

ELECTRICAL CONDUCTANCE OF LiBr IN ACETONE AT HIGH PRESSURE AND 25°C

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The electrical conductance of LiBr in anhydrous acetone was measured at 25°C up to 5000 kg/cm². The limiting equivalent conductance Λ° and the ion-pair dissociation constant K_A were determined by the Shedlovsky method: $\Lambda^\circ = 192 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{equiv.}^{-1}$, $K_A = 2.36 \times 10^{-4}$ mole/l at atmospheric pressure.

The closest approach distance of the ion pair, a , calculated by the Fuoss equation increases slightly with pressure. The volume change with the dissociation, $\Delta \bar{V}_a^\circ$, is $-25 \text{ cm}^3/\text{mole}$. Both a and $\Delta \bar{V}_a^\circ$ suggest that this ion pair would be considerably solvated.

Introduction

The dissociation constants of some salts in acetone at high pressure have been investigated by a few authors. Ershov *et al.* investigated the dissociation of KI in acetone in 1959¹⁾. Some tetraalkylammonium iodides were studied by Adams and Laidler in 1968 and the effects of pressure and temperature were discussed^{2,3)}. Now we have measured the electrical conductance of LiBr in acetone to investigate the dissociation constant and ion-solvent interaction at high pressure, and obtained Λ° and K_A by the Shedlovsky method. Furthermore the ionic Walden products, the ionic solvation numbers and the closest approach distance of the ion-pair were calculated to make some suggestions about the states of the ions and the ion pair. LiBr is often added in solution in the study of the complex ions, so the pressure effect on the dissociation of LiBr will be useful.

Experimental

The pressure vessel is similar to the one described in the previous paper⁴⁾. A jacket was attached to control the temperature at $25 \pm 0.02^\circ\text{C}$ by circulating liquid paraffin. Pressure generated up to 5000 kg/cm² was calibrated by inserting a manganin wire gauge and the inaccuracy of pressure was $\pm 2\%$. The conductance cell made of teflon⁵⁾ was fixed to the bottom plug of the vessel. The

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* $1 \text{ kg/cm}^2 = 0.9807 \times 10^5 \text{ Pa}$

- 1) Y. A. Ershov, M. G. Gonigberg, M. B. Neiman and A. A. Opekunov, *Proc. Acad. Sci. USSR (Phys. Chem. Sect. Trans.)*, **129**, 803 (1959)
- 2) W. A. Adams and K. J. Laidler, *Can. J. Chem.*, **46**, 1977, 1989 (1968)
- 3) W. A. Adams and K. J. Laidler, *ibid.*, **46**, 2005 (1968)
- 4) I. Ishihara, K. Hara and J. Osugi, *This Journal*, **44**, 11 (1974)
- 5) M. Ueno, K. Shimizu and J. Osugi, *ibid.*, **43**, 33 (1973)

platinum electrodes were slightly coated with platinum black. The cell constant at atmospheric pressure was determined by using 10^{-2} M aqueous solution of KCl⁶⁾ and the pressure effect on the cell constant was corrected for the compression of teflon⁷⁾. The resistance of each solution was measured twice by the conductivity outfit of Yanagimoto Co. Ltd. (model MY-8). The ultra pure reagent LiBr · (1~2)H₂O supplied by Merck was heated at 130~140°C for about 8 hr to make this salt completely anhydrous. The spectroscopic grade acetone (Nakarai Chemicals Ltd.) was distilled after mixing with molecular sieves (Linde Product 4A-1/16) for a day⁸⁾. The specific conductance κ° of the solvent was $(1.6\sim 3.2) \times 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$.

