

THE EFFECT OF PRESSURE ON THE WALDEN PRODUCTS OF ALKALI IODIDES IN ACETONE

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The conductivities of LiI, NaI, KI and CsI in acetone were measured at 30.0°C up to 2070 kg/cm²¹⁾ in the concentration range $3 \times 10^{-4} - 5 \times 10^{-3}$ M. The results were analysed by the Shedlovsky method in order to obtain the limiting molar conductivities and the association constants. The pressure coefficient of the Walden products are positive for all salts studied here and increase in the order of LiI < NaI < KI < CsI with increasing pressure. This trend is very different from that found in water previously.¹⁾ It is shown that this can be interpreted in terms of the Zwanzig solvent relaxation theory. The association constants also increase in the order of LiI < NaI < KI < CsI. The structure of the ion pairs is discussed on the basis of both the volume changes upon association and the closest approach distances of the ion pairs.

Introduction

Research into the ion-solvent interaction has mainly been focused on aqueous solutions. On account of the specific properties of water, ionic aqueous solutions present very interesting subjects in various fields. On the other hand, it means that the water itself introduces a number of complicating factors into the investigation of the ion-solvent interactions. To obtain the basic knowledge of these interactions, it is desirable to do experiments in normal or approximately normal liquids where any specific interactions between an ion and solvent molecules can be neglected.

In our laboratory, the ion-solvent interactions have been extensively studied in water under high pressure and the pressure dependence of the Walden products are discussed from the viewpoint of the density difference of water between in the hydration shell and in the bulk.²⁻⁴⁾ It is the purpose of this paper to propose another interpretation for the pressure dependence of the Walden products based on the Zwanzig solvent relaxation theory.

In a previous paper,¹⁾ the conductivities of NaI, KI and CsI in water were measured under various pressures and temperatures to examine the pressure and temperature effects on the Walden products of the ions of these salts. By plotting the pressure coefficient of the Walden product against the crystal radius of the ion, it was found that the pressure coefficient of the Walden product decreased

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1) E. Inada, *This Journal*, **46**, 19 (1976)

*1) 1 kg/cm² = 0.9807×10^5 Pa

2) M. Nakahara and J. Osugi, *This Journal*, **43**, 71 (1974)

3) M. Ueno, M. Nakahara and J. Osugi, *ibid.*, **45**, 9 (1975)

4) M. Ueno, M. Nakahara and J. Osugi, *ibid.*, **45**, 17 (1975)

in the order of $K^+ > Na^+ > Cs^+$. In other words, the pressure coefficient of the Walden product showed a maximum around the radius of K^+ . This is predicted by the Zwanzig solvent relaxation theory simplified with some approximations. At the lower pressure and temperature, however, the observed pressure coefficient of the Walden product was negative for each ion and it had a minimum at a specific pressure. This fact was not explained by the theory. We inferred that the discrepancies between the experimental results and the theory might be attributed to the neglect of the water structure, which is inherent to the theory.

For this reason, the present work was carried out to examine whether or not the solvent relaxation theory works better in predicting the pressure effect on the Walden product in such a solvent where the solvent molecules are expected to be less structured. The viscosities, together with the compressibilities and the dielectric constants, all at high pressures, are available for only a few non-aqueous solvents. We have chosen acetone as solvent, since all these properties have been thoroughly studied under high pressures.

At atmospheric pressure, the conductivities of many electrolytes have been measured in acetone.⁵⁻¹⁵⁾ Several authors discussed their results from the viewpoint of the Zwanzig solvent relaxation theory.^{12, 13)} In only a few studies, however, has the conductivity in acetone been measured under high pressure.¹⁶⁻¹⁸⁾ Particularly, the conductivities of alkali ions in acetone have never been measured systematically under high pressure.

In this paper, therefore, the conductivities of LiI, NaI, KI and CsI were measured at 30.0°C up to 2070 kg/cm² in the concentration range $3 \times 10^{-4} - 5 \times 10^{-3} M$. We have found an interesting relation between the pressure coefficients of the Walden products and the crystal radii of the cations of the salts, combining these results with those of Adams and Laidler on Me₄NI, Et₄NI and *n*-Pr₄NI.¹⁶⁾ The structure of the ion pairs is also discussed.

