Dielectric Studies on Colloidal Solutions. IV. The Dielectric Constant of the Solutions of Long-chain Amine Hydrochlorides

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(Received March 18, 1957)

In the first paper of this series[1], the result of the measurement of high-frequency conductivities of aqueous solutions of colloidal electrolytes has been reported; the measurement of the dielectric constants of their solutions, which is reported in this paper, must also be an important approach to the understanding of the nature of the electrolytes.

Experimental

Procedure.—The measurement of the dielectric constant (D. C.) at 2 Mc./sec. has been carried out by means of the heterodyne beat method. The main part of the apparatus consists of two separate oscillators, one of which is held at a frequency of 2 Mc./sec. by the vibration of a quartz crystal and the other is adjusted by varying its capatity to give a frequency different by a constant amount from that of the former oscillator. A liquid cell is incorporated into the circuit of the latter oscillator. The adjustment of the frequency of the latter oscillator is performed by the addition of a 700 cycles/sec. tuning-fork oscillator to the apparatus, and against that oscillator the beat note is balanced by a cathode-ray oscilloscope. Each electrical component is enclosed in an earthened metal box.

The precision condenser consists of two variable air condensers; the one has a working range of 100 pF traversed in 25 turns and the other that of 11.25 pF traversed in 90 turns. The division of the former condenser is 1/100 turns and that of the latter is 1/50 turns.

The measurement of D. C. at 30 Mc./sec has been carried out by the resonance method used for the measurement of the high-frequency conductivity[1]. The resonance point is obtained by determining the whole resonance curve of the resonant circuit containing the measruring cell, so that the precision of the resonance point is sufficiently accurate.

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

The cell used is constructed of parallel plates of platinum enclosed in a glass vessel which is immersed in a constant temperature bath of toluene, and fixed at a definite position. The cell constant is determined by using distilled water as the standard whose D. C. is taken to be 73.02 at 40°C[2].

The electrical conductivity has been measured with the impedance bridge used in the previous work[3].

Materials.—Hexadecyl- and octadecylamine hydrochloride were prepared from the corresponding amines (Armour & Co., U. S. A.) by the method given in the previous paper[4].

Ethanol was distilled over calcium oxide: b. p. 78.3°C.

Benzene was purified from a commercial sample by washing with sulfuric acid and then with water, followed by drying over calcium chloride and distillation: b. p. 80°C.

The water used is the conductivity water distilled in an nitrogen atomsphere.

Results and Discussion

1) **Electrode polarization**—In measuring D. C. of a conductive medium, the electrode polarization often causes a serious error. This error is inversely proportional to the square of the frequency at which the measurement is made[5]. The error in the present investigation is expected to be very small as the frequency employed is high, being 2 Mc./sec. In reality, D. C. of aqueous solutions of potassium chroride at various concentrations obtained has been found nearly constant as shown in Table I. A little increase in D. C. at higher concentrations may be interpreted in terms of Debye-Falkenhagen's effect of potassium chloride. Thus, it is conceivable that the values of D. C. obtained are free from the error due to the electrode polarization at the range of concentration and at the frequency at which the measurement has been carried out.

TABLE I

DIELECTRIC CONSTANT OF AQUEOUS SOLUTION OF POTASSIUM CHLORIDE (temp 40°C)

conc. (mole/l.)	ε (2Mc./sec.)
0.0001	73.02
0.0002	73.02
0.0003	73.03
0.0005	73.05
0.0008	73.21
0.001	73.45

2) **D. C. of aqueous solutions of salts.**—The result of the measurement of D. C., ε, and the equivalent conductivity (E. C.), Λ, of aqueous solutions of hexadecyl- and octadecylamine hydrochloride is shown in Table II and in Fig. 1, where the relative increase of D. C. or E. C. is plotted as ordinate against the square root of the concentration of amine salts as abscissa. The relative increase in D. C. is there expressed by

$$100\frac{\varepsilon-\varepsilon_0}{\varepsilon_0}$$

in which ε and ε_0 denote D. C. of the solution and the solvent, respectively. For both salts D. C. remains nearly constant with increasing concentration below the critical micelle concentration, but increases considerably beyond that concentration.

