953. *Some Physical Properties of Aqueous Solutions of Choline Chloride at 25°.*

By R. Fleming.

The equivalent conductance of choline chloride at infinite dilution was found to be 118·4 ohm^{-1} cm.^{2}. The plot of Λ against $\sqrt{c}$ was linear in the most dilute region, but the slope was greater than that required by Onsager's limiting law. The fluidity elevation of the choline ion is −18·9 rhes, which is close to that of the tetramethylammonium ion. The apparent molal volume at infinite dilution, ϕ^0_v, was found to be 124·9 cm.^{3} mole^{-1}.

In a general study of the conductance of quaternary ammonium compounds in nitrobenzene Taylor and Kraus [1] showed that the dissociation constants of the salts in this solvent decrease with increasing dimensions. Introducing a polar group also leads to lower dissociation constants, and for choline picrate they suggested that this was due to interaction of the hydroxyl group with the picrate ion. The conductance of choline chloride in aqueous solution has not previously been reported. Daggett, Bair, and Kraus [2] studied the conductance of symmetrical quaternary ammonium compounds in aqueous solutions at 25° and found that this type of salt obeys Onsager's limiting law.

Experimental

A Cambridge Instrument Company's conductivity bridge was used to measure the conductance of choline chloride solutions. The solutions were contained in a dipping-type conductivity cell which was supplied with the apparatus, and the cell was immersed in a thermostat kept at 25° ± 0·01°. The cell constant was determined by calibration with 0·1N- and 0·01N-potassium chloride which were made up by weight, and the specific conductivities of these solutions were taken to be 0·01288 and 0·001413 ohm^{-1} cm.$^{-1}$, respectively.[3] The cell constant varied slightly with concentration,[4] the value at 0·1N being 0·3682, and at 0·01N 0·3665.

The choline chloride (B.D.H.) was purified by two recrystallisations from absolute ethanol and then vacuum-dried. It was stored in a vacuum-desiccator over magnesium perchlorate. It is extremely deliquescent and its purity was frequently checked by potentiometric titration with silver nitrate solution. Its purity was also determined by passing a known volume of 0·1N-choline chloride through an anion-exchange resin (Amberlite IRA-400), and the resultant base was potentiometrically titrated with 0·1N-hydrochloric acid. This method of assay is

[1] Taylor and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 1731.
[2] Daggett, Bair, and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 799.
[3] Harned and Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., New York, 3rd edn., p. 195.
[4] Ref. 3, p. 195.

similar to that described [5] for ephedrine chloride. Results by the two methods agreed closely. The " AnalaR " potassium chloride used for the determination of the cell constant was dried at 110° for 2 hr. before use. The results of the conductance measurements are shown in Table 1.

TABLE 1.

c	$\sqrt{c}$	Λ	c	$\sqrt{c}$	Λ	c	$\sqrt{c}$	Λ	c	$\sqrt{c}$	Λ
0·5819	0·7628	72·7	0·1360	0·3687	89·6	0·01714	0·1309	105·8	0·00343	0·0586	112·5
0·4150	0·6442	77·5	0·08514	0·2917	94·3	0·01662	0·1289	106·3	0·00171	0·0414	114·2
0·2358	0·4856	84·6	0·06874	0·2622	96·0	0·00686	0·0828	110·1	0·00166	0·0408	114·6
0·1662	0·4077	88·0	0·04150	0·2037	100·5	0·00415	0·0644	111·8	0·00136	0·0368	114·8

The equivalent conductance of choline chloride at infinite dilution, 118·4 ohm^{-1} cm.^{2}, was found by the extrapolation of the plot of Λ against $\sqrt{c}$. Although this plot was linear in the most dilute region, the slope (101·0) was steeper than that required by the Onsager law (87·4). It being assumed that the conductance of the Cl^- ion is 76·4 ohm^{-1} cm.^{2} equiv.$^{-1}$ at infinite dilution,[6] the value for the choline ion is 42·0 ohm.$^{-1}$ cm.^{2}, which is close to that found for the tetramethylammonium ion (44·92) by Daggett *et al.*[2]

RESULTS

Viscosity.—An Ostwald viscometer was used and was immersed in a thermostat kept at 25° ± 0·01°. The results are shown in Table 2. Cols. 1 and 2 show the concentration expressed in terms of molality and molarity respectively, and col. 3 gives the relative viscosity η/η_0.

TABLE 2.

m	c	η/η_0	m	c	η/η_0	m	c	η/η_0	m	c	η/η_0
6·185	3·504	3·071	1·730	1·422	1·352	0·4369	0·4133	1·083	0·0428	0·0424	1·010
3·937	2·643	2·043	0·9869	0·8760	1·195	0·2426	0·2328	1·050	0·0417	0·0413	1·009
2·243	1·752	1·518	0·6263	0·5795	1·124	0·0866	0·0848	1·015	0·0098	0·0098	1·000

The relative viscosity of a N-solution was read off from the graph of η/η_0 plotted against $\sqrt{c}$ and found to be 1·20. From this value and that used by Bingham [7] for the viscosity of water (0·008947 poise), the fluidity of a N-solution of choline chloride is 93·4 rhes. Bingham assumed that the fluidity elevations of K^+ and Cl^- ions were both equal to +0·28 rhe and used these as a standard for calculating the fluidity elevations of a large number of electrolytes. He found that the stronger the base, the larger the fluidity elevation, and that with large elevations there was less likelihood of hydration. The fluidity elevation of the choline ion is −18·9 rhes and it lies in between the elevation of the tetramethylammonium ion (−14·0) and the tetraethylammonium ion (−34·3 rhes). Since the choline ion does not show a large negative elevation this seems to suggest that the ion is not hydrated.

Apparent Molal Volume.—The densities were determined with a Perkin-type pycnometer. The derived apparent molal volumes [8] are recorded in Table 3. The plot of ϕ_v

TABLE 3.

c	3·504	2·643	1·752	1·422	0·8760	0·5795	0·2348
d_4^{25}	1·0557	1·0404	1·0256	1·0202	1·0109	1·0062	1·0006
ϕ_v	123·3	123·6	123·7	123·7	124·2	124·2	124·9

against c was linear in the most dilute region but it had a negative slope which is unusual. Extrapolation to zero concentration gave the value of ϕ^0_v as 124·9 cm.^{3} mole^{-1}, and ϕ^0_v for

[5] Saunders, Elworthy, and Fleming, *J. Pharm. Pharmacol.*, 1954, **6**, 32.
[6] Owen and Zeldes, *J. Chem. Phys.*, 1950, **18**, 1083.
[7] Bingham, *J. Phys. Chem.*, 1941, **45**, 885.
[8] Root, *J. Amer. Chem. Soc.*, 1933, **55**, 850.

the Cl^- ion [9] being assumed to be 18·0 cm.^{3} mole^{-1}, the value for the choline is 106·9 cm.^{3} mole^{-1}. The apparent molal volumes of ammonium, tetramethylammonium, and tetraethylammonium chloride were calculated from density data given in the International Critical Tables.[10] In the first two cases ϕ_v increases with increasing concentration, but the last salt behaves like choline chloride and ϕ_v decreases with increasing concentration.

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SCHOOL OF PHARMACY, BRUNSWICK SQUARE, LONDON, W.C.1. [*Received, February 10th,* 1960.]

[9] Ref. 3, p. 397.
[10] International Critical Tables, McGraw-Hill Book Company Inc., New York, 1928, Vol. III, p. 114.