



Diffusion Coefficients of Sodium Dodecylsulfate in Aqueous Solutions of Sucrose and in Aqueous Solutions

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Abstract

Differential diffusion coefficients of sodium dodecylsulfate (SDS) in aqueous solutions of sucrose and in aqueous solutions at 298.15 K, over the concentration range 0.0018 M to 0.0817 M, have been measured using a conductimetric cell and an automatic apparatus to follow the diffusion. The results are discussed on the basis of the Onsager–Fuoss model. The cell uses an open ended capillary method, while a conductimetric technique is used to follow the diffusion process by measuring the resistance of a solution inside the capillaries, at recorded times. The influence of molecules of sucrose on the diffusion of this electrolyte was investigated. The presence of sucrose increases the diffusion coefficients of sodium dodecylsulfate both above and below the critical micelle concentration (cmc) of the surfactant.

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Introduction

Interactions of surfactants with natural products, such as sucrose, are of considerable practical importance. However, while earlier data on diffusion coefficients of sodium dodecylsulfate in aqueous solutions has been reviewed [1–3], this was only at 25 °C over the concentration range from 0.0018 M to 0.0817 M, and no data has been presented in the literature for the diffusion coefficient of this surfactant in aqueous solutions in the presence of sucrose. This paper reports experimental data for differential diffusion coefficients of sodium dodecylsulfate (SDS) at 298.15 K obtained using the previously reported open-ended capillary cell [4] over the same interval of concentrations used for other electrolytes. Data are also presented for differential diffusion coefficients of sodium dodecylsulfate in aqueous solutions of 0.0018 M, 0.0046 M, 0.0080 M, 0.0118 M and 0.0817 M in the presence of sucrose. Solutions of SDS have a well-defined critical micelle concentration (cmc) [1–3] marking the onset of surfactant

association. The effect of sucrose on the diffusion for this electrolyte above and below the cmc is reported. These results are discussed on the basis of the Onsager-Fuoss [5] model.

Experimental

The open-ended capillary cell used in this study was constructed in this laboratory and is essentially the same as that previously reported by Agar and Lobo [4]. The cell has two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 14 mm.

The upper and lower tubes, initially filled with solutions of concentrations $0.75 c$ and $1.25 c$, respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a $200 \times 140 \times 60$ mm glass tank, which was immersed in a thermostat at 298.15 K. The tank is divided internally by Perspex sheets, while a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value c , that is the physical length of the capillary tube coincides with the diffusion path, such that the boundary conditions described in [4] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl -effect [4] is reduced to negligible proportions. In a manual apparatus, diffusion is followed by measuring the ratio of resistances of upper and lower tubes by an alternating current transformer bridge. In our automatic apparatus $w = R_t/R_b$ is measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A Bradley Electronics Model 232 power source supplies a 30 V, 4 kHz sinusoidal signal (stable up to ± 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes in the top and bottom capillaries. By rapidly (< 1 s) measuring the voltages V' and V'' from top and bottom electrodes relative to the central electrode at ground potential the DVM calculates $w = R_t/R_b$.

To measure the differential diffusion coefficient D at a given concentration c , 2 litres each of a "top" solution of concentration $0.75 c$ and a "bottom" solution $1.25 c$ are prepared. The "bulk" solution of concentration c is produced by mixing 1 litre of "top" solution with 1 litre of "bottom" solution, accurately measured. The sodium dodecylsulfate solutions were prepared from *pro analysi* Merck reagent. The glass tank and the two capillaries are filled with solution c , immersed in the thermostat, and are

allowed to come to thermal equilibrium. The quantity $TR_{inf} = 10^4/(1 + w)$ is now measured very accurately, where $w = R_t/R_b$ is the electrical resistance ratio for solutions of concentration c of the top (t) and bottom (b) diffusion capillaries at infinite time. $TR = 10^4/(1 + w)$, is the equivalent, at any time t .

The capillaries are then filled with "top" and "bottom" solutions, which are allowed to diffuse into the "bulk" solution. Resistance ratio readings are taken at recorded times, beginning 1 000 min after the start of an experiment. The diffusion coefficient is finally evaluated using a linear least-squares procedure to fit the data, and subsequently an iterative process which uses 20 terms of the expansion series of the solution of Fick's second law for the present boundary conditions. The theory developed for this cell has already been described [4].

Results and discussion

Part I - Diffusion coefficients of SDS in aqueous solutions

The results of three independent diffusion experiments on 0.0046 M SDS solutions at 298.15 K are shown in Table 1. The good agreement between the data clearly shows the precision of the method for measuring differential diffusion coefficients. The accuracy of the systems has been demonstrated by measurements on 0.1 M KCl solutions using this method which agree with those of Miller within 1% [6]. Table 2 shows the results with sodium dodecylsulfate solutions from 0.0018 M to 0.0817 M at 298.15 K. These results are the average of 3 experiments performed on consecutive days. The reproducibility of the data is good, as shown by S_{Dev} , and the mean value is in excellent agreement with experimental results of Deng and co-workers [3] (deviations of ca. 2 %, except for the higher concentration), as shown in Fig. 1.

