

Ultramicroelectrode Voltammetric Investigation of Intermicellar Interaction and Micellar Growth of Sodium Dodecyl Sulfate in Aqueous NaCl Solutions

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Ultramicroelectrode voltammetric measurements have been carried out to calculate the micellar self-diffusion coefficient (D_s) and intermicellar interaction parameter (K_d) of sodium dodecyl sulfate (SDS) in aqueous NaCl solutions at 298.15 K. The hydrodynamic radius (R_h^m), the aggregation number, and the molecular weight of SDS micelles at various NaCl concentrations are also estimated. It is found that the D_s value is a function of SDS concentrations and the electrolyte concentration dependence on D_s exhibits two regions of behavior. With increasing NaCl concentration, D_s initially increases because of increasing Coulombic screening and, then, decreases linearly because of a linear spherical expansion of the micelles resulting from the increasing aggregation number. K_d is found to be a function of electrolyte concentrations. The stepwise decrease of K_d reflects that, due to Coulombic repulsion, the electrostatic interaction is gradually screened with increasing NaCl concentration. As the linear interaction theory applies rigorously over the electrolyte concentration range from 0.20 to 1.00 mol dm⁻³, it suggests that the micellar structure remains effectively spherical in the region, the linear spherical expansion of the micelle is occurring, and no dramatic structural changes have taken place in the micellar solutions. In addition, the micellar interaction energy is calculated, which implies that it is the Coulombic nature of the interaction between micellar particles that controls the micellar self-diffusion behavior in aqueous solutions.

1. Introduction

Micellar systems are of immense technological importance, as flow regulators, solubilizing agents, membrane mimetic compounds and recently as nanoreactors for enzymatic and chemical reactions.^{1–3} In general, the micellar structure (shape and size) has strongly influenced the behavior of such systems.⁴ To this end, considerable experimental and theoretical efforts have been expended to understand the phenomenological basis of the micellar behaviors on the microscopic level.^{5,6}

In these studies, micellar diffusion coefficient measurements have been widely used for characterizing the changes of micellar structure and their other properties. The usual techniques employed are light scattering,⁷ quasi-elastic light scattering,⁸ neutral scattering,^{9,10} and Taylor dispersion.¹¹ They all yielded mutual diffusion coefficients with the exception of tracer diffusion, which gives self-diffusion. Recently, the a simple electrochemical technique has been introduced to investigate the micellar systems, from which the mobility of micellar-immobilized electroactive probes in aqueous solutions is determined and the micellar self-diffusion coefficients are obtained.^{12–16} It suggests that such an electrochemical technique can provide some valuable information concerning the surfactant supramolecule structure, structural evolution, and interparticle interaction in the micellar solution, without the need for complicated parametrized fitting of the data.

Significantly, the ultramicroelectrode, often neglected in the investigation of the micellar behaviors in the solutions, has more advantages than conventional electrodes in these electrochemical measurements.^{15–17} For example, they draw extremely small

current (picoamperes to nanoamperes), the iR distortion may be substantially circumvented, and the charged current can be reduced very quickly. Due to its small size, the ultramicroelectrode may be used to conduct electrochemical measurements in minute volumes and observe discrete spatial events in microscopically small areas with high sensitivity.

In this work, ultramicroelectrode voltammetric measurements have been carried out to calculate micellar self-diffusion coefficient (D_s) and intermicellar interaction parameter (K_d) of sodium dodecyl sulfate (SDS) in aqueous NaCl solutions using Ferrocene as the electroactive probe. It is found that D_s value is a function of SDS concentrations and the electrolyte concentration dependence on D_s exhibits two regions of behavior. The decrease of K_d reflects that the electrostatic interaction due to Coulombic repulsion is gradually screened with the increase in NaCl concentration. The hydrodynamic radius (R_h^m), the aggregation number, the molecular weight of SDS micelles at various NaCl concentrations and micellar interaction energy are also estimated. It suggests that the Coulombic nature of the interaction between micellar particles controls the micellar self-diffusion behavior and the linear spherical expansion of the micelle is occurring, but the micellar structure remains effectively spherical in aqueous solutions; no dramatic structural changes have taken place in the micellar solutions.