Experimental

NaI, KI and CsI of an ultra pure reagent grade were dried to a constant weight at *ca.* 120°C for

- 5) P. Walden, H. Ulich and G. Busch, *Z. Physik. Chem.*, **123**, 429 (1926)
- 6) O.L. Hughes and H. Hartley, *Phil. Mag.*, **15**, 610 (1933)
- 7) J.F.J. Dippy, H.O. Jenkins and J. E. Page, *J. Chem. Soc.*, **1939**, 1386
- 8) J.F.J. Dippy and S.R.C. Hughes, *ibid.*, **1954**, 953
- 9) G.J. Janz and M.J. Tait, *Can. J. Chem.*, **45**, 1101 (1967)
- 10) M.J. McDowell and C.A. Kraus, *J. Amer. Chem. Soc.*, **73**, 3293 (1951)
- 11) L.G. Savedoff, *ibid.*, **88**, 664 (1966)
- 12) D.F. Evans, J. Thomas and J.A. Nadas, *J. Phys. Chem.*, **75**, 1714 (1971)
- 13) R.F. Prini and G. Atkinson, *ibid.*, **75**, 239 (1971)
- 14) M.B. Reynolds and C.A. Kraus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948)
- 15) P. C. Blokker, *Rec. Trav. Chim.*, **54**, 975 (1953)
- 16) (a) W.A. Adams and K.J. Laidler, *Can. J. Chem.*, **46**, 1977 (1968)
- (b) W.A. Adams and K.J. Laidler, *ibid.*, **46**, 1989 (1968)
- (c) W.A. Adams and K.J. Laidler, *ibid.*, **46**, 2005 (1968)
- 17) S.P. Sawin and C.A. Eckert, *J. Chem. Eng. Data*, **16**, 476 (1971)
- 18) I. Ishihara, *This Journal*, **47**, 102 (1977)

5 hours before use. Anhydrous LiI of an extra pure reagent grade was used after drying for one day *in vacuo* at 120°C without further purification, since its high solubility and high liability to oxidation when heated in solution make recrystallization difficult.¹⁹⁾ Acetone of a guaranteed grade was dried by allowing it to stay over molecular sieve 1/16" pellet of type 4A Linde overnight. The acetone was then distilled over a small amount of molecular sieve of 4A Linde through a Widmer column. The middle fraction of the distillate was kept in a dessicator and used within 24 hours after distillation. The Kahl-Fisher titrations and the gas-chromatographic measurements²⁰⁾ showed that most of the trace amount of water was effectively removed. Both measurements indicated ~0.0046% of water by weight in the treated acetone on the day after distillation.

The specific conductivities of the solvent were on the average 4.3×10^{-8} and $3.0 \times 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$ at atmospheric pressure and at 2070 kg/cm², respectively. Therefore, the solvent correction for conductivity was negligible.

The high-pressure generating apparatus and the conductivity cell under high pressure are shown in Fig. 1. The pressure in the vessel was measured with a Manganine gauge. The ground glass joint in the cell was carefully tightened to prevent the solvent from evaporating. Two cells of this type can be placed in the vessel.

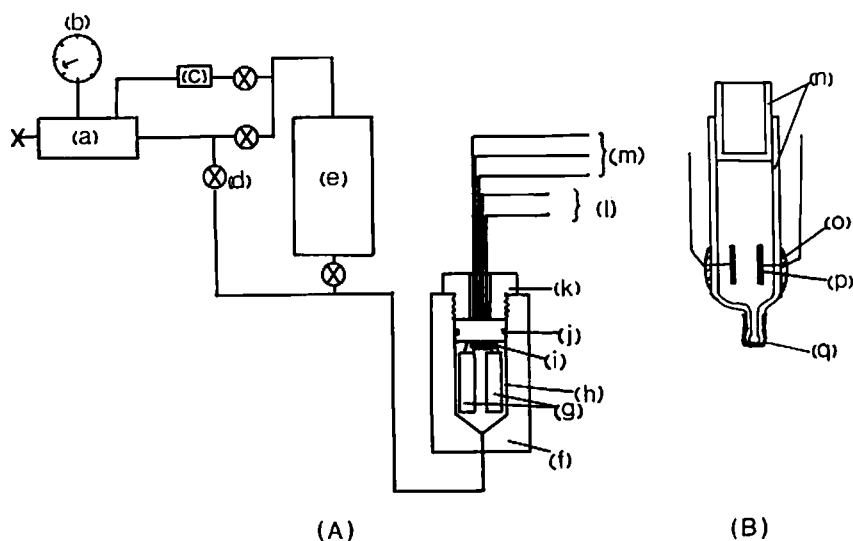


Fig. 1 High-pressure generating apparatus and conductivity cell.

(A) High-pressure generating apparatus

(a) Pressure generator, (b) Bourdon gauge, (c) Oil reservoir,

(d) Valve, (e) Intensifier, (f) High-pressure vessel,

(g) Conductivity cell, (h) Liquid paraffine, (i) Manganine coil,

(j) "O" ring, (k) Nut cover, (l) Wire leads from (i), (m) Wire leads from (g).

(B) High-pressure conductivity cell

(n) Glass syringe, (o) Araldite, (p) Platinum electrodes, (q) Teflon cap.

