Colloid Polym Sci (2006) 284: 788–794
DOI 10.1007/s00396-005-1451-x

ORIGINAL CONTRIBUTION

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Determination of the electrochemical diffusion coefficient of methylene blue in SDS/*n*-C5H11OH/H2O system by non-probe microelectrode voltammetry

Received: 17 June 2005
Accepted: 13 November 2005
Published online: 21 January 2006

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Abstract The diffusion coefficient of methylene blue (MB) is determined by the method of non-probe microelectrode voltammetry in sodium dodecyl sulfate (SDS)/*n*-$C_5H_{11}OH/H_2O$ lyotropic liquid crystal system. The results obtained show that the diffusion coefficient of MB increases with water and *n*-pentanol contents in the microemulsions and the lyotropic liquid crystal but decreases with SDS content. The diffusion coefficient of SDS droplet in the microemulsions and the diffusion coefficient of SDS molecule in the lyotropic liquid crystal with MB all are less than those without MB. The magnitude order of the diffusion coefficient of MB is as follows: the coefficient in the oil-in-water (O/W) microemulsion is greater than the coefficient in the water-in-oil (W/O) microemulsion which is greater than the coefficient in the lamellar liquid crystal (LLC), which is also greater than the coefficient in the Hex.

Keywords SDS · MB · Microelectrode · Diffusion coefficient · Micelle · Liquid crystal

Introduction

The molecular organized assembly formed from surfactants (such as micelle, microemulsion, and lyotropic liquid crystal can be applied in chemistry, chemical engineering, material, biology, and life science [1–5]. The structure of micelle is similar to that of native human cell. The lamellar liquid crystal (LLC) is like the human scarfskin [6]. Simulating life system and investigating the physical–chemical properties of bioactive substances in life system are of great significance in molecular organized assembly [7–10]. Methylene blue (MB) is a very useful bioactive substance and bio-indicator. It can treat some skin disease using photo-dynamical therapy [11]. Because the structure of MB is similar to that of hematoporphyrin, Nishisaka believed that MB might be used to tackle cancer by means of a photochemical method [12]. The study of the properties and the diffusion behaviors of MB in some simulating biological systems will provide more important information for the application of bioactive substance in life science. From the interactions between MB and the molecular organized assembly, man can obtain some illumination to understand the interactions between bioactive substance and the human native cell. We have studied the partition coefficient and the binding free energy of the MB dimerization in a sodium dodecyl sulfate (SDS) microemulsion and lyotropic liquid crystal system [9]. The content of MB monomer in micelle system is less than that in O/W microemulsion. The greatest content of MB monomer is found in lamellar liquid crystal (LLC).

The diffusion coefficient of a particle can indicate its size, shape, transporting property, microstructure, and the interactions with some other particles. The diffusion coefficient has been determined by some methods such as NMR, light scattering, and cyclic voltammetry [13–15]. However, the NMR method is expensive and complex. Light scattering is only applied to some big particles. For the cyclic voltammetry with probe, because water-soluble probe must be used in O/W microemulsion and oil-soluble probe in W/O microemulsion, the cyclic voltammetry with same probe is not used to continuously determine the diffusion coefficients of the O/W droplet and the W/O droplet. The cyclic voltammetry without probe can be applied to determine continuously the diffusion coefficients in O/W and W/O microemulsions and bicontinuous-structure (BI) region

according to the diffusion controlling progress of electroactive substance at a given electrode [16, 17]. In addition, the surface of normal electrode (big area piece electrode) cannot equably tightly contact lyotropic liquid crystals with great viscosity. The sensitivity and stability of the results determined by normal electrode are inferior in lyotropic liquid crystals. So, the cyclic voltammetry with normal electrode cannot be applied in lyotropic liquid crystals.

