Colloid Polym Sci 273:288–292 (1995)
© Steinkopff Verlag 1995

ORIGINAL CONTRIBUTION

P. C. Schulz

Effect of NaOH and NaCl on the disodium *n*-decane phosphonate micellar aggregation number

Received: 16 March 1994
Accepted: 20 June 1994

P.C. Schulz (✉)
Department of Chemistry and
Chemical Engineering
Universidad Nacional del Sur
Av. Alem 1253
8000 Bahia Blanca, Argentina

Abstract The diffusion coefficient of disodium *n*-decane phosphonate micelles was studied by polarography at 25 °C in NaCl and in NaOH solutions, and the size and aggregation number of the micelles was computed as a function of Na^+ concentration. All other conditions being equal, the addition of NaCl produces micelles with an aggregation number one order of magnitude larger than the NaOH addition. This is due to the increase of the effective charge per micellized head group produced by the reaction of OH- with the hydrolized head groups which are mainly present as $-PO_3H-$ in the micellar Stern layer.

Key words Disodium *n*-decane phosphonate – rodlike micelles – diffusion coefficients – polarography – micelle size

Introduction

Alkanephosphonic acids and their salts are surfactants which are rarely studied, and they show some unusual properties which are under investigation in this laboratory. In particular, light scattering measurements show a strange dependence of turbidity on pH [1], and there is evidence that the micelle size and shape depends on the nature of coions [1, 2].

The micellar diffusion coefficients were determined to elucidate the origin of the dependence of the micelle aggregation number on the OH– and Na^+ concentrations.

Some interest in methods for micelle size characterization led to the use of polargraphic techniques to estimate micelle diffusion coefficients via the redox behavior of associated electroactive probes [3–7]. These studies assumed that the presence of a small number of these probes per micelle will not affect its size and shape [7]. Polarographic methods have been successfully used to study the nature of concentrated microemulsions [8] and to determine the solubilization site of electroactive probes in cationic micelles [9]. Polarographic techniques give micelle self-diffusion coefficients, which are amenable to interpretation in terms of micelle shape and size. Moreover, the self-diffusion coefficient is that of the kinetic entity, without its ionic atmosphere. We applied the polarographic method to study the effect of NaCl and NaOH on the size and shape of disodium *n*-decane phosphonate micelles.

Experimental

The preparation and purification of *n*-decane phosphonic acid were both described elsewhere [10].

A concentrated solution was prepared by weighing the appropriate amount of *n*-decane phosphonic acid in a volumetric flask. NaOH aqueous solution was added only to neutralize the acid, then a CdI_2 aqueous solution was added to tag the micelles, and water was poured in to obtain the desired volume. The solutions for measurement were prepared by adding the appropriate amount of NaCl or NaOH concentrated solution to the former solution and then water was added to obtain the desired final concentration.

All solutions were prepared with double-distilled water.

pH measurements were performed with an Orion pH-meter and a glass electrode.

Polarographic measurements were performed in a Radiometer PO4 Polarograph, following the technique of Novodoff et al. [5]. Solutions were thermostatted at 25 °C.

The Ilkovic equation was used

$$i_d\ (\mu A) = 607 v D^{1/2} c m^{2/3} t^{1/6}, \tag{1}$$

where i_d is the average diffusion current in microampéres, v is the number of electrons consumed in the reduction of the probe ($v = 2$), D is the kinetic entity self-diffusion coefficient and c the probe concentration, m is the rate of flow of mercury through the capillary, and t is the time elapsed between the fall of two consecutive mercury drops. This equation may be written in the following way:

$$i_d = K c D^{1/2}, \tag{2}$$

and K may be obtained from the slope of i_d vs. Cd^{+2} concentration plot (Fig. 1), measured on solutions of CdI_2 in 0.15 M NaCl. The straight line illustrates the least-squares fitting equation:

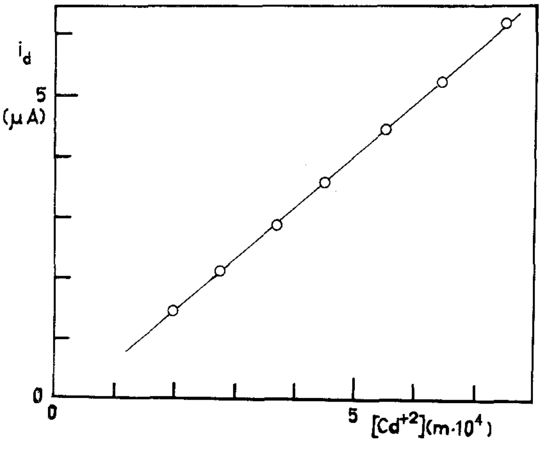
$$i_d\ (\mu A)' - 0.03 \pm 0.29 \pm (7810 \pm 570)\ [Cd^{2+}] \tag{3}$$

Correlation Coefficient $r = 0.9971$
Slope variation coefficient 7.36%
$E_{1/2} = -0.565 \pm 0.008\ V$

The Cd^{+2} diffusion coefficient was $D = 6.9 \times 10^{-9}$ $m^2 s^{-1}$ at 25 °C [10].

