Dielectric Studies on Colloidal Solutions. II. The Behavior of Small Counter Ions in the Aqueous Solutions of the Hydrochlorides of Homologous Long-chain Amines

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In the previous work¹⁾ of this series the high-frequency conductivity of aqueous solutions of paraffin-chain salts has been measured and the results have been interpreted in terms of the Debye-Falkenhagen's theory of strong electrolytes. The sudden rise of the high-frequency effect as well as the fall of the low-frequency equivalent conductivity of these solutions have been considered to be due to the electrostatic interaction between ionic micelles and small counter ions. It is, however, probable that some fraction of counter ions associate with the micelle, and consequently, the valence of the ionic micelle does not agree with the number of single ions contained in the micelle. The fraction of counter ions associated with the micelle has been estimated from the data of conductivity and transference number²,³⁾, from those of electro-

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1) M. Shirai and B. Tamamushi, This Bulletin, 28, 545 (1955).

2) G.S. Hartley, B. Collie and C. S. Samis, *Trans. Faraday Soc.*, 32, 785 (1936).

3) A.P. Brady and D.J. Salley, *J. Am. Chem. Soc.*, 70, 914 (1948).

motive force measurement[4], from those of self-diffusion coefficient[3], etc. Chandler and McBain[5] have recently estimated, based on the results of anomalous osmosis, that the effective charge on the micelle is only two or three, whereas Hartley and his collaborators[2] came to the conclusion that the micelles behave as polyvalent ions having a large number of effective charges.

In the present paper we discuss this problem on the basis of the experimental data of low-frequency and high-frequency conductivities, and those of transference number obtained for the hydrochlorides of homologous long-chain amines.

Experimental

Procedure.—The method and apparatus applied for the high-frequency conductivity measurement are the same as described in the previous paper[1].

The determination of transference number was carried out by the moving boundary method. The principle of that method was fully discussed by McInnes et al.[6], and the method suitable for the measurement of transference number of large radical-ions was developed by Hartley et al.[7] A brief outline of the method used in our present work is as follows. The micellar solution which is to be investigated acts as a following solution and potassium chloride solution is used as a leading one. The transference number of the following radical-ion, T_F, is determined by the concentration, C_L, and the transference number of the leading ion, T_L, and the concentration of the following radical-ion left behind the boundary, C_F, according to the following relation:

$$\frac{T_F}{C_F}=\frac{T_L}{C_L}$$

Thus, if C_F is determined, T_F is calculated by using the known values of C_L and T_L[8].

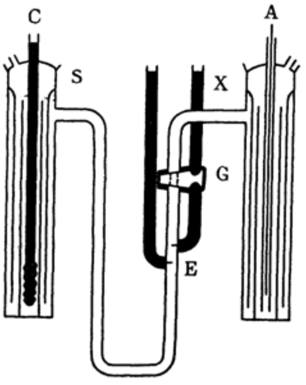

Fig. 1. Moving boundary apparatus.

The apparatus used is shown in Fig. 1. The initial boundary is formed at the position of the stopcock G. The platinum wire C immersed in a strong ferric chloride solution is used as the cathode, while the silver wire A serves as the anode. The electrodes must be nonpolarizable, which condition is fulfilled in this case. The part S of the vessel is filled with potassium chloride solution and the part X with the colloidal electrolyte solution which is to be investigated. After letting electric current flow for a few hours by connecting the apparatus in series with a constant current regulator, the concentration of the colloidal electrolyte solution left behind the boundary is determined by measuring its conductivity. This is performed by using the platinum electrodes E and the alternating-current bridge employing the frequency of 1000 cycle/sec. As it is difficult to measure the high-frequency conductivity at higher temperatures, all these measurements have been carried out at 30°C.

Materials.—Octyl-, decyl-, dodecyl-, tetradecyl-, and hexadecylamine hydrochlorides were prepared from the corresponding amines supplied by Armour & Co., U. S. A., by passing gaseous hydrogen chloride through their benzene solutions. The products were subjected to careful recrystallization from ethanol, and then they were dried in a vacuum desiccator over calcium chloride. All dissolution and dilution processes were carried out with conductivity water but no special precautions were taken to prevent access of carbon dioxide in the transference number measurement.

Results and Discussion

The experimental data of the equivatent conductivity at the frequency of 1000 cycle/sec. and the high-frequency effect at the frequency of 30 Mc./sec. for the electrolytes under investigation are tabulated in Table I, where the high-frequency effect denotes the increase of the equivalent conductivity at the applied high-frequency expressed in terms of the percentage as defined in the previous paper[1]. The measurement of the high-frequency conductivity was carried out only in the range of concentration shown in Table I, on account of the great increase of the conductance in higher concentrations.

The increase of equivalent conductivity at high-frequency is attributable to the relaxation effect of the ionic atmosphere surrounding the micelle ion, and therefore, that increase is expected to be the larger, the greater the electric charge of the micelle, and the smaller its radius. As is seen from Table I, dodecyl-, tetradecyl-, and hexadecylamine hydrochlorides show considerable increase of equivalent conductivity at high-frequency in spite of their large ionic

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[4] J.W. McBain and M.D. Betz, ibid., **57**, 1909 (1935).