There are some advantages to study the electrochemical behaviors of a particle by using microelectrode (the electrode with microscopic dimensions), such as good resistive media, higher sensitivity and stability, especially good contact with liquid crystals [18–21]. We have successfully determined the diffusion coefficient of sodium dodecyl sulfate in the SDS/*n*-$C_5H_{11}OH/H_2O$ O/W microemulsion, W/O microemulsion and lyotropic liquid crystal system by non-probe cyclic voltammetry with microelectrode [20]. In this paper, we study and determine the electrochemical diffusion behaviors of MB in SDS/*n*-$C_5H_{11}OH/H_2O$ lyotropic liquid crystals. The results obtained may provide some illumination and understanding on the properties of bioactive substance in lyotropic liquid crystals and the interactions between bioactive substance and the human native cell.

Experiment

Reagents

Sodium dodecyl sulfate was obtained from Sigma (98+%) and was recrystallized twice in ethanol. The surface tension of the SDS-recrystallized product had no lowest point around its critical micelle concentration (cmc) by the method of platinum ring. *n*-pentanol (*n*-$C_5H_{11}OH$) was from Aldrich (99+%). MB was A.R from Third Shanghai Agent Factory. Water used was sub-boiling water from sub-boiling purifier.

Determination of partial phase diagram

n-pentanol was titrated to the samples with various mass ratios of SDS/H_2O, or SDS was added to the samples with various mass ratios of *n*-$C_5H_{11}OH/H_2O$. The mono-phase region of the microemulsion was verified by observing the change between clarity and cloud. The phase boundaries between the LLC and hexagonal liquid crystal were verified with polarizing microscope (59X, Shanghai Optical Instrument Co., China) and XRD experiments The structure parameters of the LLC and hexagonal liquid crystal were studied by small-angle X-ray diffraction using a *D*/max-rc X-ray diffractometer (Japan Physics, Co.) with a Ni filter and Cu radiation (λ=0.542 nm), tube voltage 50 kV, and tube current 180 mA [16, 22].

The samples all must be placed in the thermostat (25± 0.1°C) at least 4 h to reach phase equilibrium. To guarantee the accuracy of the phase diagram, the determination differences were restricted within 0.5% for two different routes.

Preparation of microelectrode and determination of the diffusion coefficient

Microelectrode can be prepared with a fine platinum wire (ϕ=10 μm) sealed in a glass. One end of the platinum wire is polished by superfine diamond paste and fine α-alumina particle (0.05 μm). The voltammetric properties were carried out with CHI660A Electrochemical Workstation (Shanghai Chenhua Apparatus Co., China). The microelectrode was as working electrode, saturated calomel electrode as reference electrode, and the platinum electrode with 0.5-mm dimensions as auxiliary electrode. The reference electrode was kept close to the working electrode to minimize the electrolytic ohmic drop. The diffusion coefficient of $Fe(CN)_6^{4}$ calculated from the voltammetric peak current with the microelectrode [20, 23] was $(6.3\pm0.1)\times10^{-6}$ cm^2 s^{-1} in 1.00×10^{-3} mol $L^{-1}K_4Fe(CN)_6$ solution, which was completely consistent with [24]. The diffusion coefficient of SDS micelle obtained by the same microelectrode was also consistent with that by normal platinum electrodes in SDS/H_2O system [20]. These results indicated that the microelectrode prepared was reliable and steady.

According to the behaviors of the cyclic voltammetric curves of MB, the diffusion coefficient of MB was calculated by the following equations [20, 23, 25]:

$$i_p = 4nFDC\left[0.34\exp\left(-0.66P\right) + 0.66 - 0.13\exp\left(-\frac{11}{P}\right) + 0.351P\right] \quad (1)$$

Where, i_p is the anodic peak current, F is the Faraday constant, C is the concentration of MB, r is the radius of the microelectrode, D is the diffusion coefficient. In Eq. (1), n is the electron number obtained from Eq. (2) [26], $n\approx1$ for

the microelectrode process of MB. P is the characteristic parameter of the microelectrode [20] [in Eq. (3)].

$$E_P - E_{P/2} = \frac{2.2RT}{nF} \quad (2)$$

$$P = \left(\frac{nFr^2v}{RTD}\right)^{\frac{1}{2}} \quad (3)$$

E_P is peak current, $E_{P/2}$ is half peak current, v is the potential scanning rate (1.0 V s^{-1}), T is the absolute temperature, R is gas constant. Equation (1) was combined with Eqs. (2) and (3) to calculate the diffusion coefficient of electro-active substance by the Newton iterative method.