The runs on surfactant solutions were under the same conditions as those in Fig. 1, including the Cd^{2+} concentration range used as a tag. No additional supporting electrolyte was added.

Fig. 1 Dependence of i_d on Cd^{+2} concentration at 25 °C. Supporting electrolyte 0.15 mol. L^{-1} NaCl



By Eq. (2) the micelle diffusion coefficient D_M was obtained, and from the Stokes-Einstein equation the hydrodynamic radius R_H was found:

$$D = \frac{kT}{6\pi\eta R_H} \tag{4}$$

The concentration dependence of D_M is generally due to two factors, the first is the effect of intermicellar interactions while the second one is the possible change of the micelle size and shape with concentration.

To compute the intermicellar interactions the method of Corti and Degiorgio [11] was used which considers a hard-core repulsion, a screened Coulomb repulsion, and a London–Van der Waals attraction:

$$D_M = D_{M.o}[1 + k_D(c - \mathrm{CMC})], \tag{5}$$

and

$$k_D = [0.5 + 2(1 + X)^2(1 + 4X) - \frac{15}{8}(1 + X)^{-1}]\bar{V}, \tag{6}$$

where $X = k^{-1}/R_H$. k^{-1} is the Debye length and $\bar{V}$ is the partial specific volume of the micelle.

At high surfactant and/or salt concentration micelles are oblate elipsoids or rodlike [12], so we used the following equation to compute the micelle length L which corresponds to the determined hydrodynamic radius [13]:

$$R_H - \frac{L}{2\sigma - 0.19 - \frac{8.24}{\sigma} + \frac{12}{\sigma^2}} \tag{7}$$

where L is the length of the rodlike micelle, r its radius and $\sigma = \ln (L/r)$.

When error estimations were made, the confidence level was 0.90.

Results

Figure 2 shows one of the polarograms on disodium n-decane phosphonate samples. The half-wave potential was 0.76° V.

Table 1 shows the measured data and pertinent information obtained from literature. Table 2 shows the calculated micellar parameters.

The maximum radius for spherical micelles is equal to the surfactant molecule length b, which may be computed by [14]:

$$b(\mathrm{nm}) = 0.13 n_c + 0.1704 + 2 r_{ph}, \tag{8}$$

where n_c is the number of carbon atoms in the molecule hydrocarbon chain and r_{ph} is the radius of the hydrated polar head. This radius was obtained from the literature [15]: $r_{ph} = 0.2541 \pm 0.0059$ *nm*, then $b = 1.978$ nm.

The determined hydrodynamic radii are incompatible with spherical micelles.

To compute the ionic strength and then the Debye length, the concentration of free surfactant ions was taken as the CMC and the concentration of free Na^+ ions was estimated with:

$$[Na^+] = 2(c - CMC) + CMC.\alpha + [NaCl] + [NaOH] \tag{9}$$

where α is the fraction of charge per micellized polar head. We used α and cmc values from the literature [2], and these are listed in Table 1. We took $r = b = 1.97_8$ nm, obtaining the values of L listed in Table 2.

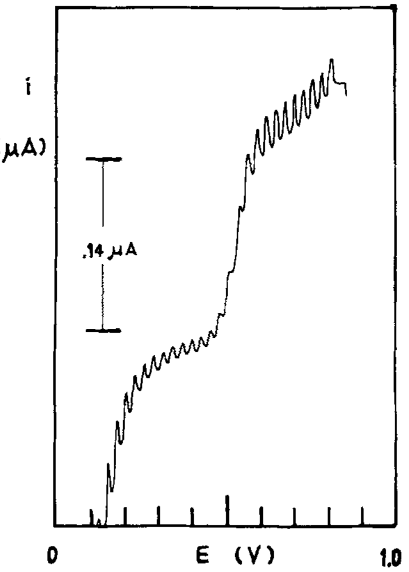


Fig. 2 Polarogram of disodium *n*-decane phosphonate + 0.001 M NaOH.