Table 1
Diffusion coefficients, D, of 0.0046 M SDS in aqueous solutions
at 298.15 K using a 250 Hz signal (see “experimental”)

| D/ /10 ⁻⁹ m ² s ⁻¹ | TRinf |
|--|--------|
| 0.780 | 4984.0 |
| 0.783 | 4983.7 |
| 0.780 | 4984.0 |

$D_{av} = 0.781 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $S_{D_{av}} = 0.001 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $Cv = 0.2 \%$
where D_{av} is the mean diffusion coefficient of 3 experiments; $S_{D_{av}}$
is the standard deviation of that mean and Cv is its coefficient of variation

Table 2
Diffusion coefficients, D, of SDS in aqueous solutions at 298.15 K
at different concentrations, c.

| c/ /mol dm ⁻³ | f/ /Hz a) | Mean value of D in 3 experiments/ /10 ⁻⁹ m ² s ⁻¹ | TRinf b) | $S_{D_{av}}$ / /10 ⁻⁹ m ² s ⁻¹ c) | D_{OF} / /10 ⁻⁹ m ² s ⁻¹ d) |
|-----------------------------|-----------------|--|-------------|--|--|
| 0.0018 | 250 | 0.795 | 4 998.7 | 0.008 | 0.822 |
| 0.0028 | 250 | 0.788 | 5 007.2 | 0.007 | 0.809 |
| 0.0034 | 250 | 0.782 | 5 002.2 | 0.007 | 0.809 |
| 0.0046 | 250 | 0.781 | 4 983.9 | 0.001 | 0.800 |
| 0.0118 | 500 | 0.234 | 4 981.7 | 0.003 | 0.040 |
| 0.0178 | 500 | 0.228 | 4 991.0 | 0.003 | 0.040 |
| 0.0249 | 500 | 0.277 | 4 994.0 | 0.004 | 0.050 |
| 0.0462 | 4 000 | 0.375 | 4 996.0 | 0.004 | 0.075 |
| 0.0817 | 4000 | 0.488 | 4 998.0 | 0.004 | 0.108 |

a) f , frequency of sinusoidal signal used in the experimental procedure; b) $TR_{inf} = 10^4/(1 + w)$, where
 $w = R_f/R_b$ is the resistance ratio; c) see table 1; d) D_{OF} represents diffusion coefficient calculated by
Onsager-Fuoss theory [5].

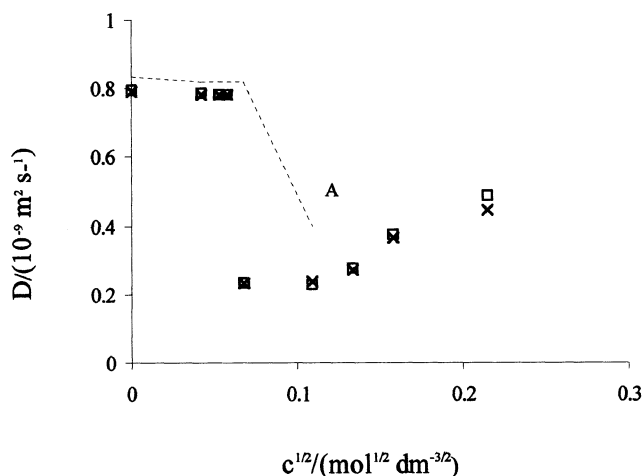


Figure 1

Comparison of our results (□) of diffusion coefficients of SDS—H₂O with those of Deng et al. (x) [3] and the Onsager-Fuoss model (curve A), for aqueous solutions, using the value for the ion size parameter, $a = 20 \times 10^{-10} \text{ m}$ [7].

The value of the diffusion coefficient of SDS at the critical micelle concentration (0.008 mol dm⁻³ [3,8]) may be estimated from the following adjustment equation

$$D/(10^{-9} \text{ m}^2 \text{ s}^{-1}) = 0.836 - 6.615\sqrt{c} + 2.045 \times 10^2 c - 1.784 \times 10^3 c^{3/2} \quad (1)$$

obtained from the data in table 2 and the Nernst limiting value D^0 , cited by Deng et al [3].