Determination of the equilibrium dimerization constant of MB

The ultraviolet spectra of MB were determined in 550–750 nm by UV-5301 spectrophotometer (Shimadzu, Japan) with the corresponding media without MB as blanks. According to the relations of the dimerization equilibrium constant K of MB with the ultraviolet absorbing spectra, the dissociation and the dimerization equilibrium constants of MB can be calculated by the least square method of Newton iterativeness (in detail in [9]).

Above experiments were all performed at 25±0.1°C. The potential scanning rate was 1.0 V s^{-1}. The cyclic voltammetric curves were all determined after the tenth cycle for the stability of the electrode processes. The MB concentration was 1.0×10^{-6} mol L^{-1}. The units used for D in this paper were cm^2 s^{-1}.

Results and discussions

The phase behavior of SDS/n-$C_5H_{11}OH$/H_2O system

The partial phase diagram of the SDS/n-$C_5H_{11}OH$/H_2O system is illustrated in Fig. 1. L_1 and L_2 represent the O/W and the W/O microemulsions, respectively; BI is the bicontinuous structure region; LLC is the lamellar liquid crystal region; and Hex is the hexagonal liquid crystal. The dash lines in Fig. 1 illustrate the determining routes.

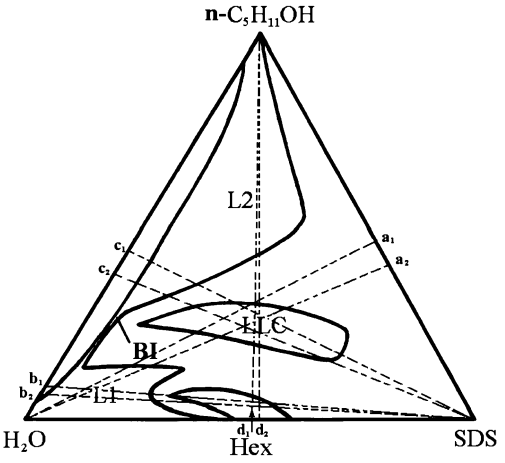

Fig. 1 Partial phase diagram of SDS/n-$C_5H_{11}OH$/H_2O system. Mass ratio of SDS/n-$C_5H_{11}OH$: a_1—55/45 a_2—60/40. Mass ratio of H_2O/n-$C_5H_{11}OH$: b_1—95/5 b_2—92/8. c_1—65/35 c_2—60/40. Mass ratio of SDS/H_2O: d_1—48/52 d_2—50/50

Voltammetric properties of MB

The cyclic voltammetric curves of MB at the microelectrode are shown in Fig. 2 in SDS/n-$C_5H_{11}OH$/H_2O LLC. The curve is not S-shaped voltammetric profile. The stable limit current does not appear at high scanning rate. The anodic and cathodic peak potential of MB did not change with the potential scanning rates v from 0.4 to 1.8 V s^{-1}. The peak current is linear with the square root of the scanning rate (Fig. 3). These results show that the electrode process of MB at the microelectrode may be a process of mass-transport control, but not the effects of the radial diffusion of the microelectrode. S-shaped voltammetric profile can also be obtained when the microelectrode is used at conventional scan rates (from 20 to 200 mV s^{-1}). But, the repetition and stability of the profile are not fine in SDS/n-$C_5H_{11}OH$/H_2O lyotropic liquid crystals, which may be the reason why the viscosity is great, the diffusion rate of MB is very slow, and the effects of the radial diffusion of the microelectrode is much less, correspondingly.