2. Experimental

2.1. Materials. Sodium dodecyl sulfate (AR, Beijing Chemical Co.) was recrystallized twice from the mixture of acetone and methanol, then washed with anhydrous dimethyl ether, and dried at 323.15 K under vacuum for at least 72 h. The purity was ensured by the absence of a minimum, in the plot of surface

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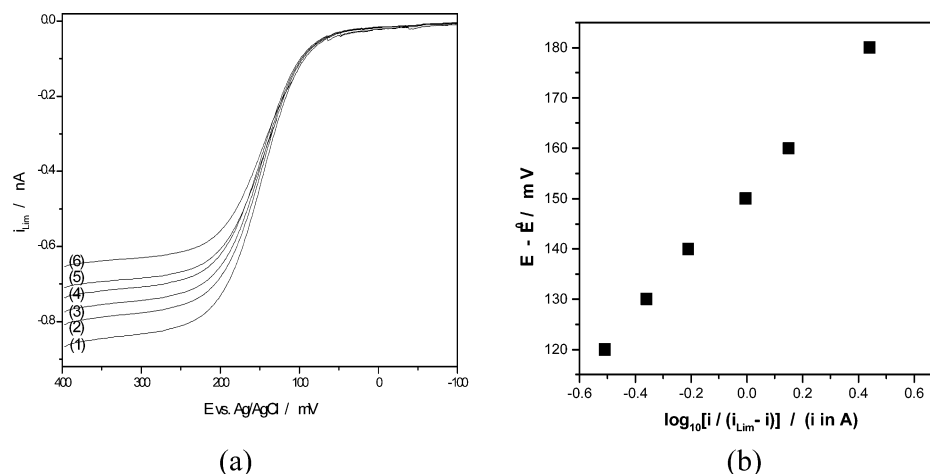


Figure 1. (a) Current–potential curves of the oxidation for Ferrocene ($C_{\text{probe}} = 0.001 \text{ mol dm}^{-3}$) in the aqueous SDS micellar ($C_{\text{SDS}} = 0.20 \text{ mol dm}^{-3}$) solution containing different NaCl concentrations: (1) $C_{\text{NaCl}} = 0.01 \text{ mol dm}^{-3}$; (2) $C_{\text{NaCl}} = 0.02 \text{ mol dm}^{-3}$; (3) $C_{\text{NaCl}} = 0.04 \text{ mol dm}^{-3}$; (4) $C_{\text{NaCl}} = 0.08 \text{ mol dm}^{-3}$; (5) $C_{\text{NaCl}} = 0.12 \text{ mol dm}^{-3}$; (6) $C_{\text{NaCl}} = 0.16 \text{ mol dm}^{-3}$. (b) Composite Nernstian plot for current–potential curves of ferrocene in the above micellar solutions.

tension versus logarithm of surfactant concentrations near the critical micelle concentration.¹⁸ Ferrocene and sodium chloride (AR, Beijing Chemical Co.) was dried at 328 and 408 K, respectively, under vacuum at least 48 h before use. The deionized water was further purified by redistilling from an alkaline permanganate solution, and the specific conductivity was $1.5 \times 10^{-6} \text{ S cm}^{-1}$ at 298.15 K.