The volume of a rodlike micelle may be computed by [16]:

$$V_{rod\cdot} = \frac{4\pi b^3}{3} + 2\pi v^2(L - 2b) \tag{10}$$

The partial molar volume of micellized disodium n-decane phosphonate was obtained from the literature [15]: $V_M = 206.166 \pm 0.022$ cm^3/mol, giving the volume of a micellized molecule: $V_s = 0.34235 \pm 0.00004$ nm^3, and the specific volume of micelles: $\bar{V} = 0.77440 \pm 0.00008$ cm^3/g.

The aggregation numbers computed by $n = V_{rod\cdot}/V_s$ are listed in Table 2.

The upper limit for stiff rodlike micelles is $L = 100$ nm [17], corresponding to $n = 3090$. This indicates that the micelles are flexible.

When log n is plotted vs. log [X], [X] being the concentration of counterions, different straight lines are obtained for spherical and rodlike micelles [16]. The data of Table 2 are plotted in such a manner in Fig. 3. The equations of the straight lines, fitted by the least squares method are:

with NaCl:

$$\log n = (2.39 \pm 0.28) \log [Na^+] + 7.58 \pm 0.27 \tag{11}$$

$r = 0.9666$

With NaOH:

$$\log n = (0.184 \pm 0.099) \log [Na^+] + 4.299 \pm 0.092 \tag{12}$$

$r = 0.5500$

Table 1 Experimental data for disodium *n*-decane phosphonate (SDP) micellar solutions.

N°	[NaOH] (m)	[NaCl] (m)	cmc^a (m)	[SDP] (m)	α^a (−)	pH (−)	i_a (μA)
1	0	0	0.0530	-	1.10	8.31	-
2	0.00010	0	0.0395	0.0605	1.078	9.24	0.161 ± .003
3	0.00015	0	0.0509	0.0700	1.081	9.24	0.182 ± .003
4	0.00030	0	0.0664	0.0874	1.133	9.25	0.157 ± .008
5	0.00100	0	0.0660	0.0870	1.133	9.29	0.145 ± .001
6	0.00300	0	0.075	0.0960	1.139	9.49	0.1401 ± .0001
7	0.0100	0	0.080	0.101	1.161	10.30	0.1485 ± .0005
8	0.0300	0	0.085	0.106	1.172	12.18	0.138 ± .002
9	0	0.000030	0.029	0.0605	1.049	9.34	0.580 ± .0006
10	0	0.000060	0.010	0.0605	0.955	9.34	0.0447 ± .0005
11	0	0.00100	0.0095	0.0605	0.950	9.33	0.0345 ± .0006
12	0	0.000200	0.0045	0.0605	0.867	9.33	0.0400 ± .0009
13	0	0.000250	0.00128	0.0605	0.800	9.32	0.0430 ± 0.0006
14	0	0.00100	0.00182	0.0605	0.800	9.33	0.0361 ± .0007

a: from ref [2].

Table 2 Diffusion coefficients, hydrodynamic radii, length, and aggregation number for disodium *n*-decane phosphonate micelles.

N°	D_M[a] ($cm^2.s^{-1}$) $\times 10^8$	R_H[a] (nm)	$D_{M.o}$[b] ($cm^2.s^{-1}$) $\times 10^8$	$R_{H.o}$[b] (nm)	L (nm)	n (–)
1	–	–	–	–	(sphere)	20.8 ± 2.8^{c}
2	8.277	29.63	10.20	24.04	183.5	12 990
3	7.904	31.02	10.30	23.80	168.0	11 870
4	7.089	34.58	9.949	24.65	190.0	13 450
5	6.714	36.51	9.561	25.65	202.0	14 320
6	6.27	39.1	9.23	26.6	211	15 000
7	7.042	34.81	10.34	23.71	180.1	12 740
8	6.05	40.5	9.43	26.0	203	14 400
9	1.074	228.3	1.574	155.8	1 960	140 500
10	0.6878	384.4	1.238	198.1	2 740	196 600
11	0.6848	358.0	1.323	185.3	2 490	178 600
12	0.5596	437.4	1.091	225.0	3 050	218 800
13	0.5109	478.8	0.9992	245.4	3 380	242 500
14	0.417	588	0.825	297	4 300	308 600

a: uncorrected values; b: corrected by Eq (5); c: from ref. [21]