19) R.F. Prini and J.E. Prue, *Trans. Faraday Soc.*, **62**, 1257 (1966)

20) C.K. Mann, "Electroanalytical Chemistry," p. 69, ed. by A.J. Bard, Marcel Dekker, Inc., New York (1969) vol. 3

The conductivities in acetone were measured in the concentration range $3 \times 10^{-4} - 5 \times 10^{-3} \text{M}$. LiI, NaI and KI were readily soluble in this concentration range, but in the case of CsI, the solution had to be cooled with ice to increase its solubility and was stirred for several hours until a sufficient amount of CsI was dissolved. These solutions were kept in the dark in order to prevent them from decomposing.

The measurements were carried out at 30.0°C and at the pressures up to 2070kg/cm^2 where Bridgman's data on the viscosity of acetone are available.²¹⁾

Results

In order to analyse the data, the Shedlovsky extrapolation method was used.²²⁾ This is an iterative procedure to give the optimum values of the limiting molar conductivity, Λ° , and the association constant, K_A . These quantities are related by the following equations,

$$\begin{aligned} 1/\Lambda S(z) &= 1/\Lambda^\circ + C\Lambda S(z)f_{\pm}^2 K_A/\Lambda^{\circ 2}, \\ S(z) &= (z/2 + \sqrt{1 + (z/2)^2})^2, \\ z &= \alpha\sqrt{CA}/\Lambda^{\circ 3/2}, \\ \gamma &= S(z) \times \Lambda/\Lambda^\circ, \\ \log f_{\pm} &= -1.8246 \times 10^6 \times \sqrt{CT}/(\epsilon T)^{3/2}, \end{aligned} \quad (1)$$

where f_{\pm} is the mean rational activity coefficient and α is the Onsager coefficient.

The compressibilities, viscosities and dielectric constants of acetone under high pressure were taken from the data of Adams and Laidler,²³⁾ Bridgman²¹⁾ and Hartmann *et al.*,²⁴⁾ respectively. These

Table 1 Physical properties of acetone under high pressure^{21, 23, 24)}

$P, \text{kg/cm}^2$	$V(P)/V(1)$	$\eta(P)$, poise	$\epsilon(P)$
1	1.0000	0.00295	20.25
260	0.9722	0.00355	21.01
520	0.9508	0.00407	21.61
780	0.9334	0.00457	22.11
1040	0.9188	0.00504	22.54
1560	0.8950	0.00607	23.28
2070	0.8764	0.00713	23.88

values under high pressures are given in Table 1. The values of Λ° and K_A calculated from eq. (1) by the Shedlovsky extrapolation method at several pressures are given in Table 2.

In Fig. 2, the molar conductivity, Λ , is plotted against the square root of the concentration,

21) P.W. Bridgman, *Proc. Amer. Acad. Arts. Sci.*, **61**, 67 (1926)

22) R.M. Fuoss and T. Shedlovsky, *J. Amer. Chem. Soc.*, **71**, 1496 (1949)

23) W.A. Adams and K.J. Laidler, *Can. J. Chem.*, **45**, 123 (1967)

24) H. Hartmann, A. Neumann and G. Rinck, *Z. Physik. Chem. Neue Folge*, **44**, 204 (1965)