2.2. Voltammetric and Rheological Measurements. The ultramicroelectrode is prepared by sealing Pt wire ($r = 10 \mu\text{m}$) into a soft glass tube. The surface of the electrode is polished with metallographic abrasive paper W₁₄ (No. 03#), W₁₀ (No. 04#), and the alumina powder of $0.05 \mu\text{m}$ and then cleaned with pure water in an ultrasonic bath. A Pt wire ($r = 0.5 \text{ mm}$) is used as an auxiliary electrode and an Ag wire ($r = 0.5 \text{ mm}$) as the pseudoreference electrode. The ultramicroelectrode ($1.3 \times 10^{-9} \text{ m}^2$ in area) is used as the working electrode and is determined electrochemically by ferricyanide (diffusion coefficient $= 7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in aqueous solution containing 1.0 mol dm^{-3} KCl at 298.2 K). All voltammetric measurements are carried out with an electrochemical working station (CHI 900) using a conventional single-compartment Pyrex glass cell. The cell, of 50 mL capacity, is equipped with a water circulating jacket, and the temperature is controlled within $\pm 0.1 \text{ K}$ with a superthermostat (Shanghai Experimental Instrument Factory). The scanning rate is 0.005 V s^{-1} in the experiments at 298.2 K. Before the measurements, each of the solutions is deoxygenated with bubbling nitrogen for at least 15 min, and each measurement is repeated at least three times. Ferrocene is added to the solutions and used as micelle immobilized electroactive probe; due to its very low solubility in water, it resides almost entirely within the hydrophobic core of the micelles. By keeping a small electroactive probe concentration ($1 \times 10^{-3} \text{ mol dm}^{-3}$) in SDS micellar solutions, the perturbation of the micellar structure by the probe has been minimized.^{19–23} All solutions are used freshly.

Viscosity measurements are made by a precise digital viscometer (Scott, 310 PVI) at 298.15 K. The experimental details have been described elsewhere.^{24–26}

3. Results and Discussion

3.1. Self-Diffusion Coefficient (D_s) of SDS Micelles. Current–potential profiles for the one-electron oxidation of ferrocene (eq 1) in the 0.20 mol dm^{-3} SDS solutions with different

NaCl concentrations are shown in Figure 1.



The traces exhibit sigmoidal shaped limiting-current versus voltage behavior, as expected for a diffusion-controlled redox process at an ultramicroelectrode; similar profiles are obtained for all SDS/NaCl solutions examined. Such i – V behaviors are analyzed in terms of electrochemical reversibility using Nernstian plots of $E - E^\circ$ vs $\log(i/(i_{\text{Lim}} - i))$, where E° is the ferrocene formal potential ($E^\circ \approx E_{1/2}$ (the half-wave potential) $= 0.160 \text{ V}$ vs $\text{Ag/AgCl}_{\text{sat}}$) and i is the current at any point along the i – E wave. The $E_{1/2}$ value obtained in this work can be comparative with the results of Mandal¹² and Rusling et al.²⁷ in 0.05 and 0.10 M SDS micellar environments, respectively. It suggests that $E_{1/2}$ decreases gradually with the increase in the SDS micellar concentrations. The Nernstian plot obtained from the solutions with various NaCl concentrations is also shown in Figure 1b. It is found that the average value of the Nernstian slope here is $\approx 0.060 \text{ V}$, which is close to that expected for a simple reversible electroactive probe such as ferricyanide.²⁸ These results demonstrate that it is possible to carry out respectable voltammetric measurements in micellar solutions, and significantly, the reversible electrochemical responses facilitate the measurement of self-diffusion coefficient of micelle. As the limiting-current represents the steady-state self-diffusion of micelles to the electrode surface, these results can reflect the average mobility of micellar size and the extent of interparticle interaction and can be used to probe micelle structures and observe micellar structural changes.