[5] C. Chandler and J.W. McBain, *J. Phys. & Colloid Chem.*, **53**, 930 (1949).

[6] D.A. McInnes and L.G. Longsworth, *Chem. Reviews*, **11**, 171 (1932).

[7] G.S. Hartley, E. Drew and B. Collie, *Trans. Faraday Soc.*, **36**, 648 (1934).

[8] L.G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

TABLE I

LOW-FREQUENCY CONDUCTIVITY AND HIGH-FREQUENCY EFFECT

Substance	Conc. (mole/l.)	Equivalent Conductivity at 1000 c./sec.	High-frequency Effect at 30 Mc./sec.
Octylamine Hydrochloride	0.005	133	0
	0.01	129	0
	0.02	120	0
	0.05	99	—
	0.1	85	—
	0.2	78.5	—
Decylamine Hydrochloride	0.005	122	0
	0.01	116	0
	0.02	108	0
	0.05	76	—
	0.1	64	—
	0.2	59	—
Dodecylamine Hydrochloride	0.005	110	0
	0.01	105	0
	0.02	75	4.2
	0.05	52	—
Tetradecylamine Hydrochloride	0.002	107	0
	0.005	102	0
	0.01	68	4.5
	0.02	48.5	6.6
Hexadecylamine Hydrochloride	0.0001	102	0
	0.001	100	0
	0.003	64	4.8
	0.005	40.4	8.6

micelles. This result can be accounted for only if the micelles behave themselves as polyvalent ions. In the case of octyl- and decylamine hydrochlorides the high-frequency effect is very small, and this fact can be considered to be due to the imperfect formation of micelles on account of the shortness of their paraffin-chains. Moreover, throughout all these electrolytes, the lower the low-frequency equivatent conductivity, the higher the high-frequency effect. This experimental fact is also in accord with the conclusion that the critical fall of equivalent conductivity is mainly due to the electrostatic interaction between large micelle ions and small counter ions, which has been inferred in the previous paper[1].

The results of transference number measurements are listed in Table II. The values of transference numbers shown in Table III are obtained from those in Table II by interpolation. For all the solutions under investigation, the transference number at an infinite dilution is about 0.2 or 0.3, but it rises very rapidly in the range where the total conductivity falls, and then tends towards a constant value. However, for the solutions of tetradecyl- and hexadecylamine hydrochlorides, the constant values could not be determined on account of their small solubilities. The mobility of each ion in the free state can be determined by using the value of the transference number and that of the equivalent conductivity at an infinite dilution, the result of calculation being shown in the last column of Table II. The mobility of chlorine ion at an infinite dilution for each solution is almost constant as is to be expected.

The critical rise of the transference number should come mainly from the association of counter ions to micelle ions. This association may take place mainly by electrical force in the low potential region around each micelle, because some other interactions, such as chemisorption or van der Waals adsorption, are unlikely to take place, taking into account the small effect of the nature of counter ions on the critical micelle concentration. The fact that the transference number reaches a nearly constant value with increasing concentration can be interpreted as follows: The fraction of counter ions which associate to the micelle will be governed by their

TABLE II

TRANSFERENCE NUMBER

Substance	Conc. (mole/l.)	Transference Number of Cation	Mobility at Infinite Dilution ($\times 10^4$ cm^2/v.sec.)	
			Cation	Anion
Octylamie Hydrochloride	0.008	0.39	(5.6)	(8.8)
	0.0166	0.40		
	0.032	0.40		
	0.050	0.42		
	0.090	0.45		
Decylamine Hydrochloride	0.0068	0.34	(4.4)	(8.7)
	0.014	0.34		
	0.057	0.71		
	0.086	0.72		
Dedecylamine Hydrochloride	0.00053	0.26	(3.1)	(8.7)
	0.0053	0.26		
	0.0172	0.42		
	0.052	1.04		
	0.067	1.11		
	0.090	1.12		
Tetradecylamine Hydrochloride	0.00092	0.23	(2.5)	(8.7)
	0.0019	0.23		
	0.0033	0.27		
	0.018	1.12		
Hexadecylamine Hydrochloride	0.000074	0.181	(2.0)	(8.7)
	0.0014	0.34		
	0.0042	0.84		

