Expermiental

Tetraethylammonium chloride, Et_4NCl was obtained by using anion exchange resin from its bromide which was first synthesized by the Menschutkin reaction. Et_4NCl salt was three times recrystallized from its methanol solution by adding chilled ether, and dried in vacuum at about 50°C for a week. Tetraethylammonium perchlorate was precipitated by adding excess amount of perchloric acid to the aqueous solution of Et_4NBr*, recrystallized twice from its aqueous solution, and dried in vacuum at room temperature for 3 days after heated up to 100°C for 2 hours with great care to avoid explosion. The dilute sample solutions were prepared from stock solutions just in the same way as before[1,21].

The high-pressure apparatus and the conductivity cell were already described elsewhere.

Results and Discussion

Determination of $\Lambda^{\circ(P)}$

The equivalent conductances, $\Lambda^{(P)}$ of Et_4NCl and Et_4NClO_4 in dilute aqueous solution at pressure P were determined, after the corrections for the solvent conductivity and changes in concentration and cell constant with pressure had been made just in the same manner as the previous study[1]. Then, the equivalent conductances at infinite dilution at pressure P, $\Lambda^{\circ(P)}$ were obtained with the aid of Onsager's equation for conductance,

$$\Lambda=\Lambda^{\circ}-(\alpha\Lambda^{\circ}+\beta)\sqrt{C}; \tag{1}$$

that is,

$$\Lambda^{\circ}=\frac{\Lambda+\beta\sqrt{C}}{1-\alpha\sqrt{C}}, \tag{2}$$

from which $\Lambda^{\circ(P)}$ of Et_4NCl at 25 and 40°C and Et_4NClO_4 at 25°C were calculated and given in Tables 1~3. The adequacy of this method to obtain $\Lambda^{\circ(P)}$ from $\Lambda^{(P)}$ in the dilute concentration range would be supported by the approximate constancy of $\Lambda^{\circ(P)}$ around their mean value within the experimental error, which was already found in the previous study on Me_4NCl and Bu_4NCl[2]. However, it was reported[22,23] that the direct graphical extrapolation of the conductance data of Et_4NCl to infinite dilution with the aid of the theoretical limiting slope was not satisfactory exceptionally. When the conductances of Et_4NCl shown in Table 1 are compared with those measured at a higher concentration by Horne and Young[24], there are rather large discrepancies between them as found

* This salt was kindly supplied by Mr. T. Hori, Laboratory of Analytical Chemistry of our Department.

21) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)
22) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 1763 (1968)
23) S. B. Brummer and A. B. Gancy, "Water and Aqueous Solutions", Chap. 19, Part I, ed. by R. A. Horne, Wiley-Interscience, New York (1972)
24) R. A. Horne and R. P. Young, *J. Phys. Chem.*, **72**, 1763 (1968)

in the cases of Me_4NCl and Bu_4NCl[2].

Table 1 $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Et_4NCl in H_2O at 25°C

Pressure, atm \ Sample*	A	B	C	D	Average
1	108.9	108.9	108.8	108.8	108.9
500	110.9	110.6	110.7	110.8	110.8
1,000	111.4	111.1	111.4	111.1	111.3
1,500	111.2	110.6	110.9	110.2	110.7
2,000	109.9	109.3	109.7	109.1	109.5
2,500	108.3	107.6	107.8	107.1	107.7
3,000	106.2	105.3	105.7	105.1	105.6
3,500	103.3	102.9	103.1	102.8	103.0
4,000	100.8	100.3	100.3	100.1	100.4
4,500	98.3	97.6	97.7	97.5	97.8
5,000	95.6	95.0	94.9	94.6	95.0

* A: 3.866×10^{-4} N, B: 6.201×10^{-4} N, C: 8.536×10^{-4} N, D: 11.598×10^{-4} N at 1 atm

Table 2 $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Et_4NCl in H_2O at 40°C

Pressure, atm \ Sample*	A	B	C	D	Average
1	143.9	143.9	143.8	143.9	143.9
500	143.6	143.7	143.7	143.6	143.7
1,000	142.6	142.6	142.6	142.5	142.6
1,500	141.2	141.2	141.0	141.1	141.1
2,000	139.6	139.1	138.9	139.2	139.2
2,500	137.2	136.5	136.4	136.6	136.6
3,000	134.6	133.8	133.5	133.7	133.9
3,500	131.4	130.5	130.3	130.4	130.7
4,000	128.2	127.2	126.9	127.0	127.3
4,500	124.9	123.6	123.4	123.4	123.8
5,000	121.5	120.1	119.9	119.8	120.4

* A: 3.847×10^{-4} N, B: 5.992×10^{-4} N, C: 8.495×10^{-4} N, D: 11.542×10^{-4} N at 1 atm

Obtaining of $\lambda^{\circ(P)}$ from $\Lambda^{\circ(P)}$

The single-ion equivalent conductances at pressure P, $\lambda^{\circ(P)}$ were calculated on the basis of the same postulate used in Ref. (2); it was assumed that the Walden product of Bu_4N^+ is approximately independent of pressure. In the present calculation, the previous[25] interpolations of the values of water viscosity measured by Cappi[3] have been corrected as shown in Table 4, because the interpolation from the direct plot of water viscosity, η° against pressure was found to be less accurate than

25) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)