Dielectric Studies on Colloidal Solutions. I. High-frequency Conductivity of Aqueous Solutions of Paraffin-chain Salts

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It is a well-known fact that the equivalent electrical conductivity of aqueous solutions of the various types of paraffin-chain salts shows a sudden fall when the concentration is increased beyond a certain value corresponding to the micelle formation and then, after passing through a minimum point, it increases gradually with increasing concentration. This latter phenomenon was considered by McBain[1] to be due to the change in the dissociation state of the electrolyte contained in micelles. On the other hand, Hartley[2] pointed out that it should come out from the electrostatic interaction.

Some years ago, Schmid and Larsen[3] measured the electrical conductivity of aqueous solutions of some paraffin-chain salts at frequencies of 15 and 25 Mc./sec. by means of Deubner's method[4], and found that the high-frequency effect showed itself at the concentration corresponding to the sudden fall of the equivalent low frequency conductivity. Recently, the authors have investigated the high-frequency conductivities of sodium dodecyl sulphate, sodium oleate, and dodecyl amine hydrochloride at frequencies of 15 and 30 Mc./sec. by means of the resonance method over a wider range of concentration. Our experimental method and result may be useful for further discussion of the problem of micelle structures.

Experimental

Method of measurement. — The method of measurement lies in the determination of the

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[1] J.W. McBain and M.D. Betz, *J. Am. Chem. Soc.*, 57, 1905 (1935).

[2] G.S. Hartley, ibid., 58, 2347 (1936).

[3] G. Schmid and E.C. Larsen, *Z. Elektrochem.*, 44, 651 (1938).

[4] A. Deubner, *Physik. Z.*, 30, 946 (1929).

width of the resonance curve of a resonant circuit coupled to a high-frequency oscillator[5]. The stabilized oscillator supplies a high-frequency wave of constant amplitude and of fixed frequency to a resonator, to which is connected a valve voltmeter. The block diagram of the whole apparatus is indicated in Fig. 1.

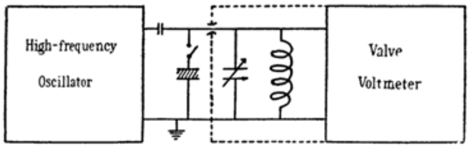

Fig. 1. Block-diagram of the apparatus.

The resonator consists of a parallel plate condenser containing the test liquid parallel to a variable condenser across an inductance. This variable condenser is an eccentric cylindrical one adjusted by a micrometer. The condenser containing the test liquid is immersed in a thermostatically controlled bath. Each part is screened in a metal box. The coupling of the resonator to the oscillator is so loose as to eliminate any pulling of the oscillator by the resonator. The high-frequency voltage of the resonator tuned to the oscillator is measured by the valve voltmeter. The circuit of the valve voltmeter is indicated in Fig. 2. The sensitivity of the galvanometer used is 2.8×10^{-9} amp./mm., and its deflection must be proportional to the square of the input voltage. This can be done by adjusting the grid bias of the valve.

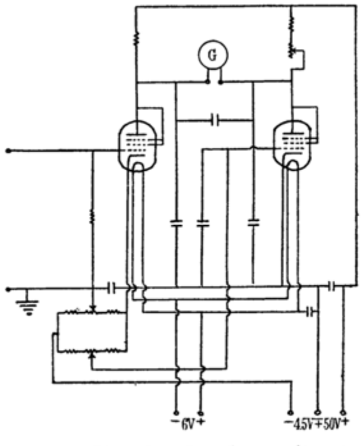

Fig. 2. Circuit of valve voltmeter.

Thus, the shape of the resonance curve for various test liquids placed in the parallel plate condenser is determined. The conductance of the resonator, G, is determined by the following formula[5]:

$$G=\frac{\omega(C-C_R)}{\sqrt{\left(\frac{V_R}{V}\right)^2-1}},$$

where, ω =frequency at which measurement is made.
V_R=voltage at resonance.
C_R=capacitance at resonance.
V =voltage at any other point.
C =capacitance at any other point.

