

force of interaction is assumed proportional to the relative velocity, a simple force balance for a fully developed (steady-state) flow of solvent through an ion-exchange membrane induced by osmotic pressure difference yields

$$(\Delta P)A = (f_{iW} + f_{wW})U_w \quad (2)$$

where ΔP is the osmotic pressure difference across the ion-exchange membrane, atm; U_w is the velocity of solvent relative to the membrane pore wall ($=\Delta V/At$), cm/sec; f_{iW} and f_{wW} are the interaction coefficients (dynes sec/cm) between ion-water and water-membrane, respectively. Similar considerations for ion and water transport during the interchange of univalent cations with hydrogen lead to the relationship³

$$\frac{w_T}{W_D} = \frac{f_{iW*}}{f_{iW*} + f_{wW}} \quad (3)$$

where w_T/W_D is the ratio of net water transport (in the direction of the large counterion) to membrane equivalent moisture content, and f_{iW*} is the interaction coefficient between the large counterion and water. (Since the large counterion exerts the major control over the magnitude of net water transport during ion interchange, the interaction coefficient between hydrogen-water is assumed negligible in this development.) By combination of eq 2 and 3 individual interaction coefficients between counterion-water and water-membrane pore wall may be estimated.

Samples of such values of friction coefficients calculated by eq 2 and 3 for the interchange of potassium, sodium, and lithium with hydrogen are given in Table V. It may be noted that the value for the interaction be-

(10) K. S. Spiegler, *Trans. Faraday Soc.*, **54**, 1409 (1958).

tween the water and the membrane pore wall does not vary markedly over a change of fourfold in the ion-water interaction for the inorganic cations. A similar calculation for the organic cations yields considerably higher values for the ion-water interaction coefficient and much lower values for the water-membrane pore wall interaction term. These results may indicate a substantial difference in the location of the organic cation from that of the inorganic one relative to the membrane pore wall. Indeed, the heteropolar nature of the organic cation would suggest its location closer to the polymer wall. The increase in the value of the ion-water interaction coefficient with increasing ionic size for the univalent inorganic and organic cations showed linear dependence of ion-water interaction coefficient on counterion diameter.

Table V. Ion-Water and Water-Membrane Interaction Coefficients

Membrane no.	Ion-pair exchange system	Interaction coefficients, dynes sec cm ⁻¹ × 10 ⁴	
		f_{iW*}	f_{wW}
1	K ⁺ -H ⁺	K ⁺ , 0.98	1.9
	Na ⁺ -H ⁺	Na ⁺ , 2.2	2.2
	Li ⁺ -H ⁺	Li ⁺ , 3.9	1.5
	(CH ₃) ₄ N ⁺ -H ⁺	(CH ₃) ₄ N ⁺ , 4.8	Av 1.9
	(C ₂ H ₅) ₄ N ⁺ -H ⁺	(C ₂ H ₅) ₄ N ⁺ , >6.3	<0

Acknowledgment. The authors are indebted to the National Research Council, Ottawa, Canada, and the President's Advisory Committee on Scientific Research, University of Toronto, for financial support.

Conductance of Electrolytes in Anhydrous Acetone

Lydia G. Savedoff¹

Contribution from the Department of Chemistry, University of California, Los Angeles, California. Received August 30, 1965

Abstract: The conductances of a number of lithium and tetra-*n*-butylammonium salts in anhydrous acetone were measured at 25° and the data analyzed by the Shedlovsky method. The limiting conductances (Λ_0) and the ion-pair dissociation constants ($K_D \times 10^4$) are as follows: LiCl, 214, 0.033; LiBr, 194, 2.19; LiI, 195.0, 69.1; lithium *p*-toluenesulfonate, 172, 0.096; tetra-*n*-butylammonium chloride, 188, 16.6; tetra-*n*-butylammonium *p*-toluenesulfonate, 151.6, 24.6. It is suggested that in the LiCl ion pair the unsolvated ions are in contact, while in LiI the ion pair is formed from fully solvated ions. LiBr represents an intermediate case with some solvent included within the ion pair.

