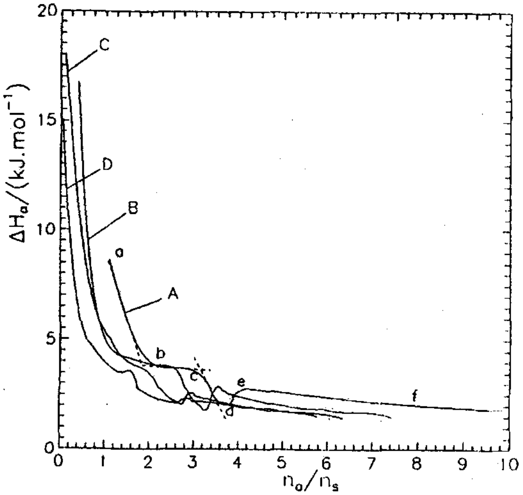

Fig. 1 Dependence of the partial mole enthalpy (ΔH_a) of *n*-pentanol upon the mole ratio n_a/n_s of *n*-pentanol to DDBS for the system DDBS/*n*-pentanol/*n*-heptane/water at 25°C. 35.00 ml *n*-heptane+2.00 ml water+0.8853 g (A) [1.4057 g (B); 1.9919 g (C); 2.8500 g (D)] DDBS

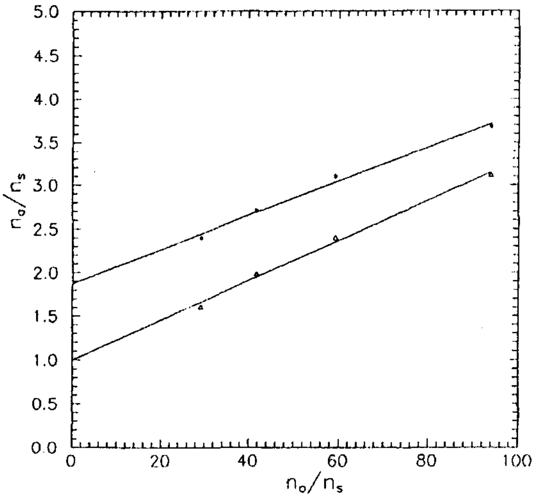

Fig. 2 The plot of n_a/n_s *vs.* n_o/n_s, where n_a, n_o and n_s are the numbers of moles of *n*-pentanol, *n*-heptane and DDBS

A sharp decrease (**ab**) then appears, followed by a reversed peak (**cde**) and a steady line (**ef**) in endothermic curve A. At the beginning, there are some undissolved DDBS crystals in the Dewar, and the solubility of DDBS in the mixed solvent of *n*-pentanol and *n*-heptane increases with increase of the *n*-pentanol content. Although the rate of injection of *n*-pentanol is even, the rate of dissolution of DDBS is not even because of the agitator; it therefore gives scattered endothermic points and disappears at point **a** when the DDBS crystals dissolve completely and, at the same time, the system turns into a water-in-oil emulsion. On the addition of *n*-pentanol, the emulsion changes into a microemulsion (**b**); most of the added *n*-pentanol molecules enter the DDBS interfacial layer before microemulsion appearance. However, the ratio of *n*-pentanol to DDBS in the interfacial layer remains constant (α_c=1.000) during period **bc** (microemulsion); the added *n*-pentanol enters the oil phase to form a mixed solvent without change in the structure of the droplets. However, it is disturbed by the further addition of *n*-pentanol: more *n*-pentanol molecules enter the interfacial layer, corresponding to the reversed peak, and the ratio α_d of *n*-pentanol to DDBS rises to 1.877 at point **d**. The microemulsion droplet structure remains steady state again during the period **ef**, and the droplets are diluted by the mixed solvent of *n*-pentanol and *n*-heptane. The section relating to the changes in the partial molar enthalpy of *n*-pentanol shows that the heat of dilution of the microemulsion is essentially constant.

It is to be seen that the curves shift downwards and to the left with DDBS content increase. The reason is that, the higher the DDBS content, the lower the mole ratio *R* of water to DDBS, the smaller the microemulsion droplets [22], and the less the *n*-pentanol can saturate the interfacial phase. We can evaluate the stand-

Table 1 Thermodynamic functions of *n*-pentanol transition from the external phase to the interfacial phase

Points	α	S	$\Delta G^{o}_{e\to s}$/kJ mol^{-1}	$\Delta H^{o}_{e\to s}$/kJ mol^{-1}	$\Delta S^{o}_{e\to s}$/J mol^{-1} K^{-1}
c	1.000	0.02284	–7.701	–3.685	13.5
d	1.877	0.01953	–8.741	–6.161	8.66

ard molar enthalpy of *n*-pentanol transition from the external phase to the interfacial phase by the extrapolation method shown in Fig. 1 (dashed line). The slope of the dashed line for period **bc** is the partial molar enthalpy change for *n*-pentanol ($\Delta H_{a,bc}$) entering the external phase, that for period **ab** is the partial molar enthalpy change for *n*-pentanol ($\Delta H_{a,ab}$) entering the interfacial phase of emulsion droplets, and that for period **cd** is the partial molar enthalpy change for *n*-pentanol ($\Delta H_{a,cd}$) entering the interfacial phase of microemulsion droplets. The standard molar enthalpy of the *n*-pentanol ($\Delta H^{o}_{e\to s,e}$) transition from the external phase to the interfacial phase of emulsion droplets, and that of the *n*-pentanol ($\Delta H^{o}_{e\to s,m}$) transition from the external phase to the interfacial phase of microemulsion droplets, are as follows:

$$\Delta H^{o}_{e\to s,e} = \Delta H_{a,ab} - \Delta H_{a,bc} \tag{22}$$

$$\Delta H^{o}_{e\to s,m} = \Delta H_{a,cd} - \Delta H_{a,bc} \tag{23}$$

By extrapolation of the ratio n_o/n_s to zero from turning points **c** and **d** (not shown in Fig. 1 for curves B, C and D), we obtained the *n*-pentanol/DDBS ratio α in the interfacial layer and slope S. The standard Gibbs free energy of the *n*-pentanol ($\Delta G^{o}_{e\to s}$) transition from the external phase to the interfacial phase can therefore be calculated from Eq. (17), and the standard molar entropy of *n*-pentanol for the transition can be estimated from $\Delta S^{o}_{e\to s} = (\Delta H^{o}_{e\to s} - \Delta G^{o}_{e\to s})/T$. The three thermodynamic functions obtained are shown in Table 1 ($\Delta H^{o}_{e\to s}$ is obtained from curve A).

Conclusions

The calorimetric results have shown that fine changes in the structure of the water-in-oil emulsion and the microemulsion droplets can be observed; further, the alcohol/surfactant mole ratio α in the interfacial layer of the droplets and also the standard thermodynamic functions of the alcohol transition from the external phase to the interfacial phase can be derived from the calorimetric data. The plot of n_a/n_s *vs.* n_o/n_s is a straight line, which means that the distribution of the alcohol in the respective phases can be measured by the dilution method and calorimetry. The intercept **I** is approximately equal to the alcohol/surfactant mole ratio α in the interfacial layer only when the alcohol/water mole ratio in the water core is so small that it can be neglected.

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