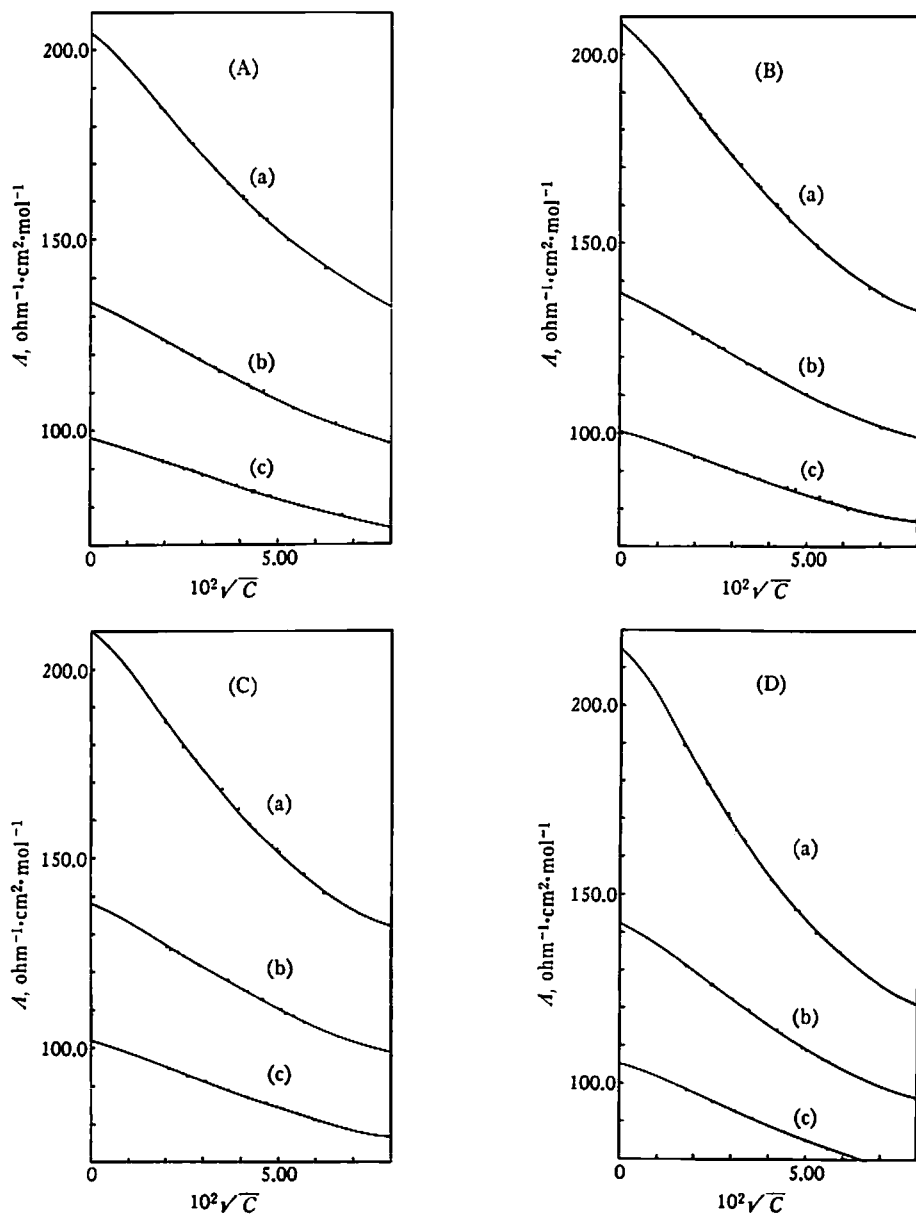


Fig. 2 Plot of Λ vs. \sqrt{C} .

(A) LiI, (B) NaI, (C) KI, (D) CsI.

(a) 1 atm, (b) 1040 kg/cm², (c) 2070 kg/cm².

Solid lines are drawn based on the Shedlovsky equation

\sqrt{C} , and the solid curves represent the relation between Λ and \sqrt{C} obtained from eq. (1) with the best fitted values of Λ° and K_A .

The Walden products, $\Lambda^\circ(P)\eta^\circ(P)$, and the relative Walden products, $\Lambda^\circ(P)\eta^\circ(P)/\Lambda^\circ(1)\eta^\circ(1)$, un-

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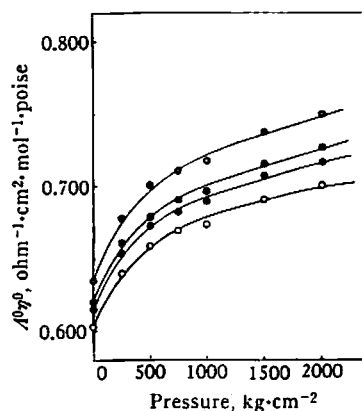


Fig. 3 Walden product vs. pressure.
○: LiI, ●: NaI, ⊗: KI, ⊙: CsI.

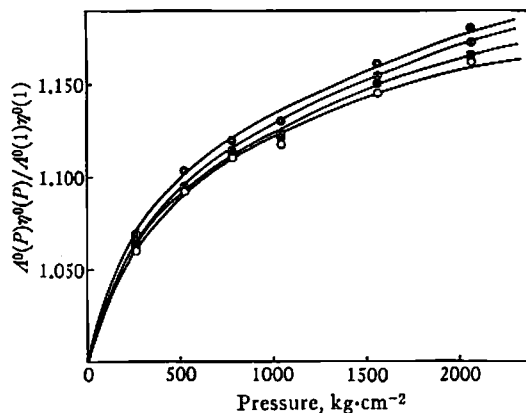


Fig. 4 Relative Walden product vs. pressure.
○: LiI, ●: NaI, ⊗: KI, ⊙: CsI.

der pressures are shown in Figs. 3²⁾ and 4, respectively. Unfortunately, the single ion mobility in acetone has not yet been determined under high pressure, so that the ionic solvations have to be discussed on the basis of these Walden products. From Figs. 3 and 4, the following features can be recognized.

1. The Walden products for all salts studied increase with increasing pressure.
2. The pressure coefficients of the Walden products increase in the order of $\text{LiI} < \text{NaI} < \text{KI} < \text{CsI}$.

