212. Dielectric Properties of Apolar Micelle Solutions Containing Solubilized Water

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Summary. Varying amounts of water have been solubilized in a micelle solution of sodium di-2-pentyl-sulfosuccinate in benzene and the complex permittivity has been observed in the range 200 KHz to 10 MHz. Part of a dielectric dispersion is seen, which extends to higher frequencies with a broad distribution of relaxation times. Due to association processes, the static dielectric increment is found to vary non-linearly with hydrated micelle concentration and with the amount of solubilized water, whereas a linear variation with micelle concentration is found if no water is added. These effects are explained on the assumption that part of the solubilized water increases the dipole moment of the micelle.

Additionally, at higher water concentrations, a sudden increase in the conductivity of the solution is observed, which is taken to indicate a conformational change of the solubilized micelle.

Introduction. – In relation to a general investigation into the properties of micelles in apolar media, it is of particular interest to study the effects of solubilizing water or other polar systems in the micellar phase¹). This could give valuable general information with regard to the catalytic effects of micelles and with respect to lipids in membranes.

Previous work on micelle forming amphiphilic compounds in apolar media includes some light scattering, vapour pressure, viscosity and NMR. measurements [1]–[8], but no dielectric measurements have been published. Since the unsolubilized micelle has a considerable dipole moment, it was felt that a dielectric investigation would be valuable because of the expected interactions with added water.

The model system (Aerosol AY = sodium di-2-pentyl-sulfosuccinate) chosen was found to be particularly suitable for these experiments and had been previously investigated [9]. The number and weight averages of the apparent molecular weight of the micelles, determined by vapour pressure osmometry and light scattering [9] indicate that the aggregation number is ∼15 in benzene and that the unsolubilized micelle solution is approximately monodisperse. Such a size has also been shown to be probable by theoretical considerations of stability [10]. (Additional confirmation is given by means of ultracentrifuge measurements in the present work.) Without added water, the critical micelle concentration (CMC) was known from DC and AC conductivity measurements [9]. The dipole moment per monomer, and the contribution per monomer to the total dipole moment of the micelle had also been determined [11].

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²) For further discussion see *e.g. Hall* [13].

Preliminary measurements indicated a considerable increase in the static permittivity of the solution as water was solubilized in the micellar phase. Therefore it was thought worthwhile to determine the variation of dielectric increment with water and aerosol AY concentration, to measure the dielectric dispersions and their temperature variation, to find the effects of adding aqueous electrolyte solutions and to investigate the stability of the solubilized micelle from a determination of its CMC.

Experimental Part. – The aerosol AY used was a commercial product (*Cyanamid Co.*) of analytical quality, which had been dissolved in benzene with added charcoal for further purification [14]. The mixture was stirred for at least 24 h. Finally the solution was filtered (D5-glass filter), the solvent evaporated and the product dried in a desiccator under vacuum and over phosphorus pentoxide. The benzene employed was analytical grade quality (*Merck AG*) and had been dried over a sodium/potassium alloy in a distilling apparatus with circulation of the benzene. Its specific conductivity of 7.10^{-15} ohm^{-1} cm^{-1} at 20° was sufficiently low compared with the conductivities of the solutions of the colloidal electrolyte in benzene. Bi-distilled water was used (conductivity $\sim 10^{-6}$ ohm^{-1} cm^{-1}, at 20°) and the solubilization in the micelles was assisted by means of a *MSE* ultrasonic generator. By inserting the probe of this instrument into the solution for about 10 min, the water or electrolyte solution was more easily solubilized and stationary conditions were attained. It was checked that the ultrasonification had no other effect than that of speeding up the solubilization.

The experimental cell consisted of two concentric cylindrical platinum electrodes with teflon insulation and teflon thread used for sealing the screw joints. The volume of test liquid required was 6 ml and this was added by means of a suitable pipette. Temperature control to less than ± 0.1° was achieved by pumping water (or ethyl alcohol at 0°) from a thermostatically controlled bath (*Haake*, Type R20, which had been additionally cooled by a refrigerator unit, *Lauda*, Type TK-30D) through an outer brass jacket on the cell. Accurate thermometers were inserted in the inlet and outlet tubes to this jacket. Their readings agreed to less than 0.1° and it was found that their mean temperature could be taken to be that of the test liquid.

For the measurements of capacity and conductance a *Wayne Kerr* type B201 transformer ratio-arm bridge was used in conjunction with a *Hewlett-Packard* type 651B test oscillator as source and a *Rhode* and *Schwarz* type USVH selective microvoltmeter as detector. This system was found to be accurate in the range 200 KHz to 10 MHz, and the effects of stray inductance and capacity were reduced as far as possible by standardizing the cell with liquids of known dielectric properties (of the same order of magnitude as those of the test liquid).

The capacity C (farads) and conductance G (mhos) measured at a particular frequency and temperature may be expressed in the form

$$C = C_0 + \varepsilon' \varepsilon_0 K \tag{1}$$

and

$$G = \varkappa K \tag{2}$$

where ε' is the relative permittivity of the test liquid and $\varkappa$ its conductivity (Ω^{-1} cm^{-1}), ε_0 is the permittivity of free space (F cm^{-1}), C_0(F) the 'empty' capacity of the cell and K(cm) a cell constant. To standardise the cell and determine C_0 and K, benzene ($\varepsilon_{20°} = 2.284$), ethanol ($\varepsilon_{20°} = 25.07$) and methanol ($\varepsilon_{20°} = 33.6$) were used. From these measurements, ε' could generally be determined to less than 1%. The measured conductance G included contributions from ionic conductivity and dielectric loss. The ionic conductivity contribution could be estimated by making measurements below the frequency at which dielectric dispersion commenced. After subtracting this part of the conductivity, the dielectric loss ε'' could then be deduced, but the estimated error ($\sim$5%) was considerably greater than for ε'.