Results and Discussion

The equivalent conductance A of the electrolyte is given by

$$A = 10^3(\kappa - \kappa^{\circ})/C, \quad (1)$$

where κ is the specific conductance of the solution and C is the concentration in equiv./l which was corrected by the compression data of acetone by Bridgman⁹⁾. The dissociation constant K_d and the limiting equivalent conductance A° were determined from the Shedlovsky equation¹⁰⁾ with computer analysis:

$$1/A S(Z) = 1/A^{\circ} + C A S(Z) f_{\pm}^2 / K_d A^{\circ 2}, \quad (2)$$

$$S(Z) = \{Z/2 + (1 + Z^2/4)^{1/2}\}^2, \quad (3)$$

$$Z = \{8.204 \times 10^5 A^{\circ} / (D^{\circ} T)^{3/2} + 82.50 / \gamma^{\circ} (D^{\circ} T)^{1/2}\} (C A)^{1/2} / A^{\circ 3/2} \quad (4)$$

and

$$\alpha = S(Z) A / A^{\circ}, \quad (5)$$

where η° , D° , T , f_{\pm} and α are the viscosity, the dielectric constant of pure acetone, the temperature, the activity coefficient, and the degree of dissociation, respectively. In order to compute the viscosity of acetone at high pressure η_p° at 25°C, the following equation was employed, using the data of Bridgman¹¹⁾:

$$\eta_p^{\circ} = C_{\eta} \exp(E/RT), \quad (6)$$

where C_{η} and the activation energy E were independent of temperature¹²⁾. The viscosity at atmospheric pressure $\eta_{p=1}^{\circ}$ was cited from literature¹²⁾. The dielectric constant of acetone at high pressure D_p° was estimated by the Tait equation.

6) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1946)

7) C. E. Weir, *J. Res. NBS*, **53**, 245 (1954)

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9) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **49**, 3 (1913)

10) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, *J. Amer. Chem. Soc.*, **71**, 1496 (1949)

11) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **61**, 57 (1926)

12) M. B. Reynolds and C.A. Klaus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948)

$$1/D_p^\circ - 1/D_{p=1}^\circ = A \log((B+P)/(B+1)), \quad (7)$$

where A and B are constants; $AD_{p=1}^\circ = 0.2577^{13)}$, $D_{p=1}^\circ = 20.70^{14)}$ and $B = 755.7 \text{ bars}^{15)}$ at 25°C . The viscosity η° and the dielectric constant D° used are given in Table 1. A with its experimental errors and A° together with the literature values $A_{p=1}^\circ$ ^{12, 16, 17, 18)} are listed in Table 2. The curve of A vs. $C^{1/2}$ is shown in Fig. 1.

It is important to separate A° into the cationic and anionic limiting conductance so that we may get insight into the ion-solvent interactions. The limiting ionic conductances $\lambda^\circ(\text{Li}^+)$ and $\lambda^\circ(\text{Br}^-)$ can be estimated from $A_{p=1}^\circ$ by using the limiting transference number at each pressure $t_{p=1}^\circ$, and neglecting its pressure dependence:

$$t_{p=1}^\circ(\text{Li}^+) = t_{p=1}^\circ(\text{Li}^+) = \lambda_{p=1}^\circ(\text{Li}^+) / \{\lambda_{p=1}^\circ(\text{Li}^+) + \lambda_{p=1}^\circ(\text{Br}^-)\} = 0.386, \quad (8)$$

where the values of $\lambda_{p=1}^\circ(\text{Li}^+)$ and $\lambda_{p=1}^\circ(\text{Br}^-)$ were cited from the literature¹²⁾, 72.8 and 115.9 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{equiv}^{-1}$, respectively. The obtained values of $\lambda_{p=1}^\circ(\text{Li}^+)$ and $\lambda_{p=1}^\circ(\text{Br}^-)$ are also given in Table 2. To determine the effective radius of the lithium ion, Robinson-Stokes' method was applied. The Stokes radius of the ion r_s is defined by the Stokes-Einstein equation,

$$r_s = |z|eF / 6\pi\eta^\circ \lambda^\circ(\text{Li}^+), \quad (9)$$

where z , e and F are the ionic valence, the electronic charge and the Faraday constant, respectively. The effective radius of the solvated ion r_e is obtained using r_s as follows:

$$r_e = r_s \cdot f_{R-S}, \quad (10)$$

where f_{R-S} is called as the Robinson-Stokes correction factor¹⁹⁾. Just as in the case of water solvent, f_{R-S} of the ions in acetone was read from the plot of f_{R-S} vs. r_s for tetraalkylammonium ions which

