Dielectric Studies on Colloidal Solutions. III. The Mobilities of Micelles of Long-chain Amine Hydrohalides

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In the previous paper of this series[1], the transference numbers of long-chain amine hydrochlorides were determined, and the fraction of small counter ions bound to a micelle and the mobility of a micelle were computed therefrom. In this paper, we shall present the direct measurement of the electrophoretic mobilities of the micelles of long-chain amine hydrohalides, and the relation between these mobilities and transference numbers or high-frequency effects will be discussed.

Experimental

Procedure.—The measurement of electrophoretic mobility was carried out by means of the tracer electrophoresis method designed by Mysels and his collaborators[2]. The cell used is shown in Fig. 1. Silver wire is used as the anode A, and silver wire coated with silver halides is used as the cathode C. These electrodes are unpolarizable. The central horizontal tube limited by three-way stopcocks 1 and 2 is filled with the solution of colloidal electrolytes tagged with orange OT, and the adjoining tubes on both sides are filled with an untagged solution. The apparatus is immersed in a thermostat. The electric current flowing through the cell is supplied by a constant current regulator. The electrophoretic mobility u is expressed by the following formula:[2]

$$u=\frac{\lambda}{it}\frac{(Co-C)v}{Co} \qquad (1)$$

where λ is the specific conductivity of the solution (mho/cm), i the current flowing through the cell (amp.), t the duration of the experiment (sec.), Co the concentration of the tracer in the initial solution, C the average concentration of the tracer after letting the current flow, and v the volume of the tube between stopcocks 1 and 2.

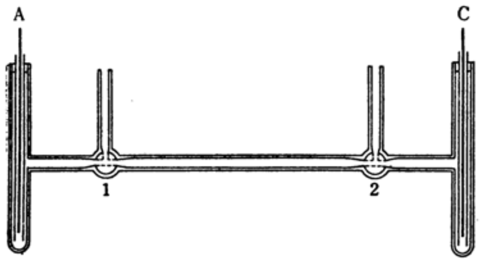

Fig. 1. The electrophoresis cell.

The conductivity of the solution was measured with the impedance bridge of Yokogawa & Co., and the concentration of the tracer with the spectrophotometer of Hitachi & Co.

Materials.—The preparation of dodecyl-, tetradecyl-, and hexadecylamine hydrochloride has been described in the previous paper[1]. Dodecylamine hydrobromide was prepared from dodecylamine (Armour & Co., U.S.A.) by the addition of hydrobromic acid to its ethanol solution and distillation with benzene to remove the water introduced by the addition of the acid. Dodecylamine hydroiodide was prepared from dodecylamine in the same way as above by adding hydroiodic acid. All these products were recrystallized from ethanol.

Orange OT was purified from a commercial sample by solution in acetone and precipitation with water, followed by recrystallization from ethanol-benzene.

Results and Discussion

The experimental results are shown in Table I and Fig. 2. As is shown in Fig. 2, the mobility of a micelle decreases with

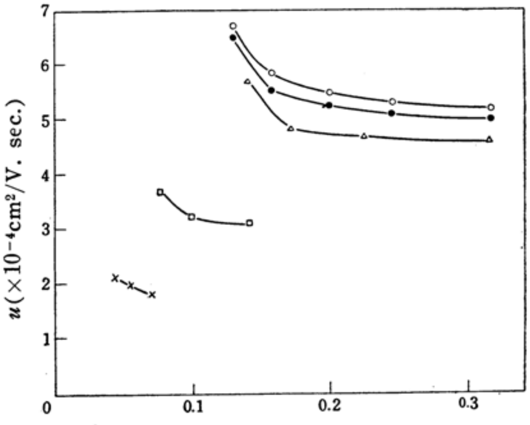

Fig. 2. The electrophoretic mobility.
○, dodecylamine hydrochloride;
●, — hydrobromide;
△, — hydroiodide;
□, tetradecylamine hydrochloride;
×, hexadecylamine hydrochloride.

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[1] M. Shirai and B. Tamamushi, This Bulletin, **29**, 733 (1956).

[2] H. W. Hoyer, K. J. Mysels and D. Stigter, *J. Phys. Chem.*, **58**, 385 (1954).

TABLE I

ELECTROPHORETIC MOBILITY AT 30°C

Substance	Concn. (mole/l.)	λ ($\times 10^{-3}$mho/cm.)	it (coul.)	$\frac{C_0-C}{C_0}$	u ($\times 10^{-4}$cm^2/v.sec.)
Dodecylamine hydrochloride	0.017	1.60	3.30	0.365	6.7
	0.025	1.88	5.28	0.430	5.8
	0.04	2.24	8.64	0.559	5.5
	0.06	2.76	6.20	0.313	5.3
	0.1	4.00	6.30	0.216	5.2
Dodecylamine hydrobromide	0.017	1.46	2.24	0.262	6.5
	0.025	1.75	3.85	0.320	5.5
	0.04	2.08	4.62	0.310	5.3
	0.06	2.64	4.49	0.228	5.1
	0.1	3.60	7.11	0.260	5.0
Dodecylamine hydroiodide	0.02	1.12	1.86	0.249	5.7
	0.03	1.34	2.67	0.252	4.8
	0.05	1.65	2.40	0.180	4.7
	0.1	2.52	7.05	0.339	4.6
Tetradecylamine hydrochloride	0.006	0.558	1.08	0.187	3.7
	0.01	0.681	1.27	0.158	3.2
	0.02	0.970	1.37	0.115	3.1
Hexadecylamine hydrochloride	0.002	0.174	0.507	0.162	2.1
	0.003	0.192	0.648	0.169	1.9
	0.005	0.202	0.648	0.152	1.8