The micellar self-diffusion coefficient (D_s) may be obtained from the steady-state limiting-current equation²⁹

$$i_{\text{Lim}} = 4nFD_rC \quad (2)$$

where n is the number of electrons, F is the Faraday constant, r is the radius of ultramicroelectrode, and C is the concentration of the electroactive probe. The micellar self-diffusion coefficients, as a function of NaCl concentration, for different SDS concentrations are shown in Figure 3. It is obvious that D_s is a function of both SDS and NaCl concentrations. It is known that the diffusion coefficient for ferrocene in water is $10.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.¹² However, the values reported in SDS micelles are typically over an order of magnitude smaller than those expected

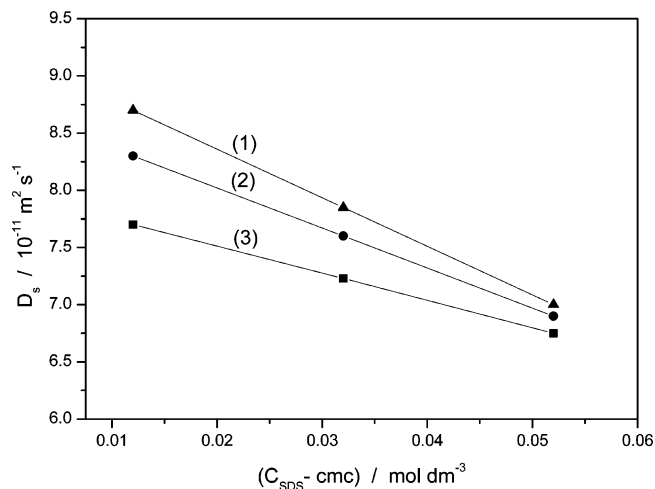


Figure 2. Plots of D_s vs $(C_{\text{SDS}} - \text{cmc})$ in the presence of various concentrations of NaCl: (1) 0.02, (2) 0.16, and (3) 1.00 mol dm⁻³.

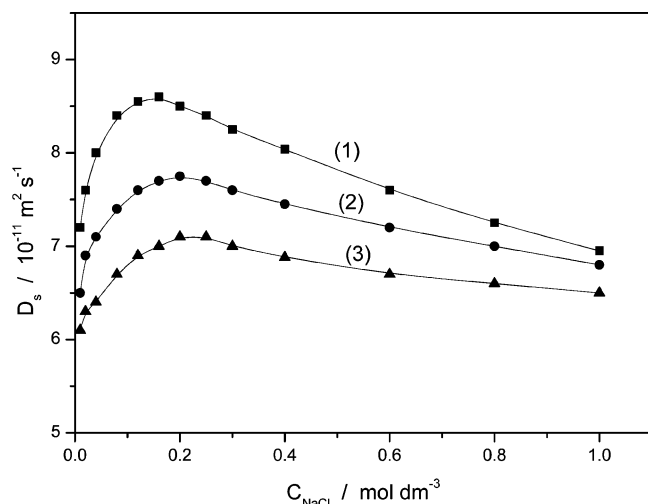


Figure 3. Plots of D_s vs C_{NaCl} in the presence of various concentrations of SDS: (1) 0.02, (2) 0.04, and (3) 0.06 mol dm⁻³.

for free ferrocene molecules in aqueous solutions. It suggests that the values of D_s reflect micellar self-diffusion and not simple free ferrocene diffusion.^{13,30} The results have been corrected for the finite aqueous solubility of ferrocene (1.0×10^{-5} mol dm⁻³) as previously described.¹²

3.2. Effect of SDS Concentrations on D_s . The effect of surfactant concentration on micellar self-diffusion coefficients is usually analyzed by the linear interaction theory, as given in eq 3^{12,29}

$$D_s = D_s^0 [1 - K_d(C_s - \text{cmc})] \quad (3)$$

where K_d is the intermicellar interaction parameter, D_s^0 is the self-diffusion coefficient with the absence of micellar interaction, cmc is the critical micelle concentrations, and C_s is the surfactant concentration. The representative profiles of D_s versus $(C_s - \text{cmc})$ for several NaCl concentrations are shown in Figure 2. To avoid overcrowding of the plots, the similar profiles of D_s vs $(C_s - \text{cmc})$ for other NaCl concentrations are not shown. It is apparent that these plots are strictly linear ($r = 0.999$) with different slopes and different intercepts. It suggests that the SDS/NaCl systems adhere to the linear interaction theory; the SDS micellar particles should retain their structural integrity and remain spherical in the NaCl concentration. In Figure 2, different slopes are the result of increased SDS micellar interparticle

