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STUDIES ON THE PHASE DIAGRAM OF THE SURFACTANT/1-PENTANOL /WATER TERNARY SYSTEM 1: THE ISOTROPIC PHASES

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ABSTRACT

The phase diagram of the dodecyl dimethyl ammonium hydroxyl propyl sulfonate(DDAHPS)/1-pentanol($C_5H_{11}OH$)/water ternary system has been established. It contains two isotropic monophase regions(L_1 and L_2) and a liquid crystalline region(L.C.). The isotropic phase regions have been investigated by means of Raman spectroscopy and conductivity.

INTRODUCTION

Many studies on phase diagram of varied amphiphiles/oil/water(or brine) system, have been reported in recent literature^[1-3]. The oil used has been mainly aliphatic and aromatic hydrocarbons, and the cosurfactants used are mainly the alkanols with moderate length of hydrocarbon chains (from three to eight carbon atom). Because the microemulsion has been widely used in detergent, chemistry and oilfield industries, these alkanols are used as oil substitutes in order to gain microemulsions for

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amphiphiles with low HLB value. Butanol and pentanol are frequently used for this purpose ^[4,5].

Recently, R. Elivira et al ^[6,7] has used conductometry and viscosimetry methods to study the phase behavior, transport properties and thermodynamics of the microemulsions in ternary system of amphiphiles / aliphatic alcohol/ water. This has led us to use the DDAHPS, which is a new surfactant with high surface activity and anti-precipitating ability for calcium ion and magnesium ion and has been widely used in ternary oil recovery in China, as the amphiphiles, and the pentan-1-ol as the oil to investigate the phase diagram of the DDAHPS/C₅H₁₁OH/H₂O system. In the present paper, conductometry and Raman spectrometry methods are used to investigate the physicochemical properties of the o/w type microemulsion (in L₁ phase region of the above ternary system) and w/o type microemulsion (in L₂ phase region).

MATERIALS AND METHODS

DDAHPS was purchased from the Nanjing Chem. Co., and recrystallized twice with the mixture of alcohol and ether; Pentan-1-ol was of A. R. grade and used as receive; Water was deionized and distilled.

The phase diagram was constructed using macroscopic samples prepared by weighing the components in glass tubes. Samples were mixed and homogenized by shaking and storing in WMK-10 Vibrator(Shandong Uni. Apparatus Co.) thermostated at $30 \pm 0.1^{\circ}$ C for at least one week. The micellar areas were determined by water titration of mixture of the remaining components noting point of turbidity and clarity. The liquid crystals were checked by visual inspection through crossed polarizers in order to determine their boundary in phase diagram^[8].

The L_1 phase region was investigated by a SPEX1403 Raman spectrophotometer (SPEX,USA) with an argon-ion laser for excitation. The spectra were recorded with spectral slitwidths of 3-5cm⁻¹ and varying running conditions according to the peak intensities. In general, the laser was operated to give about 200-500mW power of the 5145Å green line on the samples which were contained in 1 mm melting point capillaries.

The L_2 phase region was investigated with DDS-11A conductometer (Shanghai Optical Apparatus Co.) in addition to the SPEX1403 Raman spectrophotometer. In this paper, we only measure the Raman spectral intensities and frequencies of the hydrocarbon C-H stretching modes(2800-2970cm⁻¹) for each sample.

All the experiments were conducted at 30 \pm 0.1°C.

RESULTS AND DISCUSSION

Ternary phase diagram

The isothermal ternary phase diagram obtained at 30 ± 0.1 °C for the system of DDAHPS/C₅H₁₁OH/H₂O is given in Figure 1. It contains two isotropic solution phases, one rich in water(L₁) and the other rich in pentano1(L₂) and one liquid crystalline phase(L.C.). The other part in this phase diagram is the multiphase region.

The following is the description of the L_1 and L_2 phases and their phase behaviors.