D. C. of aqueous solutions of colloldal electrolytes involves many factors. (1) Sack[6] concluded that in an externally applied, field the electric fields of ions should hinder the orientation of water molecules, thus resulting in lower D. C. (2) According to the predictions of Debye-Falkenhagen's theory[7], the relaxation of ionic atmosphere should increase D. C. (3) If the solute molecules have dipole moments, such as ion-pairs[8], they will act to increase D. C., whereas (4) long hydrocarbon chains contained in the molecules will act to decrease it.

The volume fraction of the hydrocarbon chains is, however, only about 0.2 percent. at the concentration of 0.005 mole/l., assuming that their density is nearly the same as that of pure liquid paraffins, and according to Bruggeman's theory[9], the lowering of D. C. due to the hydrocarbon chains in this case is estimated to 0.3 percent,, so that we can consider this effect to be small at the range of concentration at which the measurement is carried out. Sack's effect should also be very small at the frequency of 2 Mc./sec. employed in this work, taking into account the results obtained with aqueous solutions of various electrolytes[10,11]. The rise of D. C. beyond the critical micelle concentration shown in Fig. 1 may be due to Debye-Falkenhagen's effect or the orientation of dipoles

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[2] J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

[3] M. Shirai and B. Tamamushi, This Bulletin, **30**, 411 (1957).

[4] M. Shirai and B. Tamamushi, *ibid.*, **29**, 733 (1956).

[5] J. F. Johnson and R. H. Cole, *J. Am. Chem. Soc.*, **73**, 4536 (1951).

[6] H. Sack, *Physik. Z.*, **27**, 206 (1926); **28**, 199 (1927).

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

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

[9] D. A. G. Bruggeman, *Ann. d. Phys.*, **24**, 636 (1935).

[10] F. H. Drake, G. W. Pierce and M. T. Dow, *Phys. Rev.*, **35**, 613 (1930).

[1] R. T. Lattey and W. G. Davies, *Phil. Mag.*, **12**, 1111 (1931); **13**, 444 (1932).

TABLE II

DIELECTRIC CONSTANT AND EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF AMINE SALTS

substance	concn. (mole/l.)	ε (2 Mc./sec.)	Λ (1000c./sec.)
solvent: water	temp. 40°C		
hexadecylamine hydrochloride	0.0005	73.0	126
	0.0008	73.0	124
	0.001	73.0	123
	0.0012	73.0	111
	0.0015	73.0	92.0
	0.002	73.4	78.5
	0.003	73.9	60.6
	0.005	74.6	47.8
	0.01	75.2	35.4
octadecylamine hydrochloride	0.0001	73.0	118
	0.0002	73.0	117
	0.00025	73.4	112
	0.0003	73.8	106
	0.0005	74.8	79.8
	0.0008	75.3	50.9
	0.001	75.7	42.0
	0.002	76.7	31.5
	0.005	78.0	20.0
solvent: 2 mole/l. aq. ethanol			temp. 40°C.
hexadecylamine hydrochloride	0.0005	70.5	82.2
	0.0008	70.5	81.0
	0.001	70.5	80.1
	0.0012	70.4	79.0
	0.0015	70.5	76.0
	0.002	70.7	70.3
	0.003	71.0	58.3
	0.005	71.2	48.0
	0.01	71.5	34.4
octadecylamine hydrochloride	0.0001	70.5	72.2
	0.0002	70.5	72.0
	0.00025	70.5	71.5
	0.0003	70.7	71.0
	0.0005	71.1	67.9
	0.0008	71.5	64.0
	0.001	71.7	61.0
	0.002	72.3	45.0
	0.005	72.9	24.0
solvent: 4 mole/l. aq. ethanol			temp. 40°C.
hexadecylamine hydrochloride	0.0005	67.8	56.6
	0.0008	67.8	56.6
	0.001	67.8	57.2
	0.0012	67.8	58.0
	0.0015	67.8	59.0
	0.002	67.9	59.5
	0.003	67.9	59.7
	0.005	68.0	55.8
	0.01	—	45.7
octadecylamine hydrochloride	0.0001	67.8	47.5
	0.0002	67.8	47.5
	0.00025	67.8	47.0
	0.0003	67.8	47.0
	0.0005	67.8	46.6
	0.0008	67.8	47.5
	0.001	67.8	48.0
	0.002	68.0	50.6
	0.005	68.2	48.1