Table 1 η° and D° of acetone at 25°C

P (kg/cm ²)	$\eta^\circ \times 10^3$ (poise)	D°
1	3.040	20.70
880	4.730	22.63
1950	6.899	24.10
2910	9.085	25.09
4030	12.7	26.02
4970	15.59	26.70

- 13) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943)
 14) A. A. Mayott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids", NBC Circular, 514, Aug. 10 (1951)
 15) W. A. Adams and K. J. Laidler, *Can. J. Chem.*, **45**, 123 (1967)
 16) L. G. Savedoff, *J. Amer. Chem. Soc.*, **88**, 664 (1966)
 17) D. Dobos, "Electrochemical Data", Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York (1975), p. 89
 18) H. Ulich, *Trans. Faraday Soc.*, **23**, 388 (1927)
 19) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed., Butterworth and Co. Ltd., London (1959), p. 120-126

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Table 2. A , A' , λ^* (Li⁺) and λ^* (Br⁻) ($\Omega^{-1}\text{-cm}^2 \cdot \text{equiv}^{-1}$)

P (kg/cm ²)	$C \times 10^3$ (mole/l)	A	A'	λ^* (Li ⁺)	λ^* (Br ⁻)
1	8,889	6.833	3.078	0.9453	0.6448
	35.25 ± 0.05	38.72 ± 0.04	52.86 ± 0.06	80.38 ± 0.05	89.47 ± 0.04
880	9,495	7.299	3.288	1.010	0.6887
	36.11 ± 0.14	39.47 ± 0.04	52.32 ± 0.06	73.92 ± 0.03	79.81 ± 0.03
1950	10,05	7.724	3.480	1.069	0.7289
	33.09 ± 0.03	36.00 ± 0.03	46.15 ± 0.07	61.31 ± 0.27	64.92 ± 0.45
2950	10,41	8.005	3.606	1.107	0.7554
	29.67 ± 0.04	32.07 ± 0.02	39.89 ± 0.06	51.04 ± 0.09	53.52 ± 0.23
4030	10,76	8.270	3.725	1.144	0.7804
	25.79 ± 0.00	27.76 ± 0.02	33.95 ± 0.01	41.80 ± 0.02	42.83 ± 0.02
4970	11,00	8.459	3.810	1.170	0.7982
	22.70 ± 0.05	24.37 ± 0.01	29.12 ± 0.07	35.24 ± 0.07	35.96 ± 0.22

a) From ref. (16)

b) From ref. (12)

c) From ref. (17)

d) From ref. (18)

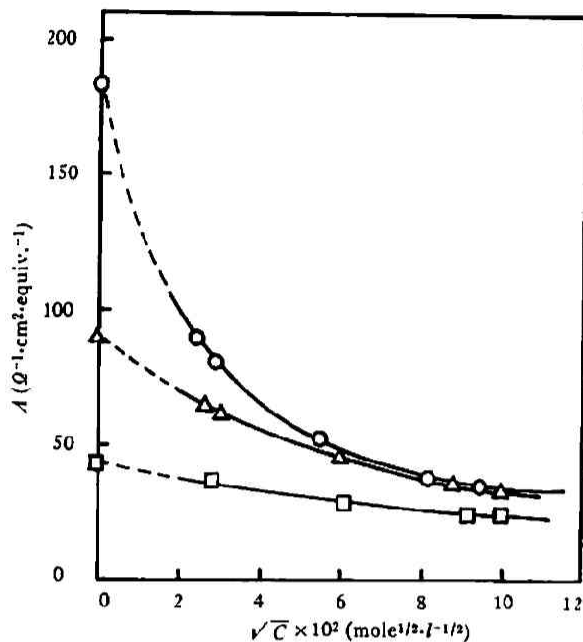


Fig. 1 Equivalent conductance of LiBr in acetone at 25°C

○: 1 kg/cm²
 △: 1950 kg/cm²
 □: 4970 kg/cm²

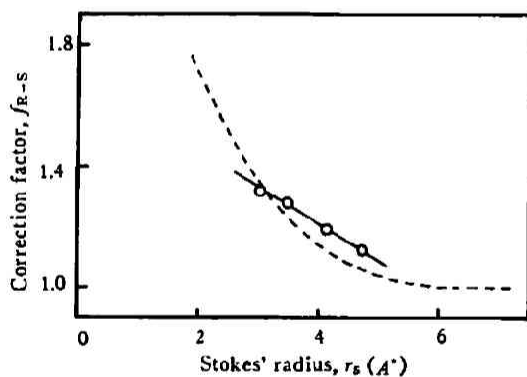


Fig. 2 Correction factor for Stokes' law at 25°C

The full line is based on the data for acetone of Table 3, the broken curve is for water by Robinson and Stokes¹⁹.