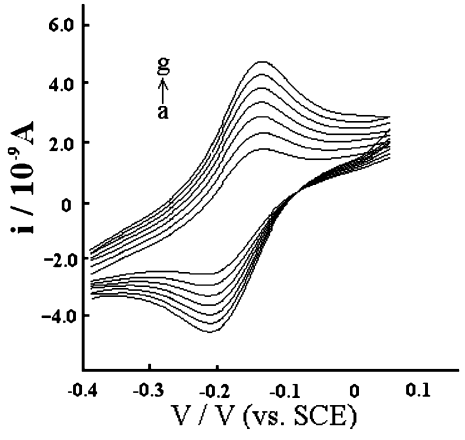

Fig. 2 Voltammogram of MB in the microelectrode at different scanning rates. Scanning rate (V s^{-1}): a—0.4, b—0.5, c—0.75, d—1.0, e—1.3, f—1.5, g—1.8

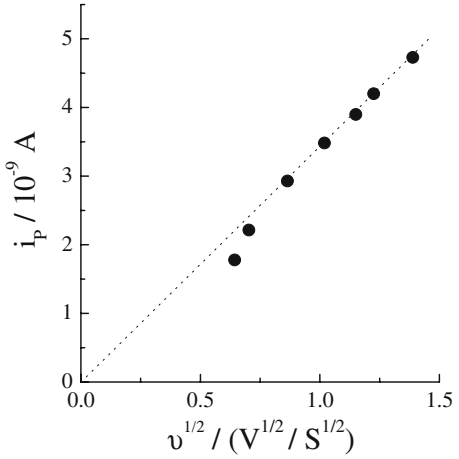

Fig. 3 Variety of the peak current of MB with square root of scanning rate

Influence of water content on the diffusion coefficient of MB

Figure 4 shows the relation of the common logarithm of the diffusion coefficient of MB (log *D*) with water content at constant mass ratios of SDS/*n*-$C_5H_{11}OH$. With water content increasing, the diffusion coefficient of MB increases lightly in the O/W microemulsion. MB can easily dimerize in water. The dimerization constant *K* of MB in the O/W microemulsion is less than that in water [9] (Table 1). Cosurfactant *n*-$C_5H_{11}OH$ can promote the solubilization of MB in the O/W droplet and, also, make the MB molecules to combine easily with the microemulsion droplet. On one hand, the dimerization of MB is affected by the polar–polar interaction [27]. There is electrostatic attraction between negative-ion SDS and positive-ion MB. The highly organized assembly structure of the membrane phase in the microemulsion can contribute to the dissociation of MB but not easily dimerize to the dimer in O/W droplet. The increase of MB monomer content leads to the increase of the apparent diffusion coefficient of MB with water content. One the other hand, the concentrations of MB and SDS all go down with water content increasing. The decrease of the electrostatic interaction between SDS and MB results in the increase of the diffusion coefficient as well.

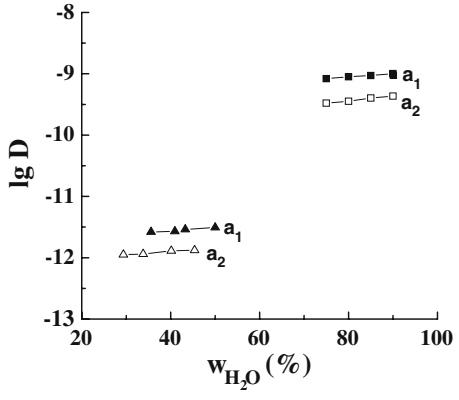

Fig. 4 Variety of the logarithm of the diffusion coefficients of MB with water content. Mass ratio of SDS/*n*-$C_5H_{11}OH$: ▪▲—55/45, □—60/40. Systems: ▪□— O/W microemulsion, ▲□—lamellar liquid crystal

The organized assembly structure of the amphiphilic layer in LLC is much greater than that of the membrane phase in the microemulsion. The dissociation of MB dimmer increases remarkably. This result makes the dimerization constant of MB in LLC decrease. The value of the dimerization constant in the LLC system is less than about seven times that in the microemulsions (Table 1), i.e., more monomer of MB exists in the amphiphilic layer of the LLC [9]. In the same condition, the more monomer there is, the greater is the diffusion coefficient. The diffusion coefficient of the monomer is greater than that of the dimer because the volume of the dimer is greater than that of the monomer. But, the spaces of the amphiphilic layer and the interlayer space are very small in the LLC. The interaction between SDS and MB is greater in the LLC than in the microemulsion. The moving resistance of MB molecule in the LLC is much greater than that in the microemulsion. So, the diffusion coefficient of MB in the LLC is less than that in the microemulsion.