of ion-pairs, but below the critical micelle concentration the effect of both factors will become insignificant. The orientation of a micelle as a whole need not be considered, provided that the micelle is supposed to be in a liquid state of aggregation[1].

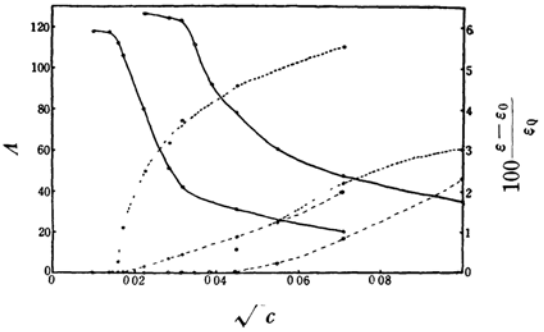

Fig. 1. The relative increase in D. C. and E. C. of amine salts in aqueous solution.
○, hexadecyl-;
●, octadecylamine hydrochloride.
— — equivalent conductivity at 700 c./sec.
-----, -·-·- } the relative increase in D. C. at { 2 Mc./sec. / 30 Mc./sec.

3) **D. C. of solutions of salts in aqueous ethnol.**—D. C. and E. C. of solutions of hexadecyl- and octadecylamine hydrochloride in aqueous ethanol of 2 mole/l. and 4 mole/l. are shown in Table II as well as in Figs. 2 and 3. The rise of D. C. of these solutions beyond the critical micelle concentration is considerably reduced in the case of aqueous ethanol of 2 mole/l. and almost diminished in the case of aqueous ethanol of 4 mole/l. And, from the conductivity curves in Figs. 2 and 3, it is seen that the micelle formation is inhibited by the increase in alcoholic content of the solution of electrolytes. In aqueous ethanol solutions an anion and a cation of electrolytes tend to associate on account of the lower D. C. of the solvent medium, and therefore, the increase in D. C. due to the orientation of ion-pairs will become significant. On the other hand, in aqueous ethanol solutions the association of counter ions will be promoted and the micelle structure will become loose, and accordingly, Debye Frankenhagen's effect is expected to be reduced considerably.

4) **Effect of solubilization on D. C. of the solution.**—It is well known that water-insoluble substances, such as benzene, are dissolved in the interior of micelles, and

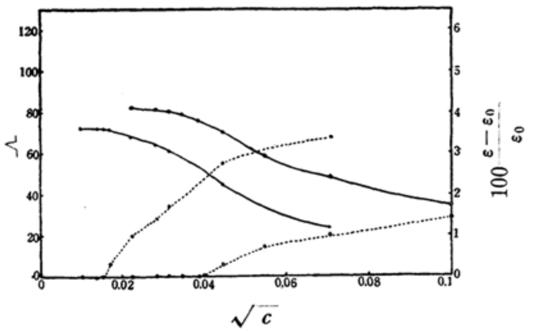

Fig. 2. The relative increase in D. C. and E. C. of hexadecyl- and octadecylamine hydrochloride in 2 mole/l. aq. ethanol.