are assumed to be little solvated in acetone. Fig. 2 shows the curves for tetraalkylammonium ions in water by Robinson and Stokes¹⁹), and in acetone based on the literature values^{12,20)} (Table 3). The latter was applied in the calculation of $r_s(\text{Li}^+)$.

The ionic Walden product, $W = \lambda^\circ \gamma^\circ$, can be expressed by the modified Stokes equation²¹⁾

$$W = \lambda^\circ \gamma^\circ = |z|eF/C_s r_s \quad (11)$$

where C_s is the hydrodynamic parameter which is a function of r_s . The Walden products of both

20) M. J. McDowell and C. A. Kraus, *J. Amer. Chem. Soc.*, **73**, 3293 (1951)

21) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **92**, 785 (1971)

Table 3 f_{R-S} of tetraalkylammonium ions in acetone at 25°C

ion	λ^*	r_s	f_{R-S}
(C ₂ H ₅) ₄ N ⁺	91.2 ^{a)}	2.96	1.35
(C ₃ H ₇) ₄ N ⁺	78.3 ^{b)}	3.44	1.31
(C ₄ H ₉) ₄ N ⁺	67.1 ^{a)}	4.02	1.23
(C ₅ H ₁₁) ₄ N ⁺	58.5 ^{b)}	4.61	1.15

a) From ref. (12)

b) From ref. (20)

Table 4 Walden product of each ion at 25°C

P (kg/cm ²)	$\lambda^*\eta^*(Li^+)$	$\lambda^*\eta^*(Br^-)$
1	0.225	0.358
880	0.241	0.383
1950	0.245	0.390
2910	0.246	0.391
4030	0.251	0.400
4970	0.262	0.416

ions increase with pressure (Table 4).

The solvation number of lithium ion, $h(Li^+)$ is calculated as follows :

$$h(Li^+) = (4/3)\pi\{r_o^3(Li^+) - r_c^3(Li^+)\} / V_{ac}^{shell} \quad (12)$$

where $r_c(Li^+)$ is the crystal radius of lithium ion (0.60 Å²²) and V_{ac}^{shell} is the molecular volume of acetone in the solvation shell. Two trials (i) and (ii) were made in the estimation of V_{ac}^{shell} to calculate $h(Li^+)$ as follows.

(i) If V_{ac}^{shell} could be assumed to be equal to the molecular volume of the bulk acetone V_{ac} at each pressure, it was calculated by the compression data of Bridgman⁹⁾ and V_{ac} at atmospheric pressure and 25°C²³⁾. These results are given in Table 5 as trial (i). The approximation of this method being taken into account¹⁹⁾, it is reasonable to regard that the solvation number to change scarcely with pressure: the average value is 3.2.

(ii) If the acetone molecule in the shell could be assumed to be compressed ultimately, V_{ac}^{shell} might be regarded as almost independent of pressure. The bulk acetone at 20°C is compressed by a factor of about 0.76 at 8000 kg/cm² and it freezes at higher pressure. So, V_{ac}^{shell} was assumed to be less than V_{ac} by a factor of 0.75 at atmospheric pressure and 25°C and estimated to be 92 Å³/molecule. The solvation number $h(Li^+)$ seems to decrease with pressure as given in Table 5 as trial (ii).