TABLE 1: Data of the Size of SDS Micelles in Aqueous Solution with Different Electrolyte (NaCl) Concentrations at 298.2 K ($C_{\text{SDS}} = 0.20$ mol dm⁻³)

$C_{\text{NaCl}}/\text{mol dm}^{-3}$	R_h^m/nm	N	M_m
0.01	2.47	97	27900
0.02	2.49	99	28500
0.04	2.54	108	31000
0.08	2.59	116	33300
0.12	2.66	127	36900
0.16	2.71	136	39200
0.20	2.71	136	39200
0.40	2.75	144	41400
0.60	2.76	146	41900
0.80	2.81	155	44700
1.00	2.85	164	47300

interaction in the aqueous NaCl solution, and different intercepts reflect the changes of the SDS micellar sizes. The mean hydrodynamic radius of micelles (R_h^m) at different SDS concentrations can be calculated from D_s^0 by a formula analogous to the Stokes–Einstein relation for spherical particles¹⁵

$$D_s^0 = \frac{kT}{6\pi\eta_0 R_h^m} \quad (4)$$

where D_s^0 is found using eq 3 by extrapolation of the plots of D_s versus C_s to the cmc. k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solution viscosity (without surfactant and probe). For example, for $D_s^0 = 0.90 \times 10^{-10}$ m² s⁻¹ ($C_{\text{SDS}} = 0.20$ mol dm⁻³, $C_{\text{NaCl}} = 0.02$ mol dm⁻³), $\eta_0 = 1.01 \times 10^{-3}$ Pa s, $T = 298.15$ K, we have $R_h^m = 2.49 \times 10^{-9}$ m (2.49 nm). To connect the radius (R_h^m) with that of the hydrocarbon core of a micelle, and take the thickness of the stern layer to be 4.60×10^{-10} m,³¹ the core volume of a micelle is then

$$V = [4\pi \times (2.49 \times 10^{-9} - 4.60 \times 10^{-10})^3]/3 = 3.47 \times 10^{-26} \text{ m}^3 \quad (5)$$

The SDS carbon chain has a volume, $v = 3.5 \times 10^{-28}$ m³.³² Thus we have the micelle aggregation number

$$N = V/v = 3.47 \times 10^{-26} \text{ m}^3 / 3.5 \times 10^{-28} \text{ m}^3 = 99 \quad (6)$$

and the molecular weight of the micelle, M_m , is 26 500. Quantitative results of the experiments are listed in Table 1. It shows that the sizes of SDS micelles increase with increasing NaCl concentrations. This observation is supported by the studies of quiescent light scattering (QELS).³³ It is known that the QELS technique measures the mutual diffusion coefficients, whereas in the ultramicroelectrode voltammetric experiments the self-diffusion coefficient is measured. However, in the absence of interactions, the mutual and self-diffusion coefficients of the micellars are indistinguishable.^{4,34,35} The results suggest that SDS micellar aggregation number does change gradually with increasing electrolyte concentrations. Furthermore, the aggregation numbers obtained in this work are also in good agreement with the results of fluorescence quenching studies.^{36–38}

3.3. Effect of NaCl Concentration on D_s . It can be seen from Figure 3 that there exist two distinct regions of behaviors for D_s versus NaCl concentrations in SDS micellar solutions. At low electrolyte concentrations, D_s exhibits an initial increase. Then D_s decreases approximately linearly with increasing NaCl concentration. Such nonmonotonic behavior is not unusual in micellar systems, and similar behavior has been shown previ-