The first feature has also been noted for the Walden products of Me_4NI , Et_4NI and $n\text{-Pr}_4\text{NI}$ ¹⁶⁾ and LiBr ¹⁸⁾ in acetone. By contrast, the Walden product of tri-*n*-propyl methyl ammonium iodide has been found to decrease with increasing pressure up to 3000atm.¹⁷⁾ Such a decrease in the Walden product with pressure disagrees with the tendency found for the other iodides. The reason for this

Table 2 $A^0(\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1})$ and $K_A(\text{mol}^{-1}\cdot\text{l})$ in acetone

Salt $P, \text{kg/cm}^2$	LiI		NaI		KI		CsI	
	A^*	K_A	A^*	K_A	A^*	K_A	A^*	K_A
1	204.5	161	208.4	193	210.0	210	215.2	344
260	180.3	125	184.2	145	186.3	165	190.9	261
520	162.0	105	165.4	117	166.9	131	172.2	213
780	146.5	87	149.4	89	151.2	107	155.5	165
1040	133.8	75	136.9	79	138.3	91	142.5	139
1560	113.8	56	116.7	60	117.9	69	121.6	106
2070	98.3	45	100.5	50	101.9	57	105.2	82

*2) It is well known that at 1atm the Walden product plotted against the reciprocal crystal radius of an ion lies on a curve with a maximum between the radii of Cs^+ and Me_4N^+ . Combining our results with those in Ref. 16, this is found to be the case for similar plots under high pressures.

discrepancy might be that Sawin and Eckert used much smaller pressure coefficient of the viscosity of acetone.

As can be seen from Table 2, the association constants increase with increasing crystal radius of the ion at any pressure investigated, *i. e.*, $K_A(\text{LiI}) < K_A(\text{NaI}) < K_A(\text{KI}) < K_A(\text{CsI})$. The reverse order of the association constants has been reported for NaI and KI at atmospheric pressure. This will be discussed below.

Discussion

Walden products

As is shown above, the sequence in the magnitude of the pressure coefficients of the Walden products for LiI, NaI, KI and CsI in acetone is very different from that observed in water.¹⁾ It will be shown here that the solvent relaxation theory²⁵⁾ can explain the sequence in the Walden products found in acetone as well as in water, when some approximations are introduced.

The Zwanzig equation is expressed in the form

$$\lambda^\circ \eta = Fe / (A_V \pi r + A_D \phi r^{-3}). \quad (2)$$

Then its pressure coefficient is written as follows,

$$\{\partial(\lambda^\circ \eta) / \partial P\}_T = -Fe(\partial \phi / \partial P)_T A_D / \{r^3(A_V \pi r + A_D \phi r^{-3})^2\}, \quad (3)$$

where

$$\phi = e^2(\epsilon_\infty - \epsilon_0)\tau / \{\epsilon_\infty(2\epsilon_\infty + 1)\eta\}. \quad (4)$$

In eqs. (2)–(4), F and e are the Faraday constant and the protonic charge, respectively; r is the ionic radius and is taken to be the crystal radius of an ion; A_V and A_D are the proportional constants of the viscous and dielectric friction coefficients; ϵ_0 and ϵ_∞ are the low- and infinite-frequency dielectric constants, and τ is the solvent relaxation time. To derive eq. (3), only ϕ is taken to depend on pressure, and A_V and A_D are assumed to be independent of pressure. Since eq. (3) is a function of an ionic crystal radius, r , the right-hand side of eq. (3) can be put as $f(r)$,

$$f(r) = \{\partial(\lambda^\circ \eta) / \partial P\}_T. \quad (5)$$

Then the first derivative of $f(r)$ with respect to the radius, r , can be given by,

$$f'(r) = Fe(\partial \phi / \partial P)_T A_D r^{-3} (A_V \pi r + A_D \phi r^{-3})^{-2} \times (5A_V \pi - 3A_D \phi r^{-4}). \quad (6)$$

In order to evaluate ϕ , the values of the relaxation times, τ , must be known. Since there is no available data on the relaxation time under high pressure, the following theoretical equation for τ derived by Debye is adopted in the calculation of ϕ ,

$$\tau = 4\pi a^3 \eta / kT, \quad (7)$$

where a is the effective dynamic radius of an acetone molecule and is taken to be equal to 1.5 \AA ¹³⁾. In eq. (4), neglecting unity which is small as compared with ϵ_∞ in the present case, the following expression for ϕ is obtained,

$$\phi \approx 2\pi e^2 a^3 (\epsilon_\infty - \epsilon_0) / (\epsilon_\infty^2 kT), \quad (4')$$

25) R. Zwanzig, *J. Chem. Phys.*, **52**, 3625 (1970)

and hence for its pressure coefficient, eq. (5) can be derived,

$$(\partial\phi/\partial P)_T \approx -2\pi e^2 a^3 \{ (\partial\epsilon_\infty/\partial P)_T + (\partial\epsilon_\infty/\partial P)_T - 2\epsilon_\infty (\partial\epsilon_\infty/\partial P)_T / \epsilon_\infty \} / (\epsilon_\infty^2 kT). \quad (5)$$