In the course of an investigation of second-order rates for SN₂ reactions of lithium and tetra-*n*-butylammonium halides in acetone, Winstein and co-workers² observed that the nucleophilicities of the tetra-*n*-butylammonium halides showed the order Cl > Br > I, the exact opposite of the commonly accepted order

which was based on the reactions of lithium halides as nucleophiles.³ Their results could be explained upon assuming an order of Cl > Br > I for the nucleophilicities of the free halide ions and that the reversal of this order, observed when lithium halides are used as nucleophiles, is a consequence of ion association. In order to

(1) National Science Foundation Science Faculty Fellow, 1959-1960; San Fernando Valley State College, Northridge, Calif. 91326.

(2) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **9**, 24 (1960).

(3) E.g., A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 258; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 160.

test this hypothesis, it was necessary to know the extent of association of the salts in question. Although data were available in the literature (see Table II and references), some were of questionable reliability. The measurements reported in this paper were undertaken to provide the information necessary for a test of the above hypothesis.

Experimental Section

The methods of purification of the solvent and for the handling of the salts used in this research follow the practices of Winstein and his associates in their kinetic studies.

Purification of the Solvent. Baker's analyzed reagent grade acetone was purified by the method of Smith, Fainberg, and Winstein.⁴ The acetone was distilled directly into the storage vessel through a 12-in. packed column. Freshly prepared solvent was used for each conductance run. Acetone purified in this way was found to give no reaction to Karl Fisher reagent when the titration was carried out in a solvent composed of equal parts of methanol and pyridine. This indicates a water content of less than 0.005%. The specific conductance of various batches of solvent varied from 0.49 to 1.66 ($\times 10^{-8}$) $\text{ohm}^{-1} \text{cm}^{-1}$. Since the density of the acetone prepared in this way was found to agree with that reported by Reynolds and Kraus,⁵ the values of the physical constants obtained by these authors were adopted for this research. These data are as follows: density, 0.7845 g ml^{-1} ; viscosity, 3.040×10^{-3} poise; and dielectric constant, 20.47.

Purification of the Salts. LiCl. Merck A.R. grade lithium chloride was recrystallized twice from distilled water and once from conductance water, then dried in a vacuum oven at 110°. Immediately before use, the salt was dried to constant weight over P_2O_5 *in vacuo* at 110° in an Abderhalden drying apparatus. (Unless otherwise indicated, this drying procedure was followed for the drying of salts throughout the research.)

LiBr. Mallinckrodt N.F. lithium bromide was recrystallized twice from conductivity water and dried in a vacuum desiccator at room temperature.

LiI was prepared by Dr. Stanley G. Smith by treating Li_2CO_3 with HI solution. The salt was recrystallized from ethyl acetate-pentane mixtures and then from conductance water.

KI. Baker's A.R. salt was recrystallized twice from conductance water.

Li *p*-toluenesulfonate was prepared by Dr. Paul E. Klinedinst, Jr.⁶

Tetra-*n*-butylammonium *p*-toluenesulfonate was prepared by Dr. Klinedinst.⁶

Tetra-*n*-butylammonium chloride was prepared by Dr. Smith from the corresponding bromide, converting it first to the methoxide by treatment with silver oxide in methanol and then neutralizing with hydrochloric acid. The solvent was removed and the salt recrystallized from a methyl acetate-pentane solution. The product was dried over KOH at 56° *in vacuo* for 20 hr. Before use, the salt was dried overnight, as above, and then at 110° over P_2O_5 for 15 min. Under the latter conditions, the salt fuses.

Preparation of Solutions. The initial concentration of each of the salt solutions was prepared by weight. The salts (except the tetrabutylammonium chloride) were weighed on an Ainsworth microbalance. All weighings were carried out in a closed container. The boat used in drying the tetrabutylammonium chloride was too heavy to be weighed on the microbalance, and a standard analytical balance was used. Large enough samples were used so that errors in weighing were limited to a maximum of one part per thousand. All subsequent solutions were prepared from the initial solution by the dilution method. The solution weighings were performed on a large capacity Seko balance. Care was taken to protect the solutions and the solvent from the moisture in the air during transfer operations.

Conductance Measurements. The apparatus used for this work is described elsewhere.^{7,8} All measurements were carried out at 25° in a cell with a constant of 0.1473 cm^{-1} . The temperature variation was less than $\pm 0.01^\circ$. The cell and contents were equilibrated

(4) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(5) M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948).

(6) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).