The diffusion coefficient of MB molecule increases also with water content in the LLC system at constant mass ratios of SDS/*n*-$C_5H_{11}OH$ (Fig. 4). In the LLC, water mostly lies in the solvent layer, the rest penetrates into the amphiphilic layer. The penetration of water from the solvent layer to the amphiphilic layer is about 30% [16]. The space of the amphiphilic layer and the interlayer space all increases with water content increasing. These results cause the moving resistance of MB to decrease and the diffusion coefficient to increase. Table 1 indicates also that the dimerization constant of MB in Hex is less than that in LLC, i.e., the monomer content of MB is great in Hex. This probably relates with the tighter structure of Hex.

The influence of *n*-pentanol content on the diffusion coefficients of MB

The diffusion coefficient of MB increases with *n*-pentanol content in the W/O microemulsion at constant mass ratios of SDS/H_2O (Fig. 5). *n*-pentanol and MB can be solubilized in the W/O droplet [28]. The concentration of MB decreases with *n*-pentanol content in the W/O microemulsion. The less the concentration is, the less the interaction, and the more the diffusion coefficient. On the other hand, the increase of *n*-pentanol content makes the dimerization constant decrease and the content of MB monomer increase (Table 1). Therefore, the diffusion coefficients of MB increase with *n*-pentanol content increasing.

Figure 5 shows that the diffusion coefficients of MB increase with the *n*-pentanol content at constant mass ratios

Table 1 The value of ε and K of MB in the SDS/*n*–$C_5H_{11}OH/H_2O$ system

Medium	Composition (%)			λ_{610}			λ_{665}		
	C_5OH	SDS	H_2O	ε_M	ε_D	K	ε_M	ε_D	K
Micelle	0	0	100	16,298	15,873	13,673	27,046	27,933	13,862
	0	0.29	99.71	14,801	14,382	11,470	32,119	31,762	11,326
	0	1.44	98.56	14,360	13,834	11,471	34,248	33,904	11,343
	0	2.88	97.12	12,466	13,043	11,384	34,223	33,087	11,362
O/W microemulsion	2.10	4.90	93.00	30,323	30,599	6,333	71,839	72,166	6,329
	4.11	9.59	86.30	30,962	31,592	6,302	70,995	72,318	6,306
	6.04	14.09	79.87	34,444	33,489	6,132	77,912	75,665	6,135
W/O microemulsion	55.62	21.30	23.08	36,723	36,551	2,532	68,356	68,421	2,498
	65.85	16.39	17.76	37,242	37,113	2,415	69,825	70,023	2,433
	72.12	13.38	14.50	38,559	38,496	2,210	69,918	70,132	2,235
LLC	20.45	47.73	31.82	17,500	16,733	960	38,269	40,656	901
	21.79	50.84	27.37	23,000	21,977	931	33,000	33,985	897
	23.08	53.84	23.08	24,824	23,522	914	34,478	32,854	889
Hex	1.22	47.41	51.37	17,213	17,229	863	36,482	36,557	852
	2.85	46.63	50.52	22,564	22,351	846	34,153	34,469	848
	4.52	45.83	49.65	23,551	23,486	815	33,582	33,673	823

ε Molar absorptivity of MB

of SDS/H_2O in the LLC system and the Hex system. With *n*-pentanol content increasing, not only the solubilization of MB increases. The dimerization constant decreases and the content of MB monomer increases (Table 1). But, also, the addition of *n*-pentanol causes the amphiphilic layer to swell [29] and the interlayer spacing in LLC to enlarge, or the interspacing of the cylinder in Hex to enlarge. Therefore, the diffusion coefficients of MB increase with the *n*-pentanol in the lyotropic liquid crystals.