Since the second and the third terms in the brackets of the right-hand side of eq. (5) are very small²⁶⁾ as compared with the first term, eq. (5) can be approximated to

$$(\partial\phi/\partial P)_T \approx -2\pi e^2 a^3 (\partial\epsilon_\infty/\partial P)_T / (\epsilon_\infty^2 kT). \quad (5')$$

When we take $\epsilon_\infty \gg \epsilon_\infty$ into account, eq. (4') is further approximated to

$$\phi \approx 2\pi e^2 a^3 / \epsilon_\infty kT, \quad (8)$$

and then eq. (5') can also be rewritten as

$$(\partial\phi/\partial P)_T \approx -\phi (\partial\epsilon_\infty/\partial P)_T / \epsilon_\infty. \quad (9)$$

Because of the positive value of $(\partial\epsilon_\infty/\partial P)_T$ under any pressure investigated, $(\partial\phi/\partial P)_T$ is always negative. Therefore, from eq. (3), it is evident that the pressure coefficient of the Walden product derived on the basis of the solvent relaxation theory is always positive for any radius and has a maximum at $r_{max} = \{3A_D\phi/(5A_V\pi)\}^{1/4}$ as is easily seen from eq. (6). The theoretical curves, $\{\partial(\lambda^\circ\eta)/\partial P\}_T$ vs. r at various pressures, can be obtained from eqs. (3), (8) and (9) in the two limiting cases,²⁵⁾

(A) perfect sticking: $A_V=6$, $A_D=3/8$

(B) perfect slipping: $A_V=4$, $A_D=3/4$

(10)

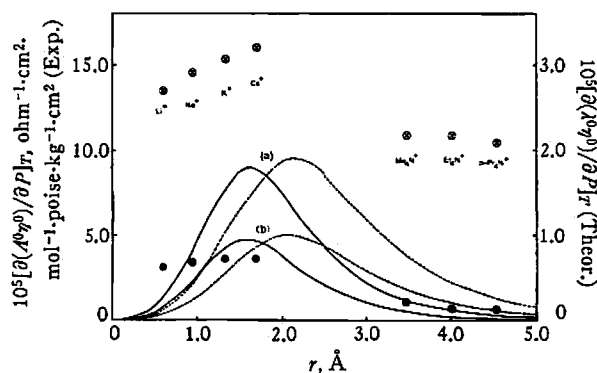


Fig. 5 Pressure coefficient of the Walden product vs. cationic crystal radius.

(a) 1 atm, (b) 1040 kg/cm².

⊗: 1 atm, ●: 1040 kg/cm².

The results calculated from the data of Adams and Laidler for Me₄NI, Et₄NI and *n*-Pr₄NI¹⁶⁾ are also shown. Solid lines (sticking) and dashed lines (slipping) represent the pressure coefficient of the Walden product calculated with eq. (3). Experimental results refer to the left-hand side scale, and theoretically drawn lines to the right-hand side scale.

They are shown in Fig. 5 together with the experimental results. The ionic radii are taken as 0.60, 0.95, 1.33 and 1.69 Å for Li⁺, Na⁺, K⁺ and Cs⁺, respectively.²⁷⁾ The results calculated from the data by Adams and Laidler for Me₄NI, Et₄NI and *n*-Pr₄NI are also shown together in Fig. 5. The values

26) R.M. Waxler, C.E. Weir and H.W. Schamp, Jr., *J. Res. Natl. Bur. Std.*, **68A**, 489 (1964)

27) R.A. Robinson and R.H. Stokes, "Electrolyte Solution," p.461, Butterworths Scientific Publications, London (1965)

of r_{max} calculated at 30°C at 1 atm are 1.6 and 2.1 Å in the case of (A) and (B), respectively.

Comparing the experimental results with the theoretical ones represented in Fig. 5, the following features are noted:

1. The experimental values of the pressure coefficients of the Walden products are positive as is predicted by the theory.
2. Each experimental curve seems to have a maximum between the radii of Cs^+ and Me_4N^+ , which is in line with the theoretically predicted results.
3. The pressure coefficient of the Walden product obtained varies with pressure in the same direction as is predicted by the theory.

Thus, as far as qualitative features are concerned, we can say that the experimental results in acetone are explained rather well from the viewpoint of the solvent relaxation theory. However, there are some remarkable discrepancies between the theory and experimental results in a quantitative sense. For example, in Fig. 5, the experimental results show much larger values than the theoretically calculated ones, even if it is taken into account that the experimental results include both cationic and anionic pressure coefficients of the Walden products. In order to get better quantitative agreement between the theory and the experimental results, the theory may have to be improved as suggested by Prini and Atkinson.¹³⁾ They emphasized the importance of dielectric saturation, dynamic viscosity and the effect of ion field on ϵ_∞ and τ of the solvent. Better agreement with the theory is seen when the experiment is carried out in acetone rather than water. This might be due to the fact that acetone is a less-structured solvent than water.