(7) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

(8) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947).

for about 1 hr before the first reading was made, then shaken, and again allowed to come to equilibrium. The average of three such readings was taken and used in calculating the conductance. A

Table I. Conductance of Several Salts in Acetone at 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Lithium Chloride			
Run A		Run B	
(31.670) ^a	(7.221)	(34.778)	(6.763)
(17.203)	(9.643)	(24.396)	(8.052)
(11.238)	(11.825)	(12.694)	(11.076)
8.1252	13.813	5.7903	16.167
5.4137	16.749	1.9792	26.755
3.4985	20.582	0.87296	38.924
2.2850	25.073	0.32520	59.170
1.7051	28.692	0.13251	83.954
0.75307	41.329		
0.45947	51.071		
0.26355	64.129		
Lithium Bromide			
Run A		Run B	
11.238	72.281	9.0925	80.131
6.2934	87.957	5.5950	94.089
2.4812	115.03	2.5883	117.85
0.97669	140.92	1.0913	143.80
0.44887	157.96	0.44101	165.94
0.16003	176.85	0.15000	182.47
		0.029678	192.89
Lithium Bromide Potassium Iodide			
Run C			
16.155	65.676	17.272	153.10
10.696	76.237	11.251	161.06
4.3180	102.69	5.8466	171.35
1.9002	128.46	2.7428	180.46
0.72475	156.12	1.2602	186.74
0.31902	173.66	0.57771	190.85
0.11170	188.61	0.23817	193.61
Lithium Iodide			
Run A		Run B	
(18.313)	(153.67)	10.473	162.54
7.8043	167.56	5.6198	171.56
4.1303	175.52	2.4658	179.70
2.2825	181.05	1.4867	183.72
0.79659	187.55	0.57895	188.34
0.46122	189.42	0.23894	190.94
0.19793	191.50	0.07753	193.78
0.10194	192.12		
Lithium <i>p</i> -Toluenesulfonate			
Run A		Run B	
(8.4379)	(16.994)	(8.8113)	(16.595)
(5.0716)	(22.149)	(5.5180)	(21.251)
(3.1300)	(28.072)	(2.8609)	(29.299)
1.1954	43.389	1.6878	37.338
0.60598	57.365	0.65220	55.716
0.31955	72.854	0.27380	76.854
0.12800	97.716		
Tetra- <i>n</i> -butylammonium Chloride			
Run A		Run B	
16.554	121.42	13.851	124.12
9.8236	134.39	9.3973	133.54
5.5206	147.29	5.8570	144.04
2.6073	161.00	3.6628	153.20
0.91857	173.73	1.9719	162.94
0.39297	179.85	0.97748	170.77
0.14557	184.06	0.40639	177.61
		0.14973	182.21
Tetra- <i>n</i> -butylammonium <i>p</i> -Toluenesulfonate			
Run A		Run B	
9.9540	113.22	7.8461	117.23
6.2603	120.92	5.7793	122.11
3.1881	130.18	3.1422	130.32
1.2616	139.32	1.4002	138.25
0.50378	144.81	0.63130	143.30
0.23106	147.64	0.24259	147.08
0.084163	150.45	0.087200	149.96

^a The points enclosed in parentheses were deleted from the final analysis because of deviations from linearity in the Shedlovsky plot.

Table II. Constants of Several Salts in Acetone at 25°

Salt	This research		Previous work			
	Λ_0	$K_D \times 10^4$	Λ_0	$K_D \times 10^4$		
LiCl ^a	214 ± 4	0.033 ± 0.001				
LiBr	194 ± 3	2.19 ± 0.07		(160) ^b		(5.0) ^c
LiI ^a	195.0 ± 0.2	69.1 ± 1.6			5.02 ^d	
Li <i>p</i> -toluenesulfonate	172 ± 2.5	0.096 ± 0.003				
KI	197.52 ± 0.08	55.7 ± 0.3	192.8	(192.8)	80.2	(67.4) ^e
			196.6	(197.0)	91.3	(62.9) ^f
Tetrabutylammonium chloride	188 ± 2	16.6 ± 1.0	172.3	(172.2)	22.8	(24.3) ^g
Tetrabutylammonium <i>p</i> -toluenesulfonate	151.6 ± 0.2	24.6 ± 0.3				