In the manner stated above, the conductances of the resonator both with and without the test liquid in the parallel plate condenser can be determined, the difference of those being the conductance of the test liquid. In order to obtain specific conductivities from these conductances, we need a "cell constant". This can be determined by making use of the aqueous solution of potassium chloride as the standard. The whole operation is repeated for a series of concentrations at each frequency-setting of the oscillator. The probable error of the measurement of conductance at each frequency is ±0.2%.

Materials. — Sodium dodecyl sulphate was a "pure" sample prepared at Nezu Chemical Laboratory, Tokyo.

Oleic acid was purified from a commercial sample by vacuum distillation. Sodium oleate was prepared by neutralizing pure oleic acid with sodium hydroxide.

Dodecyl amine hydrochloride was obtained by neutralizing dedecyl amine which came from Armour and Co., U.S.A. with hydrochloric acid, which was then recrystallized.

The dissolution and dilution of these substances were made with distilled water free from carbon dioxide and thus solutions of various concentrations were obtained.

Results and Discussion

In Tables I—III and in Figs. 3—5, the high-frequency effects of the three substances under investigation are indicated. Here the high-frequency effect is expressed by

$$H=100\frac{(\Lambda_h-\Lambda_l)}{\Lambda_l},$$

where Λ_l is the low-frequency equivalent conductivity and Λ_h is the high-frequency equivalent conductivity. Λ_l was measured at 700 c./sec. In Figs. 3—5, the low-frequency equivalent conductivity is also shown for comparison.

TABLE I

SODIUM DODECYL SULPHATE

Temp. 25°C

Concentration mol./1.	Equivalent conductivity 700c./sec.	High-frequency Effect	
		30Mc./sec.	15Mc./sec.
0.0025	79	0	0
0.005	76	0	0
0.008	71	0	0
0.01	60	1.1	0
0.015	46	2.4	0.8
0.025	37	2,5	0.3
0.05	29	2.0	0

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[5] Report of the Sub-Committee of Japan Society for the Promotion of Scientific Research, *J. I. E. E. Japan*, 59, 519 (1939).

TABLE II

SODIUM OLEATE

Temp. 25°C

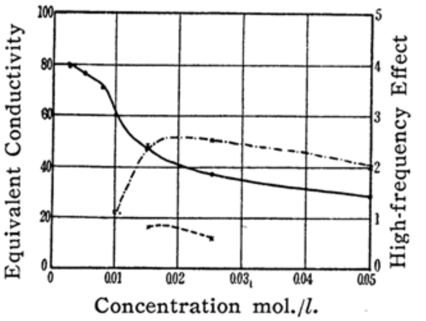
Concentration mol./l.	Equivalent conductivity 700c./sec.	High-frequency Effect	
		30 Mc./sec.	15 Mc./sec.
0.005	52	4.1	1.8
0.0075	42	5.0	2.0
0.01	39	4.5	1.7
0.015	37	3.2	1.3
0.02	34	2.5	1.1
0.025	33	2.2	1.0

TABLE III

DODECYL AMINE HYDROCHLORIDE

Temp. 25°C

Concentration mol./l.	Equivalent conductivity 700c./sec.	High-frequency Effect	
		15 Mc./sec.	30 Mc./sec.
0.0008	99	0	0
0.001	96	0.6	0.3
0.0015	85	2.0	1.5
0.0025	60	4.3	2.8
0.005	35	4.0	2.6
0.01	36	2.7	2.3
0.015	44	1.8	1.5



-·-·× 30 Mc./sec. } high-frequency effect.
---× 15 Mc./sec. }
——· 700c./sec. equivalent conductivity.

Fig. 3. Sodium dodecyl sulphate.

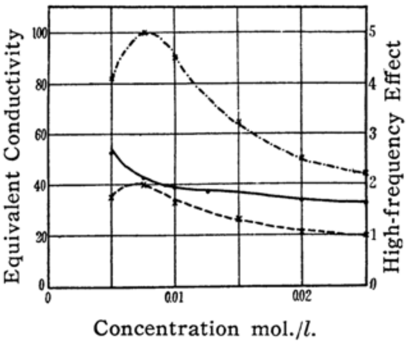


Fig. 4. Sodium oleate.