Supplementary measurements of molecular weight were made in a *Beckman* Model E analytical ultracentrifuge using *Schlieren* and *Rayleigh* interference optics. Partial specific volumes were determined with a digital density measuring device DMA 02 A (*Anton Paar KG*, Graz, Austria).

The DC conductivity at low concentrations ($\lesssim 10^{-4}$M) was measured by means of a *Keithley* electrometer, type 602 for the range $7.10^{-15} \leq \varkappa \leq 10^{-11}$ ohm^{-1} cm^{-1}; above 10^{-11} ohm^{-1} cm^{-1} a *Wayne Kerr* bridge, type B221 was employed with a constant frequency of 1592 Hz. A thermostatable cyclindrical metal cell with gold plated electrodes (type DFL 2 from *WTW*, Weilheim, Germany, cell constant $2.20.10^{-3}$ cm^{-1}) was used at 20°.

The viscosity of the solution was measured by means of a KPG-*Ubbelohde* viscometer at 20°.

Results and Discussion. – Various amounts of water were solubilized in a one molar solution of aerosol AY in benzene (*i.e.* a ~M/15 solution of micelles, since the aggregation number is known to be approximately 15 from the ultracentrifuge measurements mentioned below and from previous work [9]) and the corresponding permittivity values ε' observed at frequencies between 200 KHz and 10 MHz and at 20° are shown in Fig. 1. Above ~6.5% by volume of water added, the values of both ε' and the conductivity $\varkappa$ become unstable and $\varkappa$ increases very rapidly with increasing water content. At one fixed water concentration (5.4% or approximately three water molecules per aerosol AY monomer) the dielectric dispersion was observed at temperatures from 0° to 30° (Fig. 2). These curves show the typical temperature variation for a *Debye* type dispersion. In this case the dielectric loss ε'' has also been estimated by subtracting the low frequency ionic conductivity from the total observed conductivity and converting this difference to a loss factor ε''. It is shown plotted against ε' on a *Cole-Cole* diagram in Fig. 2a. Skewed arcs are obtained indicating an unsymmetrical distribution of relaxation times, which can be represented by the empirical *Cole-Davidson* equation for the complex permittivity

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + j\,\omega\,\tau)^\beta} \tag{3}$$

where ε_s is the static permittivity, ω the angular frequency, τ a mean relaxation time, β a spread parameter, and ε_∞, the permittivity of the solution at very high frequencies ($\varepsilon_\infty \simeq n^2$, the square of the refractive index for the solution, and since this is only slightly less than that of benzene, ε_∞ has been taken to be equal to the permittivity of benzene; thus $\varepsilon_\infty = 2.28$ at 20°). A least squares fit of the experimental values of ε' at each temperature to Eq. (3) gives the following values of the parameters (see Tables 1 and 2), corresponding to Fig. 1 and 2. The fitted and measured values of ε' agree in most cases to within the experimental error (~1%); ($\varepsilon_s - \varepsilon_\infty$) is considered to be accurate to ±2%, but the values for β and τ are less accurately determined and could have estimated errors of up to ±20%.

The dielectric dispersion in the pure micelle solutions (*i.e.* with no water added) has previously been treated as an orientation phenomenon [11], *i.e.* the micellar dipoles (~15 D) re-orientate in the applied field. The addition of water is now assumed to increase the dipole moment μ of the rotating micelles and thus cause considerably greater dielectric increments. An estimate of the size of the increased dipole moment is difficult, however, since association phenomena now occur.

From the low values of the spread parameter β in Tables 1 and 2 ($\beta = 1$ for a single *Debye* dispersion) it is seen that there is a wide distribution of relaxation times in all cases, due no doubt to aggregation and deviations from spherical form [11]. It also appears from Table 1 that the solubilization of water within the micelle first decreases the relaxation time and then with increasing quantities of water it stays approximately constant at this lower value. By diluting the water solubilized micellar

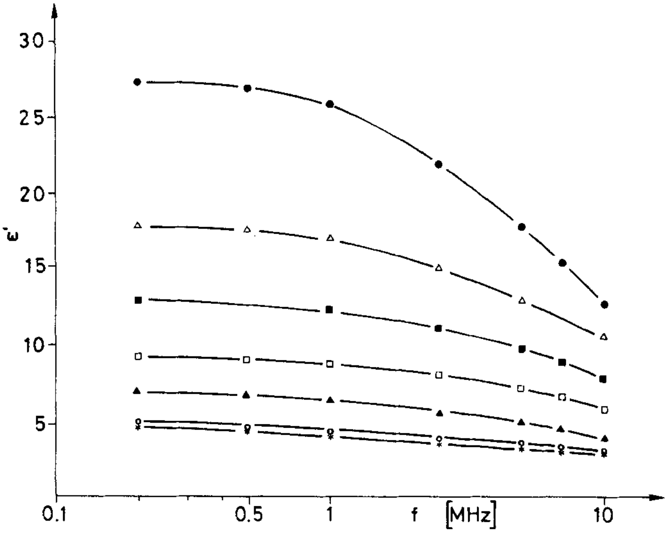


Fig. 1. *Relative permittivity ε' of a 1* M *aerosol AY solution in which the following volumes (%) of water have been solubilized*: ∗ 0; ○ 1.8; ▲ 2.7; □ 3.6; ■ 4.5; △ 5.4; ● 6.3