L₁ Phase region

The boundary of the L_1 phase region corresponds to the maximum amount of 1pentanol that the DDAHPS micelles in aqueous solution can solubilize before phase separation. With regard to the alcohol distribution between aqueous and micellar phases for short chain aliphatic alcohol, the equilibrium constant (K) is expressed in equation(1).

$$K = X_A^{mic} / X_A^{aq}$$
(1)

where X_A^{mic} is the mole fraction of alcohol in the micellar phase, X_A^{aq} is the mole fraction of alcohol in the aqueous phase. X_A^{mic} and X_A^{aq} can be expressed as follows:

$$X_{A}^{mic} = (C_{A} - C_{A}^{aq}) / [(C_{A} - C_{A}^{aq}) + (C_{s} - cmc)]$$
(2)
$$X_{A}^{aq} = C_{A}^{aq} / (C_{A}^{aq} + cmc + 55.5)$$
(3)

where all the concentrations are expressed as molarity in one liter, C_A and C_S are the total concentration of alcohol and surfactant respectively; cmc is the critical micellization concentration; 55.5 is the concentration of water. So the equation (1) can be rearranged, as follows:

$$C_{A} = C_{A}^{aq} + (C_{s} - cmc)KC_{A}^{aq}/(C_{A}^{aq} + cmc + 55.5 - KC_{A}^{aq})$$
(4)
Because of $C_{A}^{aq} + cmc << 55.5$, the equation (4) can be rescripted as follows:
$$C_{A} = [KC_{A}^{aq}/(55.5 - KC_{A}^{aq})] (C_{s} - cmc) + C_{A}^{aq}$$
(5)

Assuming that for all the solutions, the solubilities of the alcohol and the surfactant in water, namely C_A^{aq} and cmc, are constant when the temperature is fixed. So, equation (5) means that plot of C_A against (C_s - cmc) should be linear with a slop of K $C_A^{aq}/(55.5 - KC_A^{aq})$ and intercept of C_A^{aq} (shown in Fig. 2). The results follow this theoretical treatment up to a surfactant amount of 0.65 ~ 0.70 mol/L(shown in Fig.2), namely, the maximum solubilizing amount of pentan-1-ol in the o/w micelles



FIG.1 The ternary phase diagram for the DDAHPS/C₅H₁₁OH/H₂O system at 30 ± 0.1 °C. the L₁, the isotropic aqueous solution phase; the L₂, the pentanolic isotropic solution phase; the L.C., liquid crystalline phase. the sample points labeled for Raman measurement.

of DDAHPS is about 2.08 mol per liter solution at the concentrations of DDAHPS (ca.0.7 mol/L, the maximum concentration). The obtained K value is about 36.4, which also means that the pentan-1-ol mainly plays a role as an oil, not as a cosurfactant.

In L_1 phase region, the DDAHPS molecules form micelles of the ordinary type, that is, with a hydrocarbon core and hydrophilic groups facing outward toward the water. The Raman spectroscopy is used to measure the spectral intensities and frequencies of the hydrocarbon C-H stretching vibrations with environmental and conformational changes. K. Teizo et al ^[9,10] has stated that the symmetric and asymmetric stretching of the CH₂, CH₃ groups occur at about 2850 cm⁻¹ and 2880cm⁻¹, 2930cm⁻¹ and 2960cm⁻¹ respectively.



FIG.2 A maximum amount of alcohol solubilized in L_1 phase at different(C_s-cmc) value.

In reference^[11], it has been shown that:(i) the ratio of the 2880-and 2850cm⁻¹ peak intensities can be used as an order/disorder parameter to estimate the degree of disorder of the hydrocarbon chains. (ii) the ratio of the 2930-and 2850cm⁻¹ peak intensities can be used as an environment polarity parameter, implying the polar/apolar character of the hydrocarbon chains.