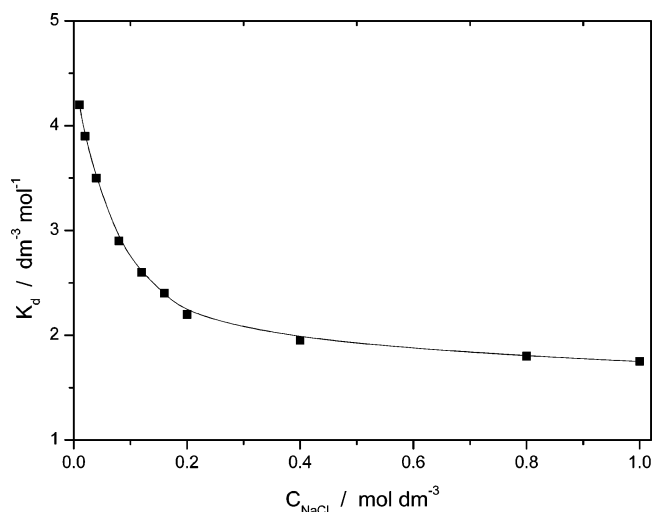


Figure 4. Plot of intermicellar interaction parameter (K_d) vs NaCl concentrations in micellar solutions at 298.15 K.

ously for CTAC/NaCl system, that is, a linear increase in D_m , and then a linear decrease in D_m with increasing NaCl concentration.³⁹

The initial increase in D_s with added electrolyte is known and has been interpreted in terms of two opposing effects: first, decreasing electrostatic drag and, second, increasing micellar hard-sphere size.⁴⁰ The addition of electrolyte causes an increase in electrostatic screening as a result of the neutralization of the micellar surface charge and causes an effective decrease in electrostatic drag. Thus, the mobility of the micellar particle increases concurrently. Therefore, the behavior observed in low NaCl concentration is considered as the net effect of decreasing electrostatic drag and micellar growth, in which the effect of reduced electrostatic drag is dominant.

The second D_s region in Figure 3 shows an approximately linear decrease in D_s in all micellar solutions. Again, the effect of micellar growth and electrostatic drag influences the observed behavior. With increasing NaCl concentration, the micellar surface charge is progressively screened, although not completely neutralized; that is, at 0.20 mol dm⁻³ NaCl, the surface potential is -77 mV.¹⁶ However, while reducing electrostatic drag, SDS micellar expansion occurs simultaneously because the aggregation number increases from 97 to 164 in the electrolyte concentration range studied in this work (Table 1). Because the values of D_s decrease gradually, it is evident that micellar growth is the predominant process and then determines the transport behavior of micelles. As the linear interaction theory applies rigorously in this region, it suggests that the micellar structure remains effectively spherical, the linear spherical expansion of the micelle is occurring, and no dramatic structural changes have taken place in the micellar solutions.

3.4. Intermicellar Interaction. Values for K_d are obtained by the linear interaction theory (eq 3) and are plotted as a function of NaCl concentrations in Figure 4. It is obvious that with the increase in NaCl concentrations K_d decreases gradually. It implies that the spherical micellar expansion due to the increase in aggregation number affects the change in K_d apparently. The effect of electrolyte concentration on intermicellar interaction parameters for several systems has been reported and interpreted in terms of DLVO theory.⁴¹ SDS micelles are highly dissociated; therefore, the surfaces of the micelles are -120 mV or more in the absence of extraneous electrolyte,^{42,43} which decreases to -77 mV at 0.20 M NaCl. The addition of electrolyte causes screening of the micellar

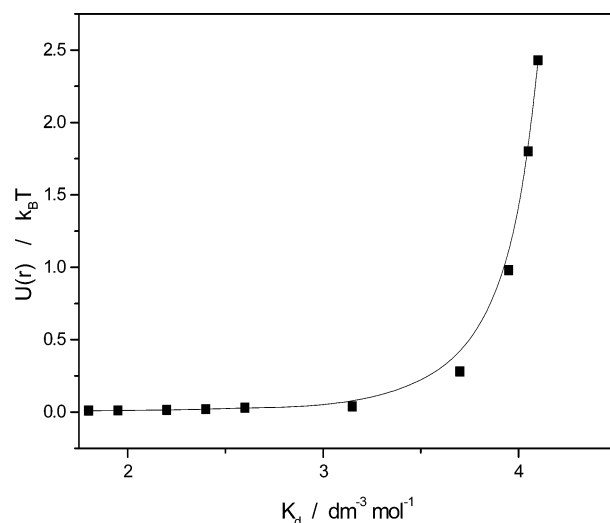


Figure 5. Plot of the micellar interaction energy ($U(r)$) vs intermicellar interaction parameter (K_d) in aqueous NaCl solutions at 298.15 K.