^a Farhat-Aziz and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 2635 (1959), give equations showing the temperature dependence of K_D from which a value at 25° may be determined. The equations are based on data of S. V. Serkov, *J. Russ. Phys. Chem. Soc.*, **40**, 413 (1908); N. L. Ross Kane, *Ann. Rept. Progr. Chem.* (Chem Soc. London), **27**, 351 (1930); and P. C. Blokker, *Rec. Trav. Chim.*, **54**, 975 (1935). These data are not of comparable reliability to the other values on which this table is based, so these values have been omitted. ^b Values in parentheses have been recalculated from the prime data by the Shedlovsky⁹ method. ^c J. F. J. Dippy, H. O. Jenkins, and J. E. Page, *J. Chem. Soc.*, 1386 (1939). ^d L. J. LeRoux and E. R. Swart, *ibid.*, 1475 (1955). ^e See ref. 5. ^f J. F. J. Dippy and S. R. C. Hughes, *J. Chem. Soc.*, 953 (1954). ^g M. J. McDowell and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 3293 (1951).

frequency of 2000 cps was used throughout except for a few solutions of very low resistance for which the Wagner ground could only be balanced at higher frequencies.

Results

The equivalent conductances at infinite dilution, Λ_0 , and the ion-pair dissociation constants, K_D , were calculated using the Shedlovsky⁹ method. The measured equivalent conductances and concentrations for all the salts included in this study are given in Table I. The reported values of Λ_0 and K_D given in Table II were determined from a plot combining all the valid data obtained in duplicate runs. The precision measure given in this table is calculated from the standard deviation of the slope and intercept of the least-squares data in the final plot. These values were obtained by applying standard statistical equations.¹⁰ The computations were programmed for the IBM 709 (later 7090) at the Western Data Processing Center. Preliminary computations were made and a Shedlovsky plot made of the results. Where necessary, high concentration points were deleted when deviations from linearity were observed and the data returned to the machine for further processing. The iteration process was terminated when the values of Λ_0 converged to 0.1% or better.

The results of this study are summarized in Table II. Constants from the literature have been included for the purposes of comparison. Much of the data had originally been extrapolated by the Fuoss¹¹ method. However, since Fuoss and Shedlovsky⁹ have shown that the two treatments yield slightly different values of the ion-pair dissociation constant, and since it was considered desirable to have a consistent set of constants, these data were recalculated by the latter method. Constants obtained by both extrapolation methods are included in Table II.

The most striking aspect of these results is the 2000-fold change observed in the ion-pair dissociation constants of the lithium halides. In order to obtain more information regarding the nature of these ion pairs, a comparison was made of the contact distance of the ions in the ion pair as estimated by the Denison-

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

(10) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p 42.

(11) R. M. Fuoss, *J. Am. Chem. Soc.*, **57**, 488 (1935).

Table III. Ionic Radii (Å)

Ion	Acetone		Crystal Gourary and Adrian ^b
	This work	Hughes and Hartley ^a	
Li ⁺	3.16	3.40	0.94
Cl ⁻	2.23	2.40	1.64
Br ⁻	2.32 ^c	2.29	1.80
I ⁻	2.40 ^c	2.36	2.05

^a Reference 16. ^b Reference 14. ^c Calculated using the ionic conductivities given by Reynolds and Kraus.⁵

Table IV. Ionic Radii and Ion-Pair Radii Comparisons (Å)

Salt	Ion-pair radius	Stokes radii sum	Crystal radii sum	
			<i>a</i>	<i>b</i>
LiCl	2.17	5.39	2.58	2.41
LiBr	3.25	5.48	2.74	2.55
LiI	5.50	5.56	2.99	2.76

^a Gourary and Adrian.¹⁴ ^b Pauling.¹⁵

Ramsey⁷ equation, with the crystal radii and the ionic radii in acetone solution. The ionic radii in solution were calculated using the Stokes¹² equation and the ionic conductivities estimated by the method of Fowler and Kraus.¹³ The conductivities for bromide and iodide ions which Reynolds and Kraus⁵ had estimated in this manner were combined with the data in this paper to obtain ionic conductivities of chloride and lithium ion. Four estimates of the lithium ion conductivity were obtained (93, 78, 83, and 88) from the limiting conductances of lithium chloride, bromide, iodide, and *p*-toluenesulfonate, respectively. The average of the four, 85.5, was then used to estimate the radius of the lithium ion in acetone. The crystal radii used for comparison are taken from Gourary and Adrian.¹⁴ These authors give a set of radii for the alkali halides, based on recent electron density maps, which reproduce observed internuclear distances to 1%. These comparisons are given in Tables III and IV. Because of

(12) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths Scientific Publications, London, 1959, p 44.