Figure 3a, 3b, 3c show the C-H stretching vibrations of solid state DDAHPS, liquid state pentan-1-ol and a sample point composed of DDAHPS, pentan-1-ol and water in L_1 phase region respectively. The polarized Raman spectra of DDAHPS solid compose of parallel bands (2844-, 2862-, 2880-, and 2900cm⁻¹) and perpendicular bands (2841-, 2865-, 2879-, and 2910cm⁻¹). According to K. Telzo et al ^[10], the 2844- and 2880cm⁻¹ lines are assigned to the CH₂ groups' symmetric and asymmetric stretching vibration respectively. The CH₃ vibration lines are almost overlapped by the background line of the Raman spectra. In the solid state, with close packing of planar



FIG.3 C-H stretching Raman spectra of samples: a), DDAHPS solid; b), pentan-1-ol liquid; c), a sample in L_1 phase region. the right curve, the perpendicular components; and the left curve, the parallel components. the I and II, the symmetric and asymmetric stretching vibrations of the CH₂ groups; the III and IV, the CH₃ groups' symmetric and asymmetric vibrations.

zigzag chains, the symmetric stretching vibration peaks of the CH_2 groups dominate in parallel and perpendicular components. The value of the order/ disorder parameter^[11], I₂₈₈₀/I₂₈₄₄ ratio, of the DDAHPS solid is 0.86.

The parallel component of pentan-1-ol polarized Raman spectrum contains 2850-, 2870-, 2900-, 2911-, 2932-, and 2953cm⁻¹ lines, and the perpendicular component contains 2850-,2877-, 2890-, 2905-, 2917-, 2930-, and 2952 cm⁻¹ lines. The 2850-and 2870 cm⁻¹ peaks are assigned to the CH₂ symmetric and asymmetric stretching vibration respectively; the 2930-, 2952cm⁻¹ peaks are assigned to the CH₃ symmetric and asymmetric stretching vibration respectively^[10]. The highest peak in the parallel component appears at 2870cm⁻¹, and the 2890cm⁻¹ peak, the highest in the perpendicular component. The values of the order/disorder parameter^[11], I₂₈₇₀/I₂₈₅₀ ratio, is 1.15, and the environment polarity parameter^[11], the ratio I₂₉₃₀/I₂₈₅₀ ratio, is 0.84.

From Fig.3c, it can be seen that the perpendicular component of sample c is too weak to measure, and its parallel component contains peaks of 2844-, 2865-, 2884- and 2933cm⁻¹. These peaks are assigned to the symmetric and asymmetric stretching vibration of the CH₂ groups and the CH₃ symmetric stretching vibration, The ratios of I_{2884}/I_{2844} and I_{2933}/I_{2844} have the values of 1.32 and 1.44.

From solid state DDAHPS to liquid state pentan-1-ol, and then to the sample c, more gauche rotational isomers are present^[12] and the asymmetric peak of the CH_2 groups becomes bigger because of the increasing mobility of methylene groups, so the values of their order/disorder parameter increase (0.86 for DDAHPS, 1.15 for 1-pentanol, 1.32 for sample c in L₁ phase region). From liquid state pentan-1-ol to sample c, the values of the environment polarity parameter increase greatly (0.84 for 1-pentanol, 1.44 for sample c), it maybe due to that the water molecules penetrate into the methylene layer of the micelles.

L₂ phase region

The specific conductivities of the samples selected from L_2 phase region versus different concentration of 1-pentanol and different water content are shown in Fig.4. With the same amount of surfactant and fixed [DDAHPS]/[H₂O] ratio (the molar concentration ratio between DDAHPS and water, and ibid.), the conductivities of these samples decrease with the increasing pentan-1-ol concentration (curve 1 in Fig.4). Because the DDAHPS is a kind of zwitteric surfactants, the conductivities of these samples are less than 270 μ S.cm⁻¹. With the same amount of DDAHPS and at



FIG.4 Specific conductivity of samples selected from L_2 phase regions versus pentan-1-ol concentration at fixed molar concentration ratio of DDAHPS and water(curve1), and versus W₀(molar ratio of water and DDAHPS) at fixed molar concentration ratio of DDAHPS and pentan-1-ol(curve 2).

the fixed [DDAHPS]/[C₅H₁₁OH] ratio, the conductivities of these samples (curve 2 in Fig.4) increase with the increasing w_0 value (where w_0 is the molar ratio of water and DDAHPS in the system), and all the samples contain less than 28wt% in water. When [DDAHPS]/[C₅H₁₁OH] ratios equal 0.54, and in w_0 region, from 3.0 to 18.5, the DDAHPS w/o pattern micelles come into being with a considerable amount of water solubilization .