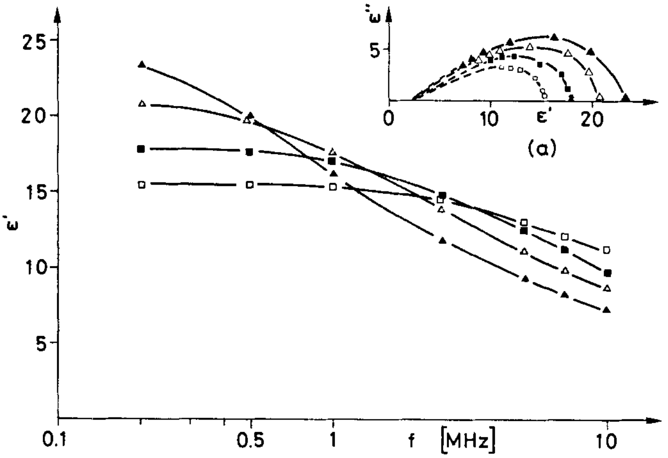


Fig. 2. *Variation of relative permittivity ε' with temperature for 1* M *aerosol AY solution with 5.4% of added water*: □ 30°; ■ 20°; △ 10°; ▲ 0°. At (a) the dielectric loss ε'' is shown plotted against ε'

Table 1. *Dielectric parameters for 1* M *aerosol AY solution with varying amounts of solubilized water* (20°; $\varepsilon_\infty = 2.28$)

Vol. % H_2O	$\varepsilon_s - \varepsilon_\infty$	τ in 10^{-8} s	β
0	2.6	38	0.33
1.8	2.9	37	0.29
2.7	4.6	8.1	0.43
3.6	6.9	6.3	0.35
4.5	10.7	6.3	0.35
5.4	15.6	7.8	0.32
6.3	25.1	6.4	0.45

Table 2. *Variation of dielectric parameters with temperature for 1* M *aerosol AY solution with 5.4% of solubilized water*

Temp. (°C)	$\varepsilon_S - \varepsilon_\infty$	τ in 10^{-8} s	β
0	22.2	36	0.39
10	18.6	16	0.37
20	15.6	7.8	0.32
30	13.3	5.0	0.27

solution, the CMC of the 'hydrated' micelle can be determined by conductivity measurements (Fig. 3). Since this CMC value is shifted by approximately one order of magnitude to a lower weighed-in aerosol AY concentration ($\sim 3.10^{-5}$ M) compared with the value ($\sim 4.10^{-4}$ M) for the unsolubilized micellar solution, the water appears to stabilize the micelle. If this process corresponds to a denser packing of the monomers in the hydrated micelle it seems reasonable to assume that this polar unit can then be orientated more easily by the applied field, in agreement with the above findings.

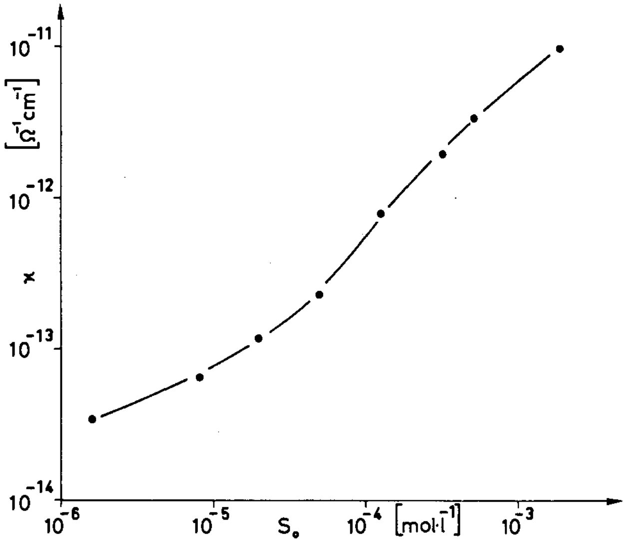


Fig. 3. *Conductivity $\varkappa$ of the solubilized aerosol AY solution at low weighed-in concentrations s_0 and with an average of 3 water molecules per aerosol AY monomer (20°)*

Considering the hydrated micelle to be a sphere as a first approximation and using *Debye*'s equation for the molecular relaxation time

$$\tau = \frac{4\pi\eta a^3}{kT} \tag{4}$$

a radius (a) of $\sim$15 Å is obtained (k is *Boltzmann*'s constant and T the absolute temperature), if η is the measured viscosity of the solution with 5.4% water added ($\sim$7.4 centipoise at 20°) and τ to be $7.8.10^{-8}$ s from Table 1. Allowing for an estimated error of ±20% in τ, this value agrees to a reasonable approximation with the radii (~12.4 Å and ~15 Å) deduced at lower hydrated micelle concentrations from the measured partial specific volume and diffusion coefficient, respectively; and with that to be expected (~15 Å) from geometrical considerations in a molecular model for the unhydrated micelle (shown in Fig. 4). Thus the mechanism of re-orientation of the micellar dipole in the field to account for the dielectric increments observed with water added seems to be confirmed.