Eq. (1) adjusts well to the above data up to $c = 0.0118 \text{ mol dm}^{-3}$ (correlation coefficient = 0.999) and using this we obtain $D_{\text{cmc}} = 0.604 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Fig.1 compares experimental results with calculations on the basis of Onsager-Fuoss [5] model. This equation for an electrolyte of this type is often written

$$D = 2000RT \frac{\bar{M}}{c} \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right), \quad (2)$$

where

$$\frac{\bar{M}}{c} = 1.0741 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0}{|z_1| \nu_1 \Lambda^0} + \frac{\Delta M'}{c} + \frac{\Delta M''}{c} \quad (3)$$

In (3), the first- and second-order electrophoretic terms are given by

$$\frac{\Delta M'}{c} = \frac{\left(|z_2| \lambda_1^0 - |z_1| \lambda_2^0 \right)^2}{|z_1 z_2| 2 \left(\Lambda^0 \right)^2} \times \frac{3.132 \times 10^{-19}}{\eta_0 (\epsilon \Gamma)^{1/2}} \frac{c \sqrt{\tau}}{(1 + ka)}$$

and

$$\frac{\Delta M''}{c} = \frac{\left(z_2^2 \lambda_1^0 - z_1^2 \lambda_2^0 \right)^2}{\left(\Lambda^0 \right)^2} \times \frac{9.304 \times 10^{-13} c^2}{\eta_0 (\epsilon \Gamma)} \phi(ka),$$

where $\Gamma = \sum c_i z_i^2$ is the ionic concentration, η_0 is the viscosity of the solvent, k is the "reciprocal of average radius of ionic atmosphere" (e.g., [9]), a is the mean distance of approach of ions, $\phi(ka) = \left| e^{2ka} E_i(2ka)/(1 + ka) \right|$ has been tabulated by Harned and Owen [9], and the other letters represent well-known quantities [9].

We use the values of thermodynamic factor $(1 + c \partial \ln y_{\pm} / \partial c)$ of aqueous sodium dodecylsulfate presented by Deng et al [3]. Table 2 shows the data calculated by these equations.

For dilute solutions (below the cmc) reasonable agreement is observed between the experimental data and this model. At higher concentrations, while our experimental data and those from other research groups [3,7] are in good agreement, the results

predicted from the above model differ markedly from experimental observation. This is not surprising if we take into account the change with concentration of parameters such as viscosity, dielectric constant and hydration, which are not taken into account in the Onsager-Fuoss model. Further, this treatment does not consider the effect of aggregation on the diffusion behaviour (i.e. formation of micelles [10]). The results obtained with the Pikal equation [11] are similar to those with the Onsager-Fuoss treatment, and do not significantly improve the fit between theory and experimental results. We may, therefore, accept that effects of short-range interactions between sodium and dodecylsulfate ions are not the main reason for the deviations shown in Fig. 1, and that micellisation plays a major role.

Part II - Diffusion coefficients of SDS in aqueous solutions of sucrose

Table 3 shows the results of diffusion experiments with 0.0018 M, 0.0046 M, 0.0080 M, 0.0118 M and 0.0817 M SDS in aqueous solutions of sucrose (0.001 M).

Table 3
Diffusion coefficients, D_{exp} , of SDS (concentration c) in aqueous solutions of sucrose (0.001 M)

| $c/$ /mol dm ⁻³ | $D_{\text{exp}}/$ /m ² s ⁻¹ | $f/$ /Hz a) | TRinf a) | D_{av} /10 ⁻⁹ m ² s ⁻¹ b) | $S_{\text{Dw}}/10^{-9}$ m ² s ⁻¹ c) | $\frac{\Delta D}{D}$ % d) |
|-------------------------------|--|-------------------|-------------|---|---|------------------------------|
| 0.0018 | 0.868 | 390 | 4 998.8 | 0.854 | 0.016 | 7.4 |
| | 0.817 | 370 | 4 999.0 | | | |
| | 0.850 | 390 | 4 997.0 | | | |
| 0.0046 | 0.859 | 750 | 4 999.2 | 0.864 | 0.018 | 10.6 |
| | 0.836 | 750 | 5 000.2 | | | |
| | 0.896 | 750 | 4 999.8 | | | |
| 0.0080 | 0.680 | 1 100 | 5 005.0 | 0.667 | 0.006 | 10.4 |
| | 0.660 | 1 100 | 4 995.0 | | | |
| | 0.662 | 1 100 | 4 998.0 | | | |
| 0.0118 | 0.314 | 1 250 | 4 999.4 | 0.311 | 0.010 | 32.9 |
| | 0.292 | 1 250 | 4 999.0 | | | |
| | 0.328 | 1 250 | 4 999.0 | | | |
| 0.0817 | 0.579 | 2 500 | 4 999.6 | 0.563 | 0.010 | 15.4 |
| | 0.546 | 3 100 | 4 999.5 | | | |
| | 0.565 | 2 750 | 5 001.0 | | | |

- a) See table 2; b) mean value of D_{exp} in 3 experiments; c) see table 1; d) ΔD is the difference between the diffusion coefficients of SDS at the specified concentration in 0.001 M sucrose, D_{w} , and that of the SDS in water, D .