TABLE III

TRANSFERENCE NUMBER AND RELATED QUANTITIES

Substance	Conc. (mole/l.)	Transference Number of Cation	Apparent Conductivity of		C^B_-/C
			Cation	Anion	
Octylamine Hydrochloride	0.005	0.39	51.9	81.1	—
	0.01	0.40	51.6	77.4	—
	0.02	0.39	50.4	69.6	—
	0.05	0.40	50.5	48.5	—
	0.1	0.45	52.7	32.3	—
Decylamine Hydrochloride	0.005	0.34	40.9	81.1	—
	0.01	0.34	39.8	76.2	—
	0.02	0.33	35.6	72.4	—
	0.05	0.60	45.6	30.4	0.23
	0.1	0.72	46.0	1.8	0.38
Deodcylamine Hydrochloride	0.005	0.26	28.6	81.4	—
	0.01	0.26	27.3	77.7	—
	0.02	0.50	37.5	37.5	0.31
	0.05	1.10	57.2	− 5.2	0.57
	0.1	1.12	44.8	− 4.8	0.66
Tetradecylamine Hydrochloride	0.002	0.22	23.6	83.4	—
	0.005	0.24	24.5	77.5	—
	0.01	0.65	44.2	23.8	0.38
	0.018	1.12	54.3	− 5.8	0.59
Hexadecylamine Hydrochloride	0.0001	0.18	18.4	83.6	—
	0.001	0.28	28.0	72.0	0.09
	0.003	0.59	37.8	26.2	0.46
	0.0042	0.84	33.9	6.5	0.65

concentration near its surface, and this must be greater than their concentration in bulk, and as the ratio of the former concentration to the latter is given by the Boltzmann-Poisson equation, the concentration of counter ions near the surface of the micelle will tend towards a constant value, and consequently, its transference number will tend towards a constant value as the bulk concentration increases. The greater-than-unity value of the transference number means, of course, that more chlorine ions are being carried towards the cathode than towards the anode.

In order to calculate the fraction of small ions bound to the micelle, some assumptions are necessary. It is first assumed, that the critical rise of the transference number arises only from the association of counter ions to the micelle. This assumption is equivatent to that of "square well potential" around the micelle. In the second place, it is assumed that, above the critical micelle concentration, the number of free cations is equal to the total number of cations existing in solution just before the critical micelle concentration. The second assumption will, however, have little effect on the result of the calculation except in the range near the critical micelle concentration. The equation obtained under these two assumptions is the same type as that obtained by Brady and Salley³⁾, which is expressed as follows:

$$\frac{C^{B}{}_{-}}{C}=1-\frac{\Lambda-(C^{0}{}_{+}/C)(T_{-}\Lambda+\Lambda^{0}{}_{+})}{\Lambda^{0}{}_{-}+T_{+}\Lambda-(C^{0}{}_{+}/C)\Lambda^{0}}$$

where C, $C^{B}{}_{-}$, $C^{0}{}_{+}$ are the concentrations of total ions, bound anions, and free cations, respectively, and Λ, Λ^{0}, $\Lambda^{0}{}_{+}$, $\Lambda^{0}{}_{-}$ denote the equivalent conductivity of total ions, total free ions, free cations, and free anions, respectively. T_{+} and T_{-} are the transference number of the cation and the anion, respectively.

In Table III, calculated values of $C^{B}{}_{-}/C$ are listed, together with the values of the apparent conductivities of the cation and the anion. It is shown here that at the concentration far above the critical micelle concentration, 60 or 70% of small ions are bound to the micelle. These bound ions can be considered to have no kinetic independence, and therefore, the valence of a micelle is about one third of the number of single molecules contained in a micelle. If we assume for dodecylamine hydrochloride the molecular weight determined by Debye[9] on the basis of his light scattering measurement, a micelle of this colloidal electrolyte is regarded to consist of 55 single molecules, so that it may possess an electrical charge of about 18 units.

If it is further assumed that the mobility of a free ion is not altered with increasing concentration; the mobility of the micelle ion of dodecylamine hydrochloride can be calculated by using the above mentioned data. The value thus obtained is 5.2×10^{-4} cm²/v.sec., which is the same order of magnitude as simple ions. According to a simple consideration, the mobility of a micelle ion is proportional to its electric charge and is inversely proportional to the cubic root of the number of molecules composing it, so that the micelle is expected to have a greater mobility than that above obtained. In order to explain the above obtained value, it should be supposed that the mobility of a micelle ion is considerably reduced by the electrostatic interaction with small ions forming an ionic atmosphere.

From Tables I and III, it is suggested that, in the solution which has a large high-frequency effect, the micelle includes many associated counter ions as its kinetic unit, and consequently, has a compact structure. Generally, the greater the number of single ions forming a micelle, the greater the number of counter ions associated and the more compact the micelle structure. The association of counter ions, being probably an evidence for the electrostatic association in Bjerrum's sense[10], should play an important role in micelle formation, in such a way that it makes the polar heads of long-chain molecules forming a micelle less repulsive to each other.

Summary

The high-frequency and low-frequency equivalent conductivities and transference numbers for aqueous solutions of octyl-, decyl-, dodecyl-, tetradecyl-, and hexadecylamine hydrochlorides have been measured.

For the latter three solutions a considerable increase of the high-frequency concuctivity was observed, and for these three solutions it has been shown that the transference numbers of cations abruptly rise at the critical concentration for the micelle formation, and then tend towards a constant value.

These experimental facts have been accounted for from the electrostatic point of view of the micelle structure. It has been inferred from the experimental results that the counter ion association may be essential to the formation of the micelle.

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[9] P. Debye, *J. Phys. & Colloid Chem.*, **53**, 1 (1949).

[10] N. Bjerrum, *Erg. exakt. Naturwiss.*, **6**, 125 (1926).