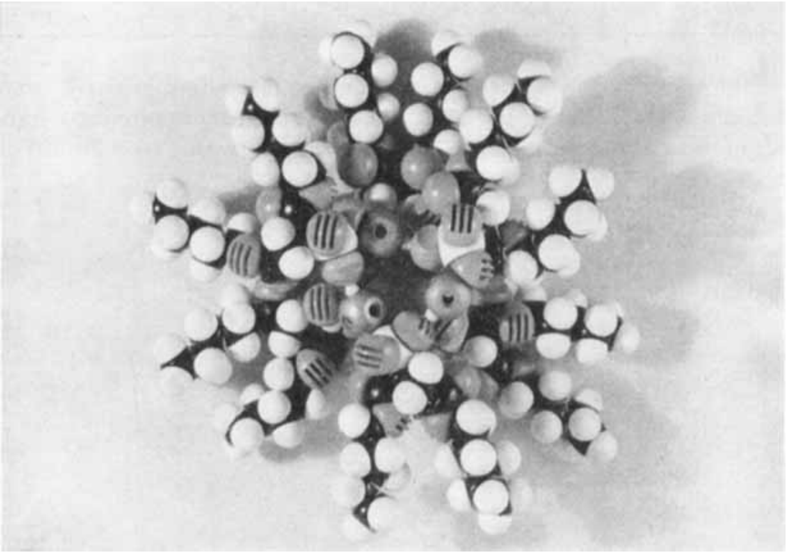


Fig. 4. *Suggested molecular model for an aerosol AY micelle in benzene.* Two of the five trimeric sub-units normally found in such a micelle are shown, stacked parallel to each other with the micelle axis perpendicular to the plane of the picture. From the axis to the tip of an apolar tail is ~15 Å and the thickness of each sub-unit is ~5 Å

Although for most highly polar liquids ($\varepsilon_s - \varepsilon_\infty$) is inversely proportional to T, it is seen from Table 2 that the product ($\varepsilon_s - \varepsilon_\infty$) T is not constant, it being 6060 at 0° and 4030 at 30°. This indicates some association of the rotating dipolar micelles, the degree of association varying with temperature. Since β decreases with increasing temperature, the micellar aggregates seem to be more monodisperse at lower temperature.

Considering now the static permittivity ε_s of the micellar solution (which at 20° may be taken to be the value of ε' at 200 KHz) the variation of ε_s with increasing water content is seen in Fig. 5. In this figure the effect of solubilizing aqueous electrolyte (1 M NaCl, KCl, CsCl, $MgCl_2$, and $CrCl_3$) in the micelle is also shown. (Once again the value of ε' at 200 KHz has been checked to be approximately equal to ε_s in each case.) The graphs demonstrate a considerable shifting of the steep parts of the curves corresponding to different electrolytes approximately in the order of increasing charge of the cations. In the case of $CrCl_3$ this correlation evidently does not hold. This might be due to the limitations in the space available for the solubilized (hydrated) electrolyte imposed by the stability requirements of the hydrated micelle. The shifting reflects the increasing amount of water which is attached to the ions and, therefore, evidently not responsible for the increase of the dielectric increment. This latter effect is thought to be due to an interaction between the 'free' water and the constituent monomers of the micelle. (To illustrate one particular case from Fig. 5, a dielectric increment of ~25 is produced by adding 0.4 ml of water to 6 ml of micelle solution, but requires a much larger quantity ~1.3 ml of $MgCl_2$ solution. Thus it can be shown that the ions from each $MgCl_2$ molecule have immobilized an average of ~33 water molecules.) In all cases there is a limiting amount of added liquid which can be solubilized before the conductivity increases sharply and ε_S becomes unstable (in the sense that it slowly changes with time over a long period).

The effect of diluting a micelle solution containing a constant amount of solubilized water per micelle is shown in Fig. 6a. In contrast to a pure 1 M aerosol AY-solution, which shows a linear increase of dielectric increment with concentration, non-linear increases are found for two different proportions of water.

To account for these non-linear variations of dielectric increment with water content (Fig. 5) and with solution concentration (Fig. 6a), the following quantitative treatment based on the assumption of 'ideal' behaviour of the investigated system is suggested as a working hypothesis. From the experiments it appears that all the water or aqueous electrolyte is solubilized in the micellar phase. Now it is assumed that a part of this water reacts with the aerosol AY micelle to form a hydrated micelle with a larger dipole moment. Thus

$$(H_2O)_{\alpha z} + S_m \underset{}{\overset{K}{\rightleftharpoons}} S_m(H_2O)_{\alpha z} \qquad (5)$$

