

is nearly independent of temperature, because in our laboratory²⁶⁾ it has been recently shown that $\tau^{\circ(P)}(\text{K}^+)$ decreases by only 0.7% with the increase in temperature from 15 to 25°C or from 25 to 40°C both at 1,000 and at 1,500 atm. By using the values of $\tau^{\circ(P)}$ at 25°C calculated from the ionic equivalent conductance values in Table 5, $\Lambda^{\circ(P)}(\text{Et}_4\text{NCl})$ in Table 2, $\Lambda^{\circ(P)}(\text{KCl})$ in Ref. (1), $\Lambda^{\circ(P)}(\text{Me}_4\text{NCl})$ in Ref. (2) and $t^{\circ(1)}(\text{K}^+)$ at 40°C in Ref. (27), the single-ion values of the limiting equivalent conductances at 40°C at high pressures were obtained and used for the calculation of the Walden Products in Table 6.

Pressure dependence of $\lambda^{\circ(P)}$

The relative variation of the limiting equivalent conductances of the ions with pressure is shown in Fig. 1. It is to be noted that the pressure dependence of $\lambda^{\circ(P)}$ of tetraalkylammonium ions such as Bu_4N^+ , Et_4N^+ and Me_4N^+ are somewhat similar to each other and, moreover, to that of the viscosity of solvent water. On the other hand, the pressure dependence of $\lambda^{\circ(P)}$ of K^+ , Cl^- and, above all, ClO_4^- are quite different with each other. Furthermore, it is surprising that ClO_4^- ion has no maximum conductance against pressure at 25°C, although all other ions so far studied have a maximum conductance against pressure at the same temperature. These facts would suggest that the limiting ionic equivalent conductance at high pressure can not be interpreted only by such a macroscopic property of the solvent as viscosity, in spite of the early finding and statement by Röntgen, Fanjung and Tamann.

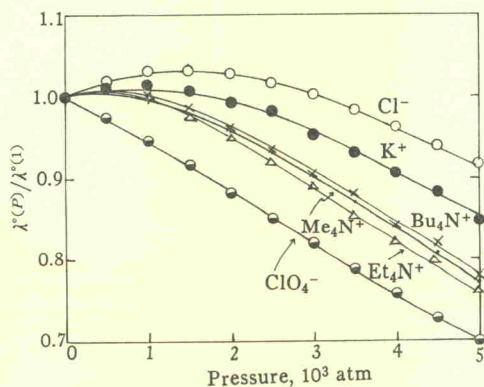


Fig. 1 $\lambda^{\circ(P)}/\lambda^{\circ(1)}$ vs. pressure at 25°C

Variation of the Walden product with pressure

In order to deduce the pressure influence on the macroscopic viscosity of water from that on the ionic conductance, the Walden products, $W = \lambda^{\circ(P)} \cdot \eta^{\circ(P)}$ of the ions at 25°C are calculated by using the values of $\lambda^{\circ(P)}$ in Table 5 and $\eta^{\circ(P)}$ in Table 4 and given in Table 7, and their relative variations with pressure are shown in Fig. 2. There, we see that the pressure coefficient of the Walden product, $\partial W/\partial P$ at 1 atm and 25°C is positive, slightly negative and remarkably negative for Cl^- and K^+ ions,

26) Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, **43**, 24 (1973)

27) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940)

Table 7 Walden products of the ions in H₂O at 25°C
 (ohm⁻¹·cm²·equiv⁻¹·cP)

| Ions Pressure, atm | Et ₄ N ⁺ | Me ₄ N ⁺ | K ⁺ | Cl ⁻ | ClO ₄ ⁻ |
|-----------------------|--------------------------------|--------------------------------|----------------|-----------------|-------------------------------|
| 1 | 29.0 | 39.9 | 65.7 | 6.83 | 60.2 |
| 500 | 29.2 | 39.9 | 66.2 | 69.1 | 58.2 |
| 1,000 | 28.9 | 39.5 | 66.4 | 70.2 | 56.8 |
| 1,500 | 28.8 | 39.7 | 67.0 | 71.4 | 55.9 |
| 2,000 | 28.6 | 39.7 | 67.6 | 72.8 | 55.2 |
| 2,500 | 28.6 | 39.7 | 68.5 | 74.1 | 54.7 |
| 3,000 | 28.6 | 39.7 | 69.1 | 75.5 | 54.5 |
| 3,500 | 28.2 | 39.4 | 69.3 | 76.2 | 53.9 |
| 4,000 | 28.4 | 39.8 | 70.5 | 77.9 | 54.1 |
| 4,500 | 28.3 | 39.3 | 70.7 | 78.2 | 53.3 |
| 5,000 | 28.4 | 39.5 | 71.5 | 80.4 | 54.1 |

tetraalkylammonium ions and ClO₄⁻ ion, respectively. Comparing Fig. 2 with Fig. 3^{28,29}), we notice that $\partial W/\partial P$ at 25°C and 1 atm does not correlate with $\partial W/\partial T$ at 1 atm 25°C for these ions. The possible view-points for the interpretation of the pressure and temperature coefficients of the ionic Walden product are summarized in Table 8, where all the view-points but the first one are relevant

 Table 8 Prediction of the sign of $\partial W/\partial P$

| Point of view | Ref. | Sign of $\partial W/\partial P$ |
|---------------------------------|--------|---------------------------------|
| C) Compression effect | 20, 21 | + |
| D) Dielectric friction theory | 18, 19 | + |
| E) Electrostriction theory | | - |
| P) Pressure-induced dehydration | 30 | + |
| S) Structural change of water | 28 | -, 0, + |

to ion-solvent interaction at any rate. Before we correlate the pressure coefficient of the ionic Walden product with the ion-solvent interaction, we now consider the theoretical background of W or λ° . Although in very dilute electrolyte solutions, λ has been successfully represented in some quantitative forms by Onsager, Fuoss and others, no satisfactory theory for ionic conductance has been established at the two extremes, at infinite dilution and at high concentration. Owing to this undeveloped stage of the theory for λ° , we could not make any completely quantitative explanation of the pressure

28) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966)

29) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London (1957)

30) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)