surface charge and diminution in the effective Coulombic interaction potential between neighboring micellar particles. According to the experimental results of Corti and Degiorgio,⁴⁴ the interaction parameter of SDS micelles (from D_m) passed through zero to yield a negative value of K_d , indicating the transition from strong Coulombic repulsive interaction to the predominance of attractive van der Waals interaction. Obviously, from Figure 4, we have been unable to detect such a transition in K_d over the entire NaCl concentration range studied, it is noticed that the K_d values are always positive and are larger than 1.80. The decrease in K_d here indicates that the electrostatic interaction due to Coulombic repulsion is gradually screened with the increase in NaCl concentration and the micellar self-diffusion behavior may be governed by Coulombic repulsive interactions between micellar particles.

To further confirm the observed behavior, the intermicellar interaction energy (Coulombic interaction potential) for two identical spherical macroions of diameter σ is calculated⁴¹

$$U(r) = \pi \epsilon \epsilon_0 \sigma^2 \psi_0^2 \exp[-\kappa(r - \sigma)]/r \quad (7)$$

where r is the micellar center to center distance, ϵ is the dielectric constant of the medium (H₂O), ϵ_0 is the permittivity of free space, κ is the Debye-Hückel inverse screening length as determined by the ionic strength of the solution, and $\sigma = 2R_h^m$, where R_h^m is the micellar hydrodynamic radius. The value for r is calculated from the micellar volume fraction (φ) (obtained from a knowledge of R_h^m and the micellar aggregation numbers)⁴⁵

$$R = 2R_h^m + l \quad (8)$$

where

$$l^3 = [8\pi/2^{1/3}] \varphi (R_h^m)^3 \quad (9)$$

A plot of $U(r)$ versus K_d is shown in Figure 5. It is evident that the intermicellar interaction parameter is a direct function of the Coulombic interaction potential, thus indicating that it is the Coulombic nature of the interaction that controls the micellar self-diffusion behavior in the aqueous NaCl solution. At low electrolyte concentration, the interaction parameter tends toward a constant value of 4.10 mol⁻¹ dm³ as the Coulombic interaction energy tends toward infinity. This behavior represents

significant unscreened Coulombic interaction between neighboring micellar particles. With increasing electrolyte concentration, the interaction parameter decreases monotonically as the Coulombic interaction energy approaches zero. Such behavior indicates the trend from Coulombic repulsion to total screening of the electrostatic interaction.

4. Conclusions

The results reported in this paper show that ultramicroelectrode voltammetry could be used to investigate the micellar self-diffusion behavior in aqueous NaCl solutions. It is sensitive to probe the structural change of SDS micelles and obtain the information of intermicellar interactions in aqueous solutions.

By ultramicroelectrode voltammetric measurements, several important micellar parameters are estimated, and intermicellar interactions and micellar growth process are analyzed. The effect of electrolyte concentration can be interpreted in terms of two opposing effects: decreasing electrostatic drag and increasing micellar hard-sphere size. In low NaCl concentration, the decrease of electrostatic drag is dominant. With increasing NaCl concentration, the linear spherical expansion of the micelles becomes predominant, but the SDS micellar structure remains effectively spherical in the electrolyte concentration range studied, no dramatic structural changes have taken place in the solutions.

It is the Coulombic nature of the interaction between micellar particles that controls the micellar self-diffusion behavior in aqueous NaCl solutions.

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