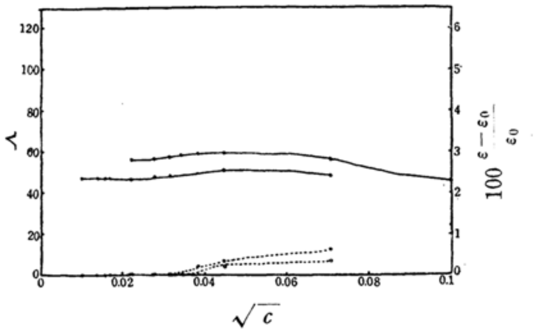

Fig. 3. The relative increase in D. C. and E. C. of hexadecyl- and octadecylamine hydrochloride in 4 mole/l. aq. ethanol.

micelles are enlarged[12]. The larger the radius of the ions, the smaller the Debye-Falkengen's effect. Accordingly, when benzene is solubilized in solutions of colloidal electrolytes, D. C. of the solutions is expected to decrease. In Table III are indicated D. C. of aqueous solutions of octadecylamine hydrochloride containing various amounts of solubilized benzene. The result agrees with the above expectation.

TABLE III

DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF OCTADECYLAMINE HYDROCHLORIDE CONTAING VARIOUS AMOUNTS OF SOLUBILIZED BENZENE temp. 40°C

conc. of octadecylamine hydrochloride 0.003 mole/l.

moles of benzene per mole of amine salt	ε (2 Mc./sec.)
0	77.4
0.11	77.3
0.34	77.2
0.57	76.8
0.86	75.9
1.1	75.8

5) **Dependence of D. C. on frequency.**—At the frequency of 2 Mc./sec., the relative increase of D. C. due to Debye-Falkenhagen's effect is significant, but at higher frequencies where the equivalent conductivity increases, the relative increase of D. C. should be diminished according to Debye-Falkenhagen's theory. In Table IV and Fig. 1 is shown the result of the measurement of D. C. of aqueous solutions of hexadecyl- and octadecylamine hydrochlorides at the frequency of 30 Mc./sec. At a certain concentration the relative increase of D. C. at 30 Mc./sec. is smaller than that at 2 Mc./sec., and this experimental fact agrees with our expectation, too. The ratio of D. C. at 30 Mc./sec. to that at 2 Mc./sec. becomes larger with increasing concentration. This is probably due to the shortening of the relaxation time of Debye-Falkenhagen's effect with increasing concentration.

TABLE IV

DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF AMINE SALTS AT 30 Mc./sec.

temp. 40°C.

substance	conc. (mole/l.)	ε (30 Mc./sec.)
hexadecylamine hydrochloride	0.0005	73.0
	0.0008	73.0
	0.001	73.0
	0.0012	73.0
	0.0015	73.0
	0.002	73.0
	0.003	73.1
	0.005	73.6
	0.01	74.7
octadecylamine hydrochloride	0.0001	73.0
	0.0002	73.0
	0.00025	73.0
	0.0003	37.0
	0.0005	73.1
	0.0008	73.2
	0.001	73.3
	0.002	73.6
	0.005	74.4

From these exerimental results, it would be reasonable to conclude that the rise of D. C. observed in the case of aqueous solutions of long alkyl amine hydrochlorides is mainly due to Debye-Falkenhagen's effect. The same effect has been inferred from the result of measurement of high-frequency conductivity[1].

Summary

The dielectric constant and the equivalent conductivity of solutions of hexadecyl-

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

and octadecylamine hydrochloride have been measured at the frequencies of 2 Mc./sec. and 30 Mc./sec. The dielectric constant of the solutions shows a considerable increase beyond the concentration for micelle formation.

The dielectric constant and the equivalent conductivity of the solutions of these amine salts in aqueous ethanol of various concentrations have been measured. The rise of the dielectric constant is diminished with increasing concentration of ethanol.

The effect of solubilization of benzene on the dielectric constant of the solutions has been investigated. The relative increase in the dielectric constant is reduced with increasing amount of solubilized benzene.

From these experimental results, it is concluded that the rise of the dielectric constant of the aqueous solutions is mainly due to Debye-Falkenhagen's effect.

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