In the trial (i) which gives $h(Li^+)$ would be almost independent of pressure, V_{ac}^{shell} and the

22) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca (1960)

23) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry", vol. 2, Organic Solvents, 3rd Ed., Wiley-Interscience, New York etc. (1970)

Table 5 $r_e(\text{Li}^+)$, V_{nc} and $h(\text{Li}^+)$ at 25°C

P (kg/cm ²)	$r_e(\text{Li}^+)$	$V_{nc}(\text{Å}^3/\text{molecule})$	$h(\text{Li}^+)$ by trial (i)	$h(\text{Li}^+)$ by trial (ii)
1	4.66	123	3.4	4.6
880	4.45	115	3.2	4.0
1950	4.41	109	3.3	3.9
2910	4.41	105	3.4	3.9
4030	4.34	102	3.4	3.7
4970	4.23	99.3	3.2	3.4

pressure dependence would be overestimated in view of the electrostriction. The trial (ii) gives the diminution of $h(\text{Li}^+)$ with increasing pressure, but this seems to be rather difficult to consider the meaning because the solvation energy increases with pressure. The assumptions in calculating the solvation number being taken into account, it would be rather hard to get definite conclusion, but, if the acetone molecule in the shell could be assumed not to be in the bulk or crystalline state but in the intermediate one, two trials would be regarded to be both extremes and the solvation number would lie between two extreme values. So it could be concluded that the solvation number would not change so much with pressure in acetone as in the case of some aqueous electrolyte solutions^{5, 24}.

In the pressure range examined, $r_a(\text{Br}^-)$ is 2.29~1.97 Å which is smaller than that of any tetraalkylammonium ions in Table 3, so that f_{B-S} of bromide ion can not be obtained without the extrapolation of Fig. 2. Thus the calculated values of $h(\text{Br}^-)$ is less reliable than $h(\text{Li}^+)$ though it would be small. The trials (i) and (ii) as used in the case of lithium ion give the solvation number of bromide ion, $h(\text{Br}^-)=0.9$ and 1.1 as average, respectively.

To study the state of the solvation of the ion pair, the closest approach distance of the ion pair, a , was calculated from the Fuoss equation²⁵,

$$K_d = (3000/4\pi N a^2) \exp\{-|z^+ \cdot z^-| e^2 / (a D k T)\}, \quad (13)$$

where N and k are Avogadro's number and the Boltzmann constant, respectively. The results are shown in Table 6. a seems to increase a little with pressure. The values of a of the ion pairs $\text{Li}^+ \cdot \text{Cl}^-$ and $\text{Li}^+ \cdot \text{I}^-$ are 1.59 Å and 4.05 Å at atmospheric pressure, respectively, when the values of K_d from literature¹⁶ are substituted in Eq. (13). $\text{Li}^+ \cdot \text{Cl}^-$ is regarded as the contact ion pair and $\text{Li}^+ \cdot \text{I}^-$ the separated one. $\text{Li}^+ \cdot \text{Br}^-$ would be in the intermediate between these two¹⁶. As a increases with pressure, the ion pair $\text{Li}^+ \cdot \text{Br}^-$ can be regarded to be more separated at high pressure.

The ion pair $\text{Li}^+ \cdot \text{Br}^-$ dissociates as



24) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970); M. Nakahara and J. Osugi, *ibid.* **45**, 69 (1976)

25) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958)

Table 6 Dissociation constant K_d and the closest approach distance of the the ion pair, a , at 25°C

P (kg/cm ²)	K_d (mole/l)	a (Å)
1	2.36×10^{-4}	2.29 (2.55)*
880	6.30×10^{-4}	2.28
1950	1.32×10^{-3}	2.30
2910	2.17×10^{-3}	2.33
4030	3.40×10^{-3}	2.37
4970	4.57×10^{-3}	2.40

* Sum of the crystal radii

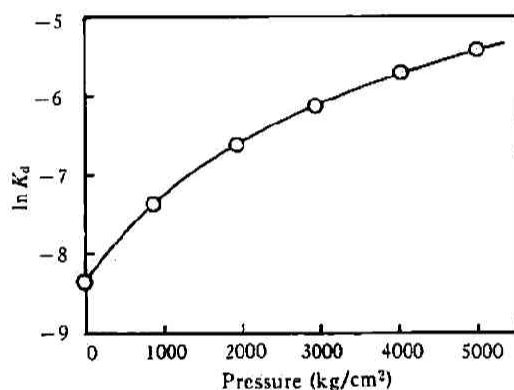


Fig. 3 Dissociation constant of LiBr in acetone at high pressure and 25°C

The volume change accompanying the dissociation is formulated²⁶⁾ by

$$\Delta \bar{V}_d^{\circ} = -RT(\partial \ln K_d / \partial P)_T + \Delta \nu RT\beta \quad (14)$$