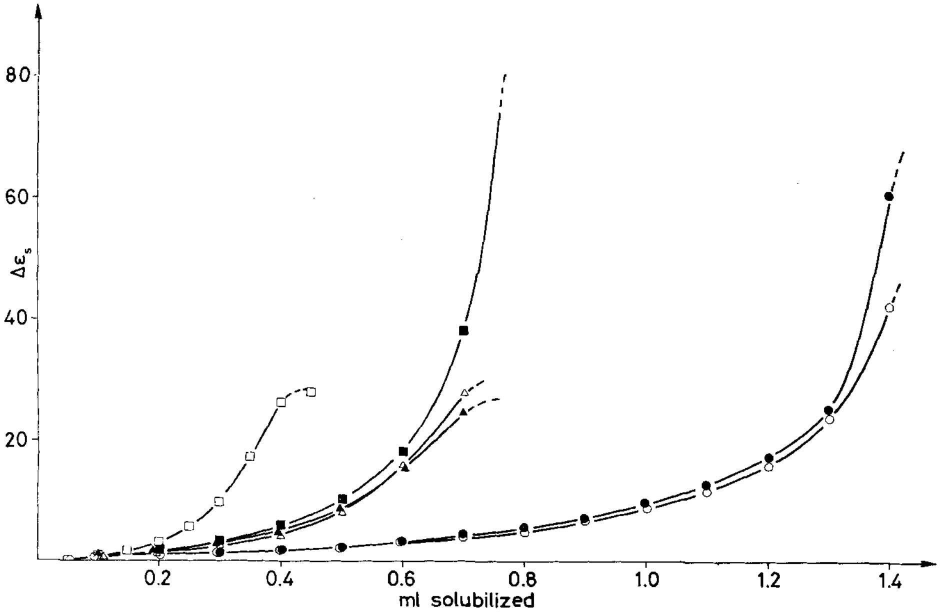
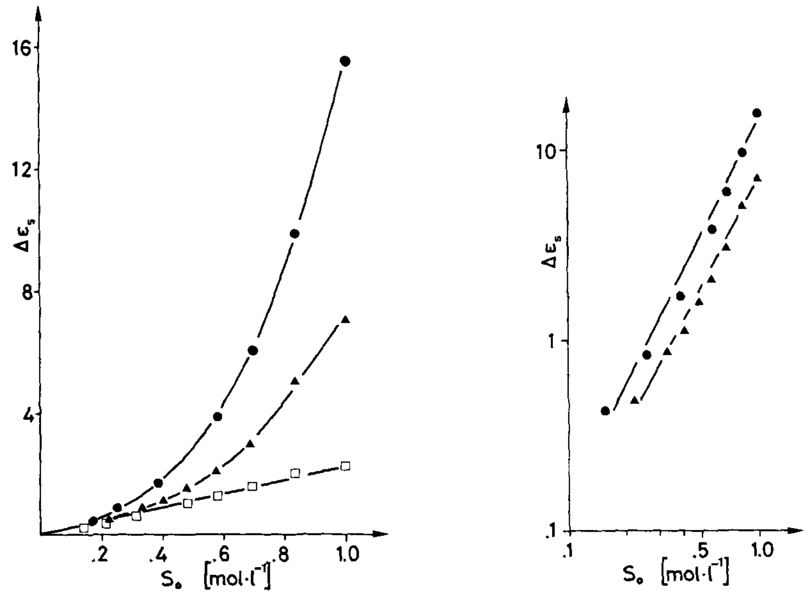


Fig. 5. *Variation of static dielectric increment $\Delta\varepsilon_S$ with volume of liquid solubilized in 6 ml of 1 M aerosol AY solution*: □ H_2O; △ 1 M NaCl; ▲ 1 M KCl; ■ 1 M CsCl; ● 1 M $MgCl_2$; ○ 1 M $CrCl_3$



(a) (b)

Fig. 6. *The curves* (a) *show the static dielectric increment* $\Delta\varepsilon_s$ *produced by various weighed-in concentrations* s_0 *of aerosol AY in benzene*: □ with no water; △ and ● with an average of two and three water molecules, respectively, per aerosol AY molecule. At (b) the variation of $\Delta\varepsilon_s$ with s_0 for these two different water concentrations is shown plotted on a log-log scale

where $(H_2O)_{\alpha z}$ is a fraction of the total water content (imagined to be aggregated with respect to the apolar environment) supplied by the hydrated electrolyte which is available for this reaction and z is the total number of water molecules (determined by the individual ions) which is solubilized by the micelle; S_m is an aerosol AY micelle and $S_m(H_2O)_{\alpha z}$ the hydrated micelle. Applying the mass action law to Eq. (5) one obtains for the equilibrium constant K

$$K = \frac{[S_m(H_2O)_{\alpha z}]}{[(H_2O)_{\alpha z}]\,[S_m]}. \tag{6}$$

The increase of the dipole moment of the hydrated micelle with the weighed-in water concentration (or aqueous electrolyte) is thought to lead to an aggregation of these micelles such as expressed by

$$n\, S_m(H_2O)_{\alpha z} \xrightleftharpoons{K'} (S_m(H_2O)_{\alpha z})_n \tag{7}$$

n being the aggregation number of the micelles and K' the association constant. The concentration of the associated micelles is expressed with the help of the mass action law

$$[(S_m(H_2O)_{\alpha z})_n] = K'[S_m(H_2O)_{\alpha z}]^n \tag{8}$$

which in turn is related to the equilibrium concentration of the 'normal' aerosol AY micelles and the available water $(H_2O)_{\alpha z}$ by

$$[(S_m(H_2O)_{\alpha z})_n] = K'K^n[S_m]^n\,[(H_2O)_{\alpha z}]^n. \tag{9}$$

The corresponding relations with respect to the weighed-in concentrations are derived with the help of the conservation of mass. Thus, the weighed-in concentration of water molecules which could participate in the reaction according to Eq. (5) is given by

$$\alpha[H_2O]_o = \alpha z[S_m(H_2O)_{\alpha z}] + \alpha z n[(S_m(H_2O)_{\alpha z})_n] + \alpha z[(H_2O)_{\alpha z}] \qquad (10)$$