Ion pairs

The observed association constant increases with increasing ionic crystal radius of the cation, *i. e.*, $K_A(\text{LiI}) < K_A(\text{NaI}) < K_A(\text{KI}) < K_A(\text{CsI})$. This is the same tendency as that obtained for LiI and KI in acetone by Savedoff.¹¹⁾ Also, Janz and Tait predicted that KI would have a larger association constant than NaI. They recalculated these constants in solvents of lower dielectric constant to obtain a self-consistent set of results for NaI and KI.⁹⁾ Dippy *et al.*⁸⁾ and Walden *et al.*⁵⁾ reported the values for NaI and KI which contradict the present results. The association constants at atmospheric pressure have been determined from the conductivity measurements for other salts, Li-Picrate, Na-Picrate and K-Picrate,¹⁴⁾ LiClO_4 , NaClO_4 ²⁸⁾ and CsClO_4 ,²⁹⁾ LiCNS, NaCNS and KCNS,⁶⁾ and Na-Salicylate and K-Salicylate.⁷⁾ Among the salts which have a common anion, the sequence of the association constants against ionic crystal radii of cations is in the reverse order to that of alkali iodides studied here. Evans *et al.* have reported that the association constants increase with decreasing crystal size of a cation in acetone and some other non-aqueous solvents.³⁰⁾ They remarked that this should be the case for alkali iodides in acetone. However, it is not clear why all the alkali series should show the same association behavior in non-aqueous solvents in spite of the wide variety in the nature of anion, since

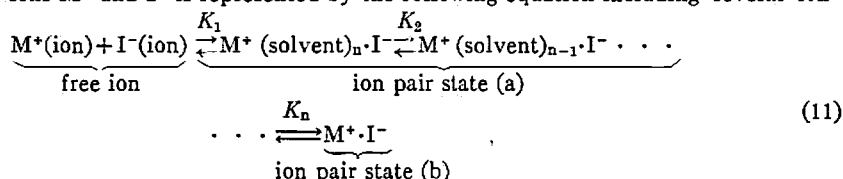
28) Accascina and Schiavo, *Ann. Chim. (Italy)*, **43**, 695(1953)

29) G. Pistoia and G. Pecci, *J. Phys. Chem.*, **74**, 1450 (1970)

30) D.F. Evans, C. Zawoyski, and R.L. Kay, *ibid.*, **69**, 3878 (1965)

as Kay has suggested, the interaction between the cation and anion is dependent on the nature of anion as well as that of cation³¹⁾.

From the IR spectroscopic studies, the association constants of LiI and NaI in acetone have been determined at 25°C to be 0.23 ± 0.02 and 0.11 ± 0.01 (mol/l)⁻¹, respectively.³²⁾ As is clear from a comparison with the values in Table 2, these values are not only smaller than those obtained here, but also inverted in magnitude, *i. e.*, $K_A(\text{LiI}) > K_A(\text{NaI})$. There is a possible explanation of the discrepancy between the results obtained from the IR measurements and those from the conductivity. In the conductivity studies, the ion pair is regarded as an entity in which the mutual electrical attraction of the opposite ions may be considerably greater than their thermal energy. On the other hand, in the spectroscopic studies so far, the ion pair has been detected only when both ions approach so closely that the perturbation on solvent molecules or the ion molecules themselves is sufficiently large to cause a spectroscopic change. Hence, the ion pair in the conductivity studies is generally defined in a wider sense than in the spectroscopic studies. Therefore, when the association process of the two opposite ions M^+ and I^- is represented by the following equation including several ion pair states,



the association constants obtained from the conductivity ($K_{A\text{cond}}$) and from the spectroscopic measurements ($K_{A\text{spect}}$) can be expressed by eqs. (12) and (13),

$$K_{A\text{cond}} = \frac{[\sum_{k=1}^n M^+(\text{solvent})_k \cdot I^-] + [M^+ \cdot I^-]}{[M^+][I^-]} \quad (12)$$

$$K_{A\text{spect}} = \frac{[M^+ \cdot I^-]}{\{[M^+] + [\sum_{k=1}^n M^+(\text{solvent})_k \cdot I^-]\} \{[I^-] + [\sum_{k=1}^n M^+(\text{solvent})_k \cdot I^-]\}} \quad (13)$$

Comparing eqs. (12) and (13), it is apparent that the association constants from the conductivity should always be larger than those from the spectroscopic measurements. Furthermore, it is not surprising to find that the association constants obtained from the two methods vary in the opposite way against ionic crystal radii because these two methods describe different equilibrium states.