where R is the gas constant, $\Delta \nu$ the change of the number of molecules on both sides of equilibrium (I) and β the compressibility of acetone. The plot of K_d against pressure is shown in Fig. 3. β is calculated by the Tait equation, *i. e.*, $\beta = C_{\beta} / (B + P)$, where B and C_{β} are the constants, B introduced in Eq. (7), $C_{\beta} = 931 \times 10^{-4}$ ¹⁵⁾. As the result, $\Delta \bar{V}_d^{\circ} = -25$ cm³/mole at atmospheric pressure. The values of $\Delta \bar{V}_d^{\circ}$ of Me₄NI, Et₄NI and *n*-Pr₄NI in acetone were reported by Adams and Laidler to be -27 ± 2 , -17 ± 1 and -15 ± 1 cm³/mole, respectively, at 26.6°C and atmospheric pressure²⁾. The volume change of Li⁺ · Br⁻ is comparable with that of Me₄N⁺ · I⁻.

The volume change $\Delta \bar{V}_d^{\circ}$ is expressed by the partial molal volume of each species

$$\Delta \bar{V}_d^{\circ} = \bar{V}^{\circ}(\text{Li}^+) + \bar{V}^{\circ}(\text{Br}^-) - \bar{V}^{\circ}(\text{Li}^+ \cdot \text{Br}^-). \quad (15)$$

If we assume that the partial molal volume of each species is given by

26) S. D. Hamann, "Physico-Chemical Effects of Pressure". Chap. 8, Butterworths Scientific Pub., London (1957)

$$\bar{V}^{\circ} = \bar{V}^{\circ}_{\text{int}} + \bar{V}^{\circ}_{\text{el}} \quad (16)$$

where $\bar{V}^{\circ}_{\text{int}}$ is the intrinsic partial molal volume and $\bar{V}^{\circ}_{\text{el}}$ is the partial molal volume due to electrostriction, and if $\bar{V}^{\circ}_{\text{int}}$ is approximated as,

$$\bar{V}^{\circ}_{\text{int}}(\text{Li}^+ \cdot \text{Br}^-) \approx \bar{V}^{\circ}_{\text{int}}(\text{Li}^+) + \bar{V}^{\circ}_{\text{int}}(\text{Br}^-), \quad (17)$$

we can get

$$\Delta \bar{V}^{\circ}_{\text{el}} = \bar{V}^{\circ}_{\text{el}}(\text{Li}^+) + \bar{V}^{\circ}_{\text{el}}(\text{Br}^-) - \bar{V}^{\circ}_{\text{el}}(\text{Li}^+ \cdot \text{Br}^-). \quad (18)$$

By the electrostriction theory, the volume change of the ionic equilibrium is estimated by

$$\bar{V}^{\circ}_{\text{el}} = -(Nz^2e^2/2r_1D^2)(\partial D/\partial P), \quad (19)$$

where N is Avogadro's number and r_1 is the ionic radius. Using the values of $r_1(\text{Li}^+)$ and $r_1(\text{Br}^-)$ which were given by Pauling²²⁾ to be 0.60 Å and 1.95 Å, respectively, the value of $\bar{V}^{\circ}_{\text{el}}$ of each ion can be calculated, and $\bar{V}^{\circ}_{\text{el}}(\text{Li}^+) + \bar{V}^{\circ}_{\text{el}}(\text{Br}^-)$ is obtained to be $-108 \text{ cm}^3/\text{mole}$ which is much more negative than the experimentally determined volume change, $\Delta \bar{V}^{\circ}_{\text{el}}$. So, $\bar{V}^{\circ}_{\text{el}}(\text{Li}^+ \cdot \text{Br}^-)$ would be rather largely negative. This would suggest that $\text{Li}^+ \cdot \text{Br}^-$ is a considerably solvated ion pair as discussed in terms of the closest approach distance.

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