The Fig. 3 for sodium dodecyl sulphate shows that in the range of very low concentrations the high-frequency effect is very small. We were unable to confirm its existence. But with increasing concentration, the high-frequency effect becomes greater and arrives at its maximum at the concentration where the low frequency equivalent conductivity is decreasing. Then it shows a gradual decrease, but on account of the high conductance of the solution we could not make a measurement at very high concentrations.

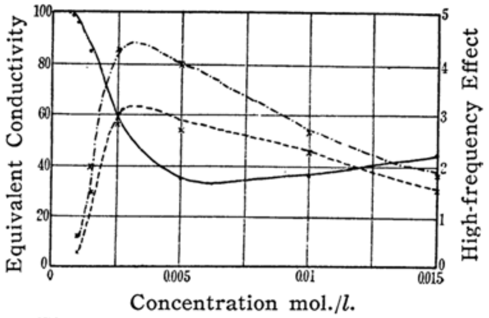


Fig. 5. Dodecyl amine hydrochloride.

The high-frequency effects of sodium oleate and sodium dodecyl amine hydrochloride show similar curves, as shown in Figs. 4 and 5.

The abnormally large values of the high-frequency effect of these solutions at the concentration corresponding to the micelle formation can be interpreted in terms of Debye-Falkenhagen's theory[6] of the dependence of the conductivity on frequency. Of course, the effect of the dielectric relaxation due to the orientation of molecules of the solvent and the solute must be considered, too. The critical frequency of the dielectric relaxation of the water molecule is about 1.5×10^4 Mc./sec., and that of the carboxyl group is about 3×10^3 Mc./sec.[7]. The critical frequencies of the sulphate group and the amino group have not been measured, but it is quite conceivable that they are nearly the same as that of the carboxyl group, considering that these polar groups have nearly the same dimensions. Thus, the critical frequencies of these groups are very high, and therefore the dielectric losses due to their orientation are negligible at frequencies of 15 and 30 Mc./sec., at which our measurement has been performed. Moreover, as molecules contained in a micelle may be rather in a liquid state of aggregation as is shown from the solvent properties of the micelle[8], the orientation of the micelle itself may not take place.

According to Debye-Falkenhagen's theory, the high-frequency effect incraeses with in-

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[6] P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928); *Z. Elektrochem.*, **34**, 562 (1928).

[7] T. J. Buchanan. *J. Chem. Phys.*, **22**, 578 (1954).

[8] cf. A.E. Alexander and P. Johnson, "Colloid Science", Oxford Press (1949), p. 685.

creasing valency of the electrolyte. Considering that ions in the solution under investigation join into a polyvalent ion on account of the formation of micelles, the high-frequency effect can be fairly great in the solutions under investigation, in spite of the loose structure of micelles. The critical fall of the low-frequency equivalent conductivity is probably due to this electrostatic interaction which comes into play with the formation of polyvalent micelle ions.

With further increasing concentration, the high-frequency effect shows a gradual decrease, as shown in Figs. 3—5. This decrease may be partly due to the shortening of the relaxation time of the ionic atmosphere with the increase of concentration, it being impossible to detect the effect at the frequency corresponding to the relaxation time at the applied frequency of 30 Mc./sec.. However, as shown in Fig. 5, there are cases where the low-frequency equivalent conductivity gradually increases with increasing concentration, and in order to account for the dependence of the low-frequency equivalent conductivity and that of the high-frequency effect on concentration consistently, we must conclude that the electrostatic interaction decreases as a whole with the concentration. Such reduction of the electrostatic interaction is presumably due to a loosening of counter ions due to the overlap of ionic atmospheres and consequently a change in the structure of micelles with increasing concentration.

Summary

The high-frequency conductivity of solutions of sodium dodecyl sulphate, sodium oleate, and dodecyl amine hydrochloride was measured at frequencies of 15 and 30 Mc./sec.. The high-frequency effect remarkably appeared at the concentration corresponding to the critical micelle concentration and the effect can be interpreted in terms of Debye-Falkenhagen's theory of strong electrolytes.

The appearance of maximum and gradual decrease in high-frequency effect may be explained by the shortening of the relaxation time or by the reduction of the electrostatic interaction due to the change of micelle structures with the increase of concentration.

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