From Fig. 5, we also see that the diffusion coefficient in LLC is more than that in Hex. The structure of Hex is tighter than that of LLC. The dimerization constants of MB in the lyotropic liquid crystals are much less than that in the microemulsions. The quantity of MB monomer is much greater in lyotropic liquid crystals; whereas, the interspacing of SDS molecules and the interspace between SDS and MB in lyotropic liquid crystals all are much less than that in the microemulsions. The interaction and the viscosity are so great in the lyotropic liquid crystals. Therefore, the diffusion coefficients of MB are much less in lyotropic liquid crystals. The sequence of the diffusion coefficient are as follows: the coefficient in the O/W microemulsion > the coefficient in the W/O microemulsion > the coefficients in the LLC > the coefficients in the Hex.

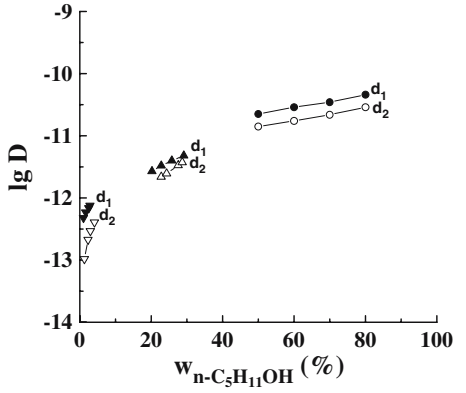

Fig. 5 Variety of the logarithm of the diffusion coefficients of MB with *n*-pentanol content. Mass ratio of SDS/H_2O: •▲▼—48/52, ○□□—50/50. Systems: •○—W/O microemulsion, ▲□—lamellar liquid crystal, ▼□—hexagonal liquid crystal

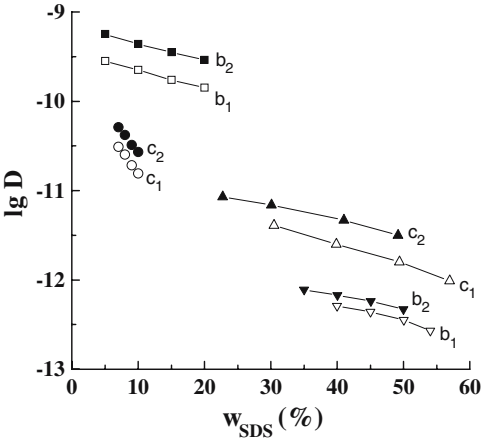

Fig. 6 Variety of the logarithm of the diffusion coefficients of MB with SDS content. Mass ratio of H_2O/*n*-$C_5H_{11}OH$: ▪▼—95/5, □□—92/8, •▲—65/35 , ○□—60/40. Systems: ▪□— O/W microemulsion, •○— W/O microemulsion, ▲□—lamellar liquid crystal, ▼□—hexagonal liquid crystal

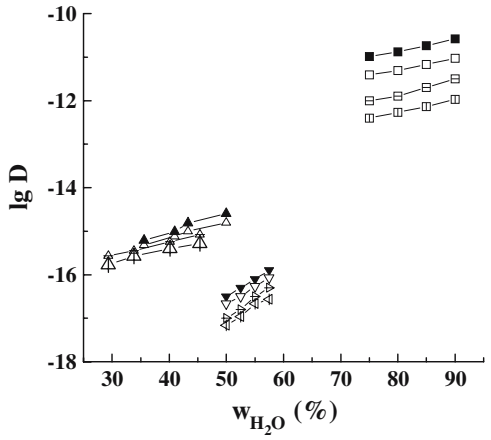

Fig. 7 Variety of the logarithm of the diffusion coefficients of SDS molecule with water content. Mass ratio of SDS/*n*-$C_5H_{11}OH$: ▪□▲□—55/45, —60/40 ▼□—90/10, —92/8. Concentration of MB (mol L^{-1}): ▪ ▲ ▼ —0 □ □ □ —1.0×10^{-6}. Systems: ▪□ — O/W microemulsion, ▲□ —lamellar liquid crystal, ▼□ —hexagonal liquid crystal