(neglecting the minute amount of water soluble in benzene) or

$$\alpha[H_2O]_o = \alpha z[(H_2O)_{\alpha z}]\,\{1 + K[S_m]\,(1 + n\,K'K^{n-1}[S_m]^{n-1}[(H_2O)_{\alpha z}]^{n-1})\}. \qquad (10a)$$

Two limiting cases of Eq. (10a) have to be discussed with respect to the reaction equilibrium (Eq. (5)) corresponding to the two conditions

$$\left.\begin{array}{ll}(1) & 1 \gg \\ (2) & 1 \ll\end{array}\right\}\ K[S_m]\,(1 + n\,K'K^{n-1}[S_m]^{n-1}[(H_2O)_{\alpha z}]^{n-1}) \qquad (10b)$$

yielding

$$[H_2O]_o \cong z[(H_2O)_{\alpha z}] \qquad (10c)$$

or

$$\cong n z\,K'K^n[S_m]^n[(H_2O)_{\alpha z}]^n \qquad (10d)$$

(to a further approximation), respectively.

The corresponding relation for the weighed-in concentration of aerosol AY reads

$$s_o = [S] + m[S_m(H_2O)_{\alpha z}] + m[S_m] + nm[(S_m(H_2O)_{\alpha z})_n] \qquad (11)$$

$$= m[S_m]\,\{1 + K[(H_2O)_{\alpha z}]\,(1 + n\,K'K^{n-1}[S_m]^{n-1}[(H_2O)_{\alpha z}]^{n-1})\}, \qquad (11a)$$

where the concentration of monomeric surfactant molecules [S] was neglected since the interesting concentration region is about four orders of magnitude above the critical micelle concentration. As in Eq. (10b) two limiting cases have to be discussed, namely

$$\left.\begin{array}{ll}(1) & 1 \gg \\ (2) & 1 \ll\end{array}\right\}\ K[(H_2O)_{\alpha z}]\,(1 + n\,K'K^{n-1}[S_m]^{n-1}[(H_2O)_{\alpha z}]^{n-1}) \qquad (11b)$$

giving

$$s_o \cong m[S_m] \qquad (11c)$$

or

$$\cong n\,m\,K'K^n[S_m]^n[(H_2O)_{\alpha z}]^n \qquad (11d)$$

(with the same approximation as in Eq. (10d)), respectively.

The experimental results from Fig. 5 and 6a give linear log-log plots of $\Delta\varepsilon_s$ against s_o and $[H_2O]_o$ (see Fig. 7 and 6b, respectively) with a slope of approximately 2 in most cases. Thus a decision can be made in favour of the first limiting case in Eq. (10b) and (11b), since by taking the second alternatives, $[(S_m(H_2O)_{\alpha z})_n]$ can be shown from Eq. (9) to be proportional to $[H_2O]_o$ or s_o respectively, and this would result in a slope of 1 in these plots. On the other hand, by taking the first alternative, it follows from Eq. (9) that

$$[(S_m(H_2O)_{\alpha z})_n] = K'K^n \left\{\frac{s_o}{m}\right\}^n \left\{\frac{[H_2O]_o}{z}\right\}^n. \qquad (12)$$

Now it can be shown from *Kirkwood*'s theory [12] that at constant temperature the dielectric increment produced by highly polar orienting units in a solution is approximately proportional to the product of their concentration and the square of their dipole moment. Thus in the frame of this treatment

$$\Delta \varepsilon_{\mathrm{S}} \approx \mathrm{n}^2 \mu^2 K' K^{\mathrm{n}} \left\{\frac{\mathrm{s}_0}{\mathrm{m}}\right\}^{\mathrm{n}} \left\{\frac{[\mathrm{H_2O}]_0}{\mathrm{z}}\right\}^{\mathrm{n}} \qquad (13)$$

if it is assumed that the micellar dipoles μ are aligned in the aggregates $(\mathrm{S_m(H_2O)_{\alpha z}})_{\mathrm{n}}$, producing a total dipole $\mathrm{n}\mu$, and that the contribution of the single micelles is neglected in this first approximation.

According to Eq. (13) $\Delta\varepsilon_{\mathrm{S}}$ is seen to depend also on the total number of water molecules added with the electrolyte. The larger the value of z, the higher the weighed-in water concentration necessary to produce a certain dielectric increment. This is precisely the behaviour which is experimentally observed (see Fig. 5). In addition, from Eq. (13) the aggregation number n of the micellar association process can be determined since

$$\left(\frac{\partial \log \Delta \varepsilon_{\mathrm{S}}}{\partial \log \mathrm{s}_0}\right)_{(\mathrm{H_2O}]_0 = \text{ const.}} = \left(\frac{\partial \log \Delta \varepsilon_{\mathrm{S}}}{\partial \log [\mathrm{H_2O}]_0}\right)_{\mathrm{s}_0 = \text{ const.}} \cong \mathrm{n} \qquad (13\mathrm{a})$$

as is experimentally verified (Fig. 6b and 7). The numerical value of n is approximately equal to 2 for water. For the electrolyte solutions n approaches 2 in all cases except for $\mathrm{MgCl_2}$ and $\mathrm{CrCl_3}$, where variations are found, probably due to the higher charges of the cations.