In order to obtain information on the nature of the ion pairs formed between the alkali ions and iodide ion, a comparison was made between the closest approach distances of the ion pairs and the sum of the crystal radii. The former values were calculated from the Bjerrum equation given by,³³⁾

$$K_A = \frac{4\pi N}{1000} \times \left(\frac{e^2}{\epsilon kT} \right)^3 Q(b) \quad (14)$$

where b is a function of the closest approach distance. The results are summarized in Table 3.

Each ion pair has a closest approach distance larger than the sum of the crystal radii of a cation and an anion, except for the ion pair of CsI at lower pressures.

31) R.L. Kay, *J. Amer. Chem. Soc.*, **82**, 2099 (1960)

32) I.S. Pereygin and M.A. Klimchuk, *Zh. Fiz. Khim.*, **49**, 164 (1975)

33) R.A. Robinson and R.H. Stokes, "Electrolyte Solution," Butterworths Scientific Publications, Chap. 14 (1965)

Table 3 Closest approach distance of ion pair (Å)

Salt <i>P</i> , kg/cm ²	LiI	NaI	KI	CsI
1	4.5	4.1	3.9	3.3
1560	5.9	5.5	5.2	4.0
sum of crystal radii	2.76	3.11	3.49	3.85

The volume changes accompanying the ion pair formation were obtained based on the following thermodynamic equation,

$$\Delta V_A^\circ = -RT \left(\frac{\partial \ln K_A}{\partial P} \right)_T - RT\beta \quad (15)$$

where β is the compressibility of the solvent. The pressure coefficients of $\ln K_A$ in eq. (13) at 1 atm and 1560 kg/cm² were obtained from the slopes of the curves shown in Fig. 6. The results for the

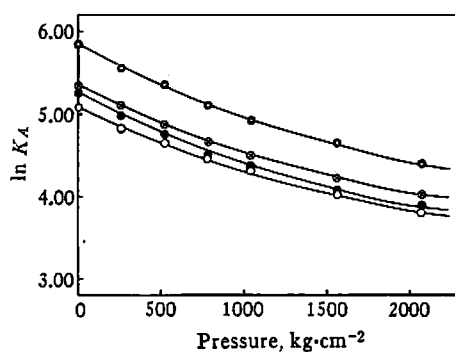


Fig. 6 Pressure dependence of $\ln K_A$.
○: LiI, ●: NaI, ⊗: KI, ⊙: CsI.

salts studied here are shown in Table 4.

Table 4 Volume change on association (cm³·mol⁻¹)

Salt <i>P</i> , kg/cm ²	LiI	NaI	KI	CsI
1	21	25	23	24
1560	12	12	11	12

When the volume change of an ion due to electrostriction in the process of dissolution is expressed in terms of the Born equation, it becomes as follows,

$$\Delta V_{el} = \left(\frac{\partial \Delta G_{el}}{\partial P} \right)_T = - \frac{Ne^2}{2\epsilon^2 r} \left(\frac{\partial \epsilon}{\partial P} \right)_T \quad (16)$$

For LiI and CsI, these values were calculated to be -99 and $-49\text{cm}^3\cdot\text{mol}^{-1}$, respectively. The absolute values for ΔV_{el} are larger compared with those for ΔV_A° . Taking into account that the sum of the intrinsic molar volumes of a cation and an anion is negligibly different from the intrinsic molar volume of the corresponding ion pair, the molar volume of the ion pair due to electrostriction is obtained as follows,

$$\bar{V}_{el}^\circ(\text{ip}) = \Delta V_A^\circ + [\bar{V}_{el}^\circ(\text{cat}) + \bar{V}_{el}^\circ(\text{an})] \quad ,$$

where

$$\begin{aligned} \Delta V_A^\circ &= \bar{V}^\circ(\text{ip}) - [\bar{V}^\circ(\text{cat}) + \bar{V}^\circ(\text{an})] \\ &= \bar{V}_{el}^\circ(\text{ip}) - [\bar{V}_{el}^\circ(\text{cat}) + \bar{V}_{el}^\circ(\text{an})] \quad , \end{aligned} \quad (17)$$

here $\bar{V}^\circ(\text{ip})$, $\bar{V}^\circ(\text{cat})$ and $\bar{V}^\circ(\text{an})$ are the partial molar volumes of the ion pair, cation and anion. The numerical values of $\bar{V}_{el}^\circ(\text{ip})$ for LiI and CsI calculated from eq. (17) are -78 and $-25\text{cm}^3\cdot\text{mol}^{-1}$, respectively. It means that the ion pairs in acetone interact considerably with the solvent molecules. From both the closest approach distances of the ion pairs and the volume changes upon association, which are given in Tables 3 and 4, it might be concluded that these ion pairs hold some solvent molecules between the cation and anion. As the crystal radius of a cation becomes larger, the fewer solvent molecules the ion pair holds, and as the pressure increases, the number of solvent separated ion pairs seems to increase.

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