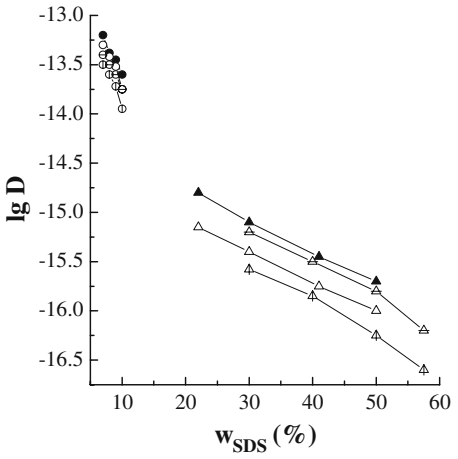

Fig. 9 Variety of the logarithm of the diffusion coefficients of W/O droplet and SDS molecule with SDS content. Mass ratio of H_2O/*n*-$C_5H_{11}OH$: •○▲□—65/35, — 60/40. Concentration of MB (mol L^{-1}): • ▲ —0, ○ □ —1.0×10^{-6}. Systems: •○ —W/O microemulsion, ▲□ — lamellar liquid crystal

The influence of SDS content on the diffusion coefficients of MB

Figure 6 indicates that the diffusion coefficients of MB decrease with SDS content. The more the SDS concentration, the less the interspace between SDS and MB, the greater the electrostatic interaction between SDS and MB, the greater MB moving resistance, and the less the diffusion coefficient of MB.

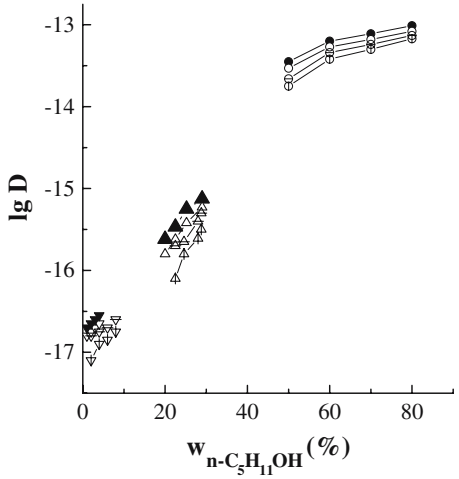

Fig. 8 Variety of the logarithm of the diffusion coefficients of W/O droplet and SDS molecule with *n*-pentanol content. Mass ratio of SDS/H_2O: •○▲□▼□—48/52, —50/50. Concentration of MB (mol L^{-1}): • ▲ ▼ —0, ○ □ □ —1.0×10^{-6}. Systems: ?○ —W/O microemulsion, ▲□ —lamellar liquid crystal, ▼□ —hexagonal liquid crystal

The influence of MB on the diffusion coefficients of SDS droplets and SDS molecule

The diffusion coefficient of O/W droplet increases with water content at constant mass ratios of SDS/*n*-$C_5H_{11}OH$ in SDS/*n*-$C_5H_{11}OH/H_2O$ system (Fig. 7), because the micellar aggregation number and the micellar volume decrease with water content increasing [16]. In the LLC, water mostly exists in solvent layer, the rest penetrates into the amphiphilic layer. The increase of water content causes the interlayer spacing of the solvent layer, the penetration of water in the amphiphilic layer, and the interspacing of SDS and MB molecules to increase. These lead to the increase of