From the above results, it is evident that sucrose molecules exert a significant influence on the diffusion of SDS in aqueous solution. The SDS-sucrose-water mixture is really a ternary system, and we are actually measuring the main diffusion coefficients D_{11} but not D_{12} , D_{21} and D_{22} . However, the present experimental conditions we may consider the system as pseudo-binary and consequently take the measured parameter as the diffusion coefficient of SDS in aqueous solutions of 0.001 M sucrose. From the experimental results, and the high precision of the diffusion measurements on SDS in aqueous solutions, in the presence and absence of sucrose, these results strongly suggest that sucrose in concentration as low as 0.001 M increases the diffusion coefficient of the SDS. This behaviour can be explained from consideration of the types of interactions that can occur: a) interactions between sucrose molecules and the dodecylsulfate anion (coulombic, etc); b) interactions between sucrose molecules and the sodium cation; c) changes in interactions between the Na^+ cation and the dodecylsulfate. It is known that sucrose decreases the cmc of SDS in aqueous solutions [12], suggesting that interactions with sucrose may increase aggregation of the dodecylsulfate chains. In addition, studies on aqueous solutions of SDS in the presence of water soluble cellulose strongly suggest surfactant binding to the carbohydrate groups [13], while it is also known that alkali metal cations can bind to small organic ligands [14]. However, sucrose can also affect the degree of hydration of species in aqueous solutions in other ways. For example, it is reported that it can stabilize proteins to thermal denaturation without directly binding to them by changing the degree of hydration [15,16]. It is probable that all these types of interaction occur, depending on the circumstances. Considering this fact, an appreciable fraction of the transport of sodium dodecylsulfate may occur as a result of larger aggregates, since these species may have a higher mobility than the dissociated part of the electrolyte. This phenomenon can be explained if we consider the loss hydration water from sodium and dodecylsulfate ions, which will lead to less resistance to motion through the liquid and, consequently, a larger diffusion coefficient. Support for such a decrease in hydration comes from calculations of the effect of sucrose on the potential of mean force between sodium and chloride ions in

aqueous solutions [17], which show that addition of sucrose decreases the number of water molecules in the first hydration sphere of the ions.

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References

- [1] D.F. Evans, S. Mukherjee, D.J. Mitchell and B.W. Ninham, *J. Colloid Interface Sci.* 93, 184 (1983).
- [2] D.G. Leaist and L. Hao, *J. Chem. Soc. Faraday Trans.*, 91, 2837 (1995).
- [3] Z. Deng, H. Lu and D.G. Leaist, *J. Chem. Eng. Data* 41, 214 (1996).
- [4] V.M.M. Lobo, Ph.D. Thesis, Cambridge (1971); J.N. Agar and V.M.M. Lobo, *J. Chem. Soc., Faraday Trans.*, I 71, 1659 (1975).
- [5] L. Onsager and R.M. Fuoss, *J. Phys. Chem.* 36, 2689 (1932).
- [6] V.M.M. Lobo, A.C.F. Ribeiro and L.M.P. Verissimo, *J. Mol. Liquids* 78, 139 (1998).
- [7] B.D. Flockhart, *J. Colloid Sci.* 17, 305 (1962).
- [8] P. Mukerjee and K.J. Mysels (*Critical Micelle Concentrations of Aqueous Surfactant Systems*), NSRDS-NBS 36, Superintendent of Documents, Washington, D.C. (1971).
- [9] H.S. Harned e B.B. Owen (*The Physical Chemistry of Electrolytic Solutions*), 3rd Ed., Reinhold Pub. Corp., New York (1964).
- [10] B. Jonsson, B. Lindman, K. Holmberg and B. Kronberg (*Surfactants and Polymers in Aqueous Solution*), Wiley, New York (1998).
- [11] M.J. Pikal, *J. Phys. Chem.* 75, 663 (1971).
- [12] M. Nakagaki and S. Kawamura, *Yakugaku Zasshi* 84, 246 (1964), quoted in ref.8.
- [13] H. Walderhaug, B. Nyström, F. Hansen and B. Lindman, *J. Phys. Chem.* 99, 4672 (1995).
- [14] D. Midgley, *Chem. Soc. Rev.* 4, 549 (1975).
- [15] J.C. Lee and S.N. Timasheff, *J. Biol. Chem.* 256, 7193 (1981).
- [16] T. Arakawa and S.N. Timasheff, *Biophys. J.* 47, 411 (1985)
- [17] V. Martorana, L. La Fata, D. Bulone and P.L. San Biagio, *Chem. Phys. Lett.* 329, 221 (2000).