A preliminary investigation by sedimentation-diffusion and conventional equilibrium methods carried out at 25°, indicated an apparent weight-average molecular weight of approximately 6000 for a micelle without water and approximately 6500 for a hydrated micelle with ~3 water molecules per aerosol AY monomer, both values as measured in the low concentration solution (0.01 M). These values agree well with the number average molecular weight corresponding to an aggregation number of approximately 15 as previously determined [9]. This agreement between number and weight averages of molecular weight again indicates a narrow distribution of micelle sizes.

By increasing the concentration of the solution it became quite clear that, whereas the apparent molecular weight of the micelles without water did not increase, the hydrated micelles aggregated and an apparent molecular weight of approximately 13,000 was reached at a solution concentration of 0.1 M. This result roughly confirms the formation of dimeric micelles. The effects of non-ideality, however, necessitate further work before the average molecular weight at higher concentrations can be deduced.

Fig. 8 shows the experimentally observed quasi-sudden increase in conductivity $\varkappa$ as more water is added (the curves for 1 M NaCl and 1 M CsCl closely follow that shown for 1 M KCl and the curve for 1 M $\mathrm{CrCl_3}$ is approximately the same as that for 1 M $\mathrm{MgCl_2}$). Now, to account for these changes of the conductivity $\varkappa$ with the weighed-in water concentration, it is hypothetically assumed that the sudden increase of $\varkappa$ is due to a change of the conformation of the aggregated (dimeric) aerosol AY micelles

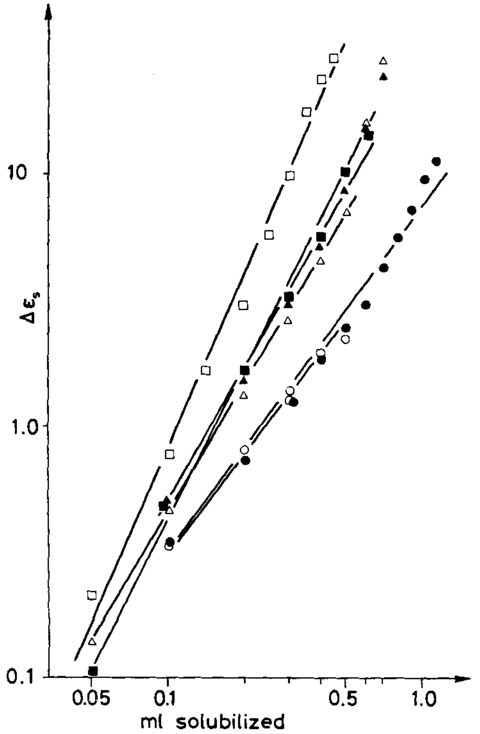


Fig. 7. *Variation of static dielectric increment $\Delta\varepsilon_S$ with volume of solubilized liquid as plotted on a log-log scale.* □ H_2O; △ 1 M NaCl; ▲ 1 M KCl; ■ 1 M CsCl; ○ 1 M $CrCl_3$

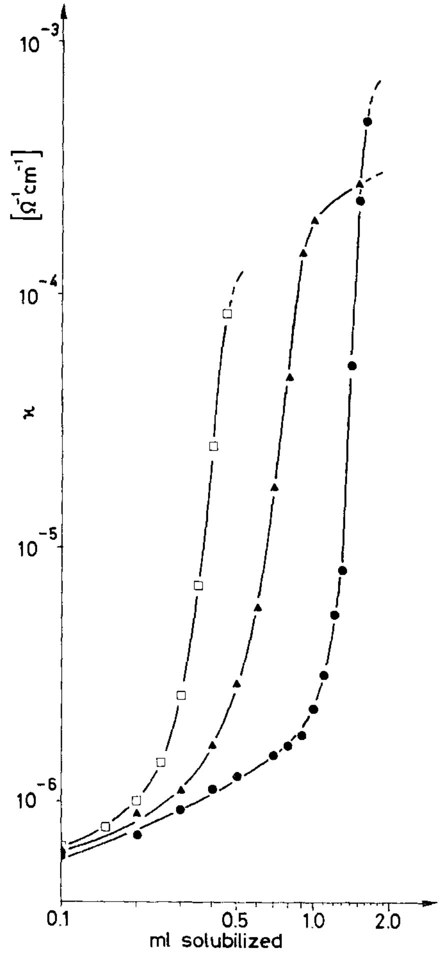


Fig. 8. *Variation of conductivity $\varkappa$ of* 1 M *aerosol AY solution with volume of solubilized liquid* (both axes on a logarithmic scale). □ H_2O; ▲ 1 M KCl; ● 1 M $MgCl_2$

analogous to the change from monomers to micelles. Thus above a certain degree of hydration a new micellar aggregate is thought to be formed by the hydrated monomers.

Starting from these aggregated hydrated micelles, which are assumed to have already formed in the region of weighed-in water concentration where the quasi-sudden increase of $\varkappa$ appears, one could formulate the new association process with respect to hydrated aerosol AY monomers by the following equation

$$\frac{r}{mn}\,(S_m(H_2O)_{\alpha z})_n \overset{K''}{\rightleftharpoons} \frac{1}{m}\,(S_m(H_2O)_{\alpha z})_r, \qquad (14)$$

where r is the corresponding association number. Application of the mass action law yields for the association constant

$$K'' = \frac{[(\mathrm{S_m(H_2O)_{\alpha z})_r}]^{1/\mathrm{m}}}{[(\mathrm{S_m(H_2O)_{\alpha z})_n}]^{\mathrm{r/nm}}} \text{ or}$$

$$[(\mathrm{S_m(H_2O)_{\alpha z})_r}] = (K'')^{\mathrm{m}}[(\mathrm{S_m(H_2O)_{\alpha z})_n}]^{\mathrm{r/n}}. \tag{15}$$