TABLE II

THE FRACTION OF BOUND IONS AND THE ζ-POTENTIAL

Substance	Concn. (mole/l.)	θ from mobility	θ from transference number	ζ-Potential (mV.)
Dodecylamine hydrochloride	0.017	0.37	0.42	119
	0.025	0.46	0.46	103
	0.04	0.59	0.56	98
	0.06	0.66	0.63	94
	0.1	0.70	0.66	92
Dodecylamine hydrobromide	0.017	0.44	—	115
	0.025	0.51	—	98
	0.04	0.62	—	94
	0.06	0.68	—	91
	0.1	0.73	—	89
Dodecylamine hydroiodide	0.02	0.60	—	101
	0.03	0.66	—	85
	0.05	0.75	—	83
	0.1	0.81	—	82
Tetradecylamine hydrochloride	0.006	0.22	—	65
	0.01	0.41	0.38	57
	0.02	0.58	0.60	55
Hexadecylamine hydrochloride	0.002	0.17	0.20	37
	0.003	0.38	0.46	34
	0.005	0.60	0.67	32

increasing concentration, the slope of the curve being considerably steep. This result is probably mainly due to the electrostatic interaction between large ionic micelles and small counter ions, as was discussed previously[3].

If we make some assumptions on the conductivity behavior of these salts, the fraction of counter ions bound to micelles can be calculated from the observed electrophoretic mobility. Those assumptions are: (1) The mobility of a free counter ion is not altered with increasing concentration, and is equal to that of a counter ion at infinite dilution; (2) beyond the critical micelle concentration there are no molecules of long-chain salts existing as single ones. Under these assumptions, if we denote the equivalent conductivity of total ions and free anions by Λ and Λ_-^0, respectively, the relation between the fraction of bound ions θ and the electrophoretic mobility u will be expressed as follows:

$$\frac{\Lambda-(1-\theta)\Lambda_-^0}{1-\theta}=Fu \tag{2}$$

where F is Faraday's constant. The solution of this equation for θ gives,

$$\theta=1-\frac{\Lambda}{\Lambda_-^0+Fu} \tag{3}$$

On account of the second assumption, equation (2) is not valid near the critical micelle concentration. Table II shows the values of θ thus obtained, together with those computed from the transference numbers for dodecyl-, tetradecyl-, and hexadecyl- amine hydrochlorides. The difference between these two series of values may arise from the assumptions (1) and (2) above settled.

For dodecylamine hydrochloride, hydrobromide, and hydroiodide, the values of electrophoretic mobility are nearly the same, but the value for dodecylamine hydrochloride is slightly greater than that for dodecylamine hydrobromide and the latter is greater than that for dodecylamine hydroiodide. And as to the fraction of bound ions θ indicated in Table II, there is the following order: dodecylamine hydrochloride $<$ dodecylamine hydrobromide $<$ dodecylamine hydroiodide. On the other hand, for the critical micelle concentration the reverse order has been demonstrated, namely[4]: dodecylamine hydrochloride$>$dodecylamine hydrobromide$>$dodecylamine hydroiodide. This shows that there is a close relation between the tendency towards association of counter ions and the critical micelle concentration, that is, the stronger the tendency towards association of counter ions, the smaller the critical micelle concentration.

The electrophoretic mobility u is related to the so-called ζ-potential, that is, the electrokinetic potential of micelle ions. However, in order to calculate the ζ-potential the knowledge concerning the thickness of the double layer, $1/\kappa$, and the radius of the micelle, a, is necessary. Considering that the relaxation effect is abnormally large in the range of concentration at which the measurement was a carried out, we assume $\kappa a\gg 1$. In such case, the relation between u and the ζ-potential has been given by Henry[5], which is shown as follows:

$$u=\varepsilon\zeta/6\pi\eta, \tag{4}$$

where η and ε denote the viscosity and the dielectric constant of the solvent, respectively. The values of ζ-potential computed from the value of u by this formula are shown in Table II. Henry's formula is valid if the relaxation effect is negligible, but in our case the relaxation effect is so great that the real ζ-potential is considerably greater than that indicated in Table II. Several formulas involving the relaxation effect have been proposed by Overbeek[6] and Booth[7], but to micelle ions which have abnormally high valency, these formulas are not valid, the theoretical solution of this problem being probably very difficult. But, if we can determine the high-frequency effect over a very wide range of frequency, more exact values of the ζ-potential will be obtained.

Summary

The electrophoretic mobilities of dodecylamine hydrochloride, hydrobromide and hydroiodide, as well as tetradecylamine and hexadecylamine hydrochlorides have been measured. They decrease with increasing concentration as is expected from the electrostatic point-of-view of the micelle structure.

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[3] M. Shirai and B. Tamamushi, This Bulletin, **28**, 545 (1955).

[4] M. Shirai, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo.* **VI**, 29 (1956).

[5] D. C. Henry, *Proc. Roy. Soc. (London)*, **A133**, 106 (1931).

[6] J. Th. G. Overbeek, *Koll. Beih.*, **54**, 316 (1943).

[7] F. Booth, *Proc. Roy. Soc. (London)*, **A203**, 514 (1950).

The fractions of counter ions bound to micelles are computed from the electrophoretic mobilities obtained. These values are found consistent with the result obtained by the transference number measurement.

The ζ-potentials of micelle ions are calculated from the electrophoretic mobilities by Henry's formula. They must be, however, less than the real values, if we take into account the expected high-frequency effects.

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