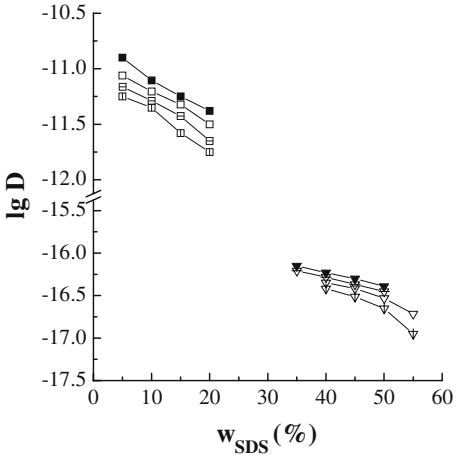

Fig. 10 Variety of the logarithm of the diffusion coefficients of O/W droplets and SDS molecule with SDS content. Mass ratio of H_2O/*n*-$C_5H_{11}OH$: ▪□▼□—95/5, —92/8. Concentration of MB (mol·L^{-1}): ▪ ▼ —0, □ □ —1.0×10^{-6}. Systems: ▪□ —O/W microemulsion, ▼□ — hexagonal liquid crystal

the moving rate and the diffusion coefficients of SDS molecules.

More MB can absorb on the surface of the O/W droplet because of the electrostatic attraction between SDS and MB. Both the increase of the O/W droplet volume and the decrease of the net charge of the O/W droplet lead to the moving rate of the O/W droplet decreasing under the condition of electric field. Moreover, the electrostatic attraction makes the moving resistance of SDS droplet increase. So, the diffusion coefficient of SDS droplet in the microemulsion without MB is greater than that with MB [30].

The diffusion coefficient of W/O droplet increases with *n*-$C_5H_{11}OH$ content at constant mass ratios of SDS/H_2O (Fig. 8), which may be the reason that the inverse micellar aggregation number and the volume decrease with *n*-$C_5H_{11}OH$ content increase. The diffusion coefficients of SDS molecule in the LLC and the Hex also increase with *n*-$C_5H_{11}OH$ content. *n*-$C_5H_{11}OH$ is mainly located in the amphiphilic layer in the lyotropic liquid crystal. The addition of *n*-$C_5H_{11}OH$ enlarges the interspacing of SDS molecules and decreases their moving resistance. When MB is added to the SDS/*n*-$C_5H_{11}OH/H_2O$ system, the electrostatic attraction between SDS and MB makes the diffusion coefficients of SDS molecule go down.

At constant mass ratios of H_2O/*n*-$C_5H_{11}OH$, the diffusion coefficients of the W/O droplet and the O/W droplet decrease with SDS content increasing (Figs. 9 and 10), a likely reason why the aggregation number and the volume of the micellar and the inverse micellar increase with SDS content. In the LLC and the Hex, the more the SDS content, the less the interlayer space, the greater the moving resistance of SDS, and the less the diffusion coefficient of SDS molecule. So, the diffusion coefficients of SDS molecule in the LLC and the Hex decrease with SDS content increasing.

Conclusion

(1) The diffusion coefficients of MB in the SDS/*n*-$C_5H_{11}OH/H_2O$ system can be determined by the non-probe microelectrode voltammetry method. The results obtained show that the diffusion coefficients of MB increase with water content and with *n*-pentanol content but decrease with SDS content in the microemulsions and the lyotropic liquid crystals. The sequence of the diffusion coefficient of MB is as follows: the coefficient in the O/W microemulsion > the coefficient in the W/O microemulsion > the coefficients in the LLC > the coefficients in the Hex.

(2) The diffusion coefficient of SDS decreases with the addition of MB. MB is likely located in the outside of the membrane phase in the microemulsion or done in the amphiphilic layer in the lyotropic liquid crystal. The electrostatic interaction between the anionic SDS and the cationic MB mainly results in the diffusion coefficients of the micellar droplets in the microemulsion, and the diffusion coefficient of SDS molecule in the lyotropic liquid crystal is greater without MB than with MB.

(3) The diffusion coefficient of the SDS molecule in the hexagonal liquid crystal is nearly one order less than that in the LLC, about three to five orders less than that of the W/O droplet and the O/W droplet.

Acknowledgement This project is supported by the National Science Foundation of China (No. 20573091, 20233010).

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