For the charge production (by monomer exchange) it is assumed that

$$\frac{2}{\mathrm{m\,r}}\,(\mathrm{S_m(H_2O)_{\alpha z})_r} \overset{K^*}{\rightleftharpoons} \frac{1}{\mathrm{m\,r}}\,(\mathrm{S_m(H_2O)_{\alpha z})_r}^{\oplus} + \frac{1}{\mathrm{m\,r}}\,(\mathrm{S_m(H_2O)_{\alpha z})_r}^{\ominus}. \tag{16}$$

Thus from the electroneutrality and the mass action law (considering, *e.g.*, the positively charged micelles)

$$[(\mathrm{S_m(H_2O)_{\alpha z})_r}^{\oplus}] = (K^*)^{\mathrm{mr/2}}[(\mathrm{S_m(H_2O)_{\alpha z})_r}], \tag{17}$$

where K^* is the corresponding dissociation constant. Substituting from Eq. (15) in the last equation

$$[(\mathrm{S_m(H_2O)_{\alpha z})_r}^{\oplus}] = (K^*)^{\mathrm{mr/2}}(K'')^{\mathrm{m}}[(\mathrm{S_m(H_2O)_{\alpha z})_n}]^{\mathrm{r/n}}. \tag{18}$$

To show that the conductivity may increase with a quasi-jump above a certain weighed-in water concentration, the ratio of the ionic concentration to that of the original aggregated (hydrated) micelles is formed. Taking the concentration of aggregated hydrated micelles to be still given approximately by Eq. (12), it follows that Eq. (18) may be expressed in the form

$$\frac{[(\mathrm{S_m(H_2O)_{\alpha z})_r}^{\oplus}]}{[(\mathrm{S_m(H_2O)_{\alpha z})_n}]} = \left\{\frac{[\mathrm{H_2O}]_0}{\mathrm{CMC}}\right\}^{\mathrm{r-n}} \tag{19}$$

where the CMC is thought to be a 'critical micelle concentration' expressed by

$$\mathrm{CMC} = \left\{\frac{\mathrm{z^{r-n}}}{(K^*)^{\frac{\mathrm{mr}}{2}}\,(K'')^{\mathrm{m}}(K')^{\frac{\mathrm{r-n}}{\mathrm{n}}}\,K^{\mathrm{r-n}}\left\{\frac{\mathrm{s_0}}{\mathrm{m}}\right\}^{\mathrm{r-n}}}\right\}^{1/(\mathrm{r-n})} \tag{20}$$

The corresponding conductivity now yields

$$\varkappa = \frac{2\bar{\mathrm{u}}\,\mathrm{F}}{10^3}\,(K^*)^{\mathrm{mr/2}}\,(K'')^{\mathrm{m}}\,(K')^{\mathrm{r/n}}\,K^{\mathrm{r}}\left\{\frac{\mathrm{s_0}}{\mathrm{m}}\right\}^{\mathrm{r}}\left\{\frac{[\mathrm{H_2O}]_0}{\mathrm{z}}\right\}^{\mathrm{r}}\,(\Omega^{-1}\,\mathrm{cm^{-1}})\,, \tag{21}$$

$\bar{\mathrm{u}}$ being the mean mobility of the positively or negatively charged micelles respectively, and F the *Faraday* constant.

From this expression for $\varkappa$ it is learned that the curves are shifted along the weighed-in water concentration scale according to the value of z.

This behaviour is shown by the experimental curves (see Fig. 8), in which the logarithm of the specific conductivity is plotted against the logarithm of the amount of solubilized aqueous electrolyte. Such a plot also permits one to determine the mean aggregation number r of the new micelles, since from Eq. (21)

$$\left(\frac{\partial \log \varkappa}{\partial \log [\mathrm{H_2O}]_0}\right)_{\mathrm{s_0\,=\,const}} = \mathrm{r}\,. \tag{22}$$

Comparing these aggregation numbers as determined by a conductivity method with values obtained by other methods, one should keep in mind that a considerable ion pair formation is to be expected in these apolar solvents and this would lead to a less steep increase of the specific conductivity.

These experiments could be considered as a first step in the investigation of larger three dimensional structures (such as membranes). A concentration has been taken, therefore, in which the hydrated micelles are interacting with each other, but still in a range where the benzene can be considered as solvent for the aerosol AY.

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213. Recherches dans la série des cyclitols XLV. Action des diazoalcanes sur la pentahydroxy-2,4,6/3,5-cyclohexanone et sur son dérivé penta-O-acétylé. I. Etude des spiro-époxydes[1][2]

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Summary. On treatment with diazomethane, 2,4,6/3,5-penta-acetoxy-cyclohexanone (penta-O-acetyl-*myo*-inosose-2 or -*scyllo*-inosose) gave only a spiroepoxide. In contrast, replacement of diazomethane by higher diazoalkanes furnished a mixture of alkylspiroepoxides and of ring expansion products (cycloheptanone derivatives). The configuration and the reactions of the spiro-epoxides have been studied.

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[1] Toutes les substances chirales sont sous forme racémique; on a supprimé dans le texte les désignations (±) ou DL.

[2] Une grande partie de ce travail avait été exécutée par *A. Giddey* en 1953–1955.

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