(13) D. L. Fowler and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 2237 (1940).

(14) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, **10**, 127 (1960).

their widespread acceptance, the Pauling¹⁵ values have also been included.

The Stokes radii in Table IV are those labeled "this work" in Table III. The iodide and bromide radii agree well with the older values given by Hughes and Hartley,¹⁶ as is shown in Table III, but the radii of the lithium and chloride ions deviate markedly. The source of the data used by these authors is not indicated but is probably that of Ross Kane¹⁷ whose values for the conductivities of the lithium and chloride ions are smaller than those reported here.

Discussion

Some interesting relationships can be determined from the data presented. First of all, the Denison-Ramsey ion-pair radius agrees remarkably well with the sum of the Stokes radii for lithium iodide, but not at all for the other lithium halides. If one adds the crystal radius of the lithium ion, 0.94 Å, to the Stokes radius of the bromide ion, 2.32 Å, a total of 3.26 Å is obtained which agrees remarkably well with the ion-pair radius of 3.25 Å obtained for the salt. This excellent agreement must be considered as fortuitous in view of the multitude of assumptions and approximations which lie behind these estimations. Nevertheless, it can be concluded that the LiI ion pair involves fully solvated ions, whereas in LiCl the unsolvated ions are in contact. LiBr must be considered as intermediate between the two extremes with some solvent trapped in the ion pair. Since the extent of association of the ions in solution is related to their distance of closest approach, the large difference in ion association of the lithium halides is readily understood.

The failure of conductance theory to provide a reasonable ion-pair radius for LiCl is not unique. This effect may be seen, for example, in some of the ion pair-crystal radii correlations shown by Kay.¹⁸ Since this failure occurs for the small ions, it is perhaps a consequence of the assumption of a continuous dielectric medium which underlies the conductance theory upon which these calculations are based.

The reappearance to be ample evidence that, in associating solvents, the conductances and the degree of associ-

ation of alkali halides¹⁸ show the order Cs > Rb > K > Na > Li, with the ionic radii of the alkali metals in the reverse order. On the other hand, the results of Reynolds and Kraus⁵ on Li, Na, and K picrates in acetone show the reverse order. Upon examining the data of Table II it may be seen, although the differences are slight, that the conductance of KI is larger than that of LiI with the dissociation constants in the expected order. Hughes and Hartley¹⁶ give the order for the ionic radii, in acetone, to be Li > Na > K. It may be, as Kay¹⁸ has suggested, that the difference is attributable to differences in cation-anion interaction rather than to solvent effects. The data given here are inadequate for any generalizations regarding this situation.

In a review of the electrolyte problem, Kraus¹⁹ reports that he had received information indicating that there was an error in the previously published value for the conductance of tetrabutylammonium chloride.²⁰ These measurements were repeated because of the importance of this salt in the kinetic studies which were in progress. The results obtained do differ from those of McDowell and Kraus²⁰ as can be seen in Table II. The new value for the limiting conductance of tetrabutylammonium chloride results in the order Cl > Br > I for the relative conductance of the halide ions, in agreement with that observed for the lithium halides.

The conductance of potassium iodide was measured primarily in order to compare the present work with earlier studies. The data at low concentrations agree well with those of Dippy and Hughes²¹ for their "Grade I" acetone. The two highest concentration points deviate somewhat giving a larger slope (and smaller dissociation constant) in the Shedlovsky analysis. The observed differences are not believed to be significant.

Acknowledgment. The author wishes to thank the National Science Foundation for the award of a Science Faculty Fellowship which made this work possible; the University of California, Professor J. B. Ramsey, and the Western Data Processing Center for the use of facilities and equipment; and Professor S. Winstein, at whose suggestion this study was instituted.

(15) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

(16) O. L. Hughes and H. Hartley, *Phil. Mag.*, **15**, 610 (1933).

(17) See footnote a, Table II.

(18) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

(19) C. A. Kraus, *J. Chem. Educ.*, **35**, 324 (1958).

(20) See footnote g, Table II.

(21) See footnote f, Table II.