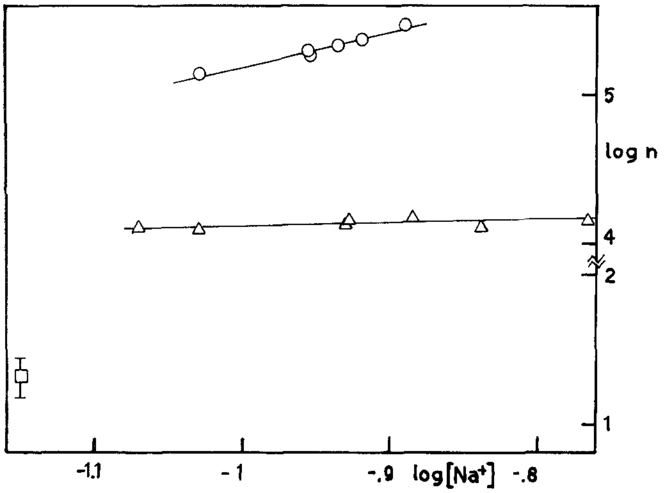


Fig. 3 Plot of log *n* vs. log $[Na^+]$ for disodium n-decane phosphonate: □: spherical micelles, from ref. [21]; △: with NaOH; ○: with NaCl.

Discussion

Figure 3 and Eqs (11) and (12) show that the addition of NaCl and NaOH to aqueous solutions of disodium *n*-decane phosphonate leads to the formation of giant micelles, all other factors being equal, NaCl produces a micellar aggregation number one order of magnitude larger than NaOH. This effect can be explianed by a variation of the effective charge of the micellized surfactant head groups [14, 16], (Table 1). Earlier work indicated that *n*-alkane phosphonate-water systems show strong hydrolysis and the micellized head groups are mainly in the $-PO_3H-$ form [1, 18, 19]. The addition of NaCl produces the well-known effect of the increment of counterion concentration on the aggregation number. The effect is almost the same at very low concentrations of NaOH, but although there is a negative adsorption of OH– ions from the (negative) micelle surface, some of them reach the Stern layer and react with the $-PO_3H-$ groups giving $-PO_3^{2-}$. This increment in the effective charge per micellized head group partially compensates the shielding effect of the increasing concentration of Na^+ counterions, which are positively adsorbed into the Stern layer. The different effect of NaCl and NaOH addition on the effective charge per micellized head group (taken from ref. [2]) can be seen in Table 1.

This effect of coion nature on the micelle properties is rare and only a few examples have been reported, which are associated with H^+ and HO^- [1, 2, 20]. This is noticeable in the systems studied because *n*-alkanephosphonic acids have a very weak second-ionization constant [10], so that the charge per micellized head group can be modified in a substantial manner.

Colloid & Polymer Science, Vol. 273, No. 3 (1995)

References

1. Miguens N (1973) Thesis, Universidad Nacional del Sur (Argentina)
2. Schulz PC (1989) Afinidad XLVI: 433
3. Zana R (1987) In: Zana R (ed) Surfactants in Solution, New Methods of Investigation Marcel Dekker New York cap 9
4. Zana R. Mackay RA (1986) Langmuir, 2: 109
5. Novodoff J, Rosano H, Hoyer H (1972) J Colloid Interface Sci 38: 426
6. Hoyer H, Novodoff J (1968) J Colloid Interface Sci 26: 490
7. Verrall RE, Milioto S, Giraudeau A, Zana R (1989) Langmuir 5: 1242
8. Mackay R, Dixit N, Agarwal R (1982) A C. S. Symp. Ser 177: 179 -Mackay R (1982): In Robb I (Ed) "Microemulsions", Plenum Press, New York, p. 207 -Makhay R, Dixit N, Argawal R, Seiders P (1983) J Dispersion Sci Technol 4: 397 -Georges J, Chen JW, (1986) Colloid Polym Sci 254: 896 -Georges J Chen JW, Arnaud W (1987) Colloid Polym Sci 265: 45
9. Hoshino K, Saji T, Osawa Y, Aoyagui S (1984) Bull. Chem. Soc. Jpn., 57: 1685
10. Schulz PC, Lelong ALM (1976) Rev Latinoamer Quím 7: 9
11. Corti M, Degiorgio V (1978) Ann Phys 3: 303
12. Tanford C (1974) J Phys Chem, 78: 2569-(1974) Proc Natl Acad Sci U.S. 71: 1811
13. Young CY, Missel PJ, Mazer NA, Benedeck GB (1978) J Phys Chem 82 (12): 1375
14. Schulz PC (1991) Colloid Polym Sci 269: 612
15. Schulz PC (1981) Anales Asoc Quím Argentina 69: 185
16. Schulz PC (1992) J Colloid Interface Sci 152: 333
17. Imae T, Ikeda S (1986) J Phys Chem 90: 5216
18. Schulz PC (1984) Anales Asoc Quím Argentina 72: 529
19. Schulz PC, Lelong ALM (1978) Anales Asoc Quím Argentina, 66: 11
20. Tikiwa F, Ohki K (1966) J Phys Chem 70: 3437
21. Lelog ALM, Schulz PC (1978) Anales Asoc Quím Argentina 66: 143