In L_2 phase region, five samples with same amount of DDAHPS and fixed [DDAHPS]/[H₂O] ratio (shown in Fig.1) are selected to conduct Raman spectroscope measurement. The feature of w/o micelles in L_2 phase region is that the polar heads of DDAHPS molecules pack together to form a polar central core, surrounded by the hydrocarbon tails, and the bulk phase is mainly composed of 1-

pentanol molecules. The Raman spectra of these selected samples show almost the same characteristic as those of liquid state 1-pentanol, so it's very easy to understand that the Raman spectra intensities of the selected samples increase with the increasing concentration of pentan-1-ol (shown in Fig.5).

Figure 5 shows the intensity of the 2870 cm⁻¹ peak, which stands up for the highest peak in the parallel component, and of the 2890cm⁻¹ peak, which stands up for the highest peak in the perpendicular component, versus the concentration of 1-pentanol, and it also shows the values of the l_{2870}/l_{2850} ratio and the l_{2930}/l_{2850} ratio for these samples.

From Fig.5, it can be seen that the intensity ratios of I_{2870}/I_{2850} and I_{2930}/I_{2850} have no significant changes, but they are bigger than those of liquid state pentan-1-ol. In these reverse micellar solutions, there is little amount of DDAHPS and H₂O presented, so their Raman spectra show the same characteristics as these of pentan-1-ol, and the increase of [C₅H₁₁OH] has no significant effect on the value of the order/disorder parameters (ca.1.20) and the environment polarity parameters (ca.1.00).

Because of the presented water, the environment polarity parameters of these samples are bigger than that of pentan-1-ol. The smaller value of the order/disorder parameter of pentan-1-ol liquid may be due to the fact that no reverse micelles are formed in liquid state pentan-1-ol.

The DDAHPS micelles in L₂ phase have smaller aggregation number than these in L₁ phase, the radius of the micelles are smaller, so there is increase in the direct chain-to-chain contact^[13,14], and a decrease in the "mobility" of the methylene groups. That is why the l_{2930}/l_{2850} and l_{2870}/l_{2850} ratios of the samples selected from L₂ phase region have smaller values, compared with the sample selected from L₁ phase region.

CONCLUSION

In this paper, the equilibrium constant (K) of pentan-1-ol distributing between aqueous and micellar phases can be calculated using the equations listed above. From the results, we can estimate the maximum amount of pentan-1-ol solubilized in the DDAHPS micellar solution according to the maximum amount of DDAHPS in the L_1 phase region, and it implies that this simple method can be used in other system for the same purpose. To investigating the properties of w/o pattern microemulsion, we measured the specific conductivities of the samples selected from the L_2 phase region.



FIG.5 The intensity of 2870 cm⁻¹ and 2890cm⁻¹ peaks, the values of I₂₈₇₀/I₂₈₅₀ and I₂₉₃₀/I₂₈₅₀ ratios versus pentan-1-ol concentration.

In literature, Raman spectroscopy method is used to estimated the order/disorder parameter and the environment polar parameter of hydrocarbon in surfactant molecule which distributes in one solvent containing no hydrocarbon chains. In this paper, we tentatively measured the two parameters of the samples selected from the L_1 and L_2 phase regions in the ternary system of DDAHPS/pentan-1-ol/water; and for comparing with them, the values of the order/disorder parameter and the environment polar parameter of hydrocarbon chain of pure samples of solid state DDAHPS and liquid state pentan-1-ol were measured and discussed.

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