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Arvin S. Quist and William L. Marshall

The Electrical Conductances of Some Alkali Metal Halides in Aqueous Solutions from 0 to 800° and at Pressures to 4000 Bars¹

by Arvin S. Quist and William L. Marshall

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 (Received May 27, 1968)

The electrical conductances of 0.01 *m* aqueous solutions of LiCl, NaI, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsCl, CsBr, and CsI were measured from 0 to 800° and at pressures to 4000 bars. Evaluation of these results, together with those from previous measurements on NaCl and NaBr, indicate that in general all of these electrolytes exhibit the same type of conductance behavior at elevated temperatures and pressures. Thus at high temperatures where most of the long-range structure of water appears to be destroyed, the relative order of the specific conductances of these electrolytes remains constant—except for some instances at the highest temperatures when association effects appear to change this order. At temperatures below 100°, comparative changes in the specific conductances of these electrolytes both with temperature and pressure can be correlated with the apparent disruption of the structure of water by the ions, by pressure, and by temperature. Thus, the present measurements indicate that the simpler behavior observed quantitatively in previous extensive measurements on several electrolytes at high temperatures and pressures probably can be extended to include all of the alkali metal halides.

The properties of electrolyte solutions have been the subject of investigations by physical chemists for many years. One of the most convenient and direct methods that has been used for obtaining information about the existence and behavior of ions in these solutions has been the measurement of the electrical conductance of these solutions. The results of these measurements have provided a significant portion of the current knowledge about the behavior of ions in solution and have permitted the testing of theoretical equations that accurately describe ion-ion interactions in dilute solutions.² However, very little quantitative information is available concerning ion-solvent interactions in electrolyte solutions. This is particularly true about the interactions between ions and water. Water is by far the most important of the ionizing solvents, but unfortunately it is also the most complex of these liquids,

probably because of the existence of tetrahedrally coordinated water molecules that form some type of structure³ in the liquid state. This structure appears to be modified by the presence of ions in solution. Therefore, a complete description of the behavior of aqueous solutions must include the effects of (1) ion-ion interactions, (2) ion-solvent interactions, and (3) modification of the water structure by ions. Much of the effect of (3) may be eliminated when studies on aqueous solutions are carried out at high temperatures and pressures. Because water appears to become less

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).

(3) H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

structured as its temperature is raised,⁴⁻⁶ at high temperature the behavior of electrolytes will be dominated by (1) and (2) with little added complications due to (3). Near room temperature, some of the water structure may also be destroyed by increasing the pressure and thus an increase in pressure will also decrease the effect of (3). Therefore, it appears that the study of aqueous solutions at high pressures at both low and high temperatures is a promising area of research that may lead to a better understanding of ion-solvent interactions in electrolyte solutions.

Much of our knowledge of the properties of aqueous solutions above 100°, and in particular in the supercritical region above 374°, has been obtained from electrical conductance studies. The first accurate studies at temperatures much above 100° were carried out by Noyes and coworkers⁷ who measured the conductances of several electrolytes to 306° at saturation vapor pressure. Fifty years later, Fogo, Benson, and Copeland⁸ extended precise conductance measurements into the supercritical region. In 1956, Franck reported the results of measurements to 750° and 2500 bars.⁹ In recent years we have measured the conductances of aqueous solutions of K₂SO₄,^{10a} KHSO₄,^{10b} H₂SO₄,^{10c} NaCl,^{10d} NaBr,^{10e} HBr,^{10f} and NH₃^{10g} to 800° and 4000 bars. Each of these electrolytes was studied at several molalities in order to calculate limiting equivalent conductances and ionization constants from the data. From these results it appears that aqueous solutions exhibit simpler behavior at elevated temperatures and pressures than at room temperature. For example, the limiting equivalent conductance in the temperature range 400–800° appears to be a linear function of density only, independent of temperature.^{10b,d-g} Although the slope of the line of Λ_0 vs. density has approximately the same value for all the salts, it is significantly different for acids and bases. However, our results indicate that the extrapolated intercept at zero solvent density is nearly the same for all uni-univalent electrolytes. As all of these electrolytes are only partially ionized at high temperatures and pressures, we were able to calculate ionization constants at zero ionic strength in the temperature region 400–800°. When the molar concentration of water was included as a variable in the ionization constant, values of the constants were obtained that were independent of solvent density (pressure) at constant temperature. Success of this principle for the high-temperature aqueous solutions led to its wide application to equilibrium constants in mixed solvents at 25°, and a questioning of the validity of conventional plots of log *K* vs. the reciprocal of the dielectric constant.^{11,12} This recent approach gave reasonable estimates for the net change in hydration number when two ions react to form an ion pair and, with additional data on solubilities at high temperatures and pressures, provided an estimate for the sum of the primary waters of hydration for the two ions.^{10a}

In a further extension of the investigation of aqueous solutions at high temperatures and pressures, we present in this paper a comparison of the conductances of 0.01 *m* solutions of most of the alkali metal halides. This summary includes data on LiCl, NaCl, NaBr, NaI, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsCl, CsBr, and CsI to 800° and 4000 bars. With the exception of KCl,^{9a} NaCl,^{8,10d} and NaBr,^{10e} to our knowledge these conductances are the first experimental measurements that have been reported for these salts at supercritical temperatures and pressures. However, estimates of ionization constants for the alkali metal chlorides under these conditions have been published, based on measurements of 0.01 *m* solutions from 450 to 750°.⁹

Experimental Section

A complete description of the equipment and procedures used for these measurements is contained in an earlier paper.^{10d} A conductance cell having no pressure seals in the high-temperature region was used for all experiments. Solutions of KCl, KBr, KI, CsBr, and CsI were prepared from single crystals (Harshaw Chemical Co., Cleveland, Ohio) and conductivity water. Solutions of NaCl, RbF, RbCl, RbBr, and RbI were prepared from 99.9% pure (or better) salts (K & K Laboratories, Plainview, N. Y.). The solution of NaI was prepared from reagent grade salt (Mallinckrodt Chemical Works, St. Louis, Mo.). With the exception of the single-crystal materials, all of the salts were dried at 110–120° prior to use. A stock solution of approximately 1.0 *m* LiCl was prepared from the hydrated, purified salt (less than 0.03 wt % of the other alkalis and alkaline earths). From this stock solution, a 0.01 *m* LiCl solution was prepared, and its conductivity was accurately measured in a glass conductance cell at 25.00 ± 0.01°. By comparison with literature values,¹³ the molality of this solution was accurately determined, and a suitable dilution was made so that the final solution had a molality of 0.01000 *m*. Several different

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- (9) E. U. Franck, (a) *Z. Phys. Chem.* (Frankfurt am Main), **8**, 92, 107, 192 (1956); (b) *Angew. Chem.*, **73**, 309 (1961).
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- (11) W. L. Marshall and A. S. Quist, *Proc. Nat. Acad. Sci. U. S.*, **58**, 901 (1967).
- (12) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968).
- (13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 697; K. A. Kreiger and M. Kilpatrick, *J. Amer. Chem. Soc.*, **59**, 1878 (1937); T. Shedlovsky, *ibid.*, **54**, 1411 (1932).

inner electrodes were used for these measurements. Their cell constants, as determined with 0.01000 demal KCl solutions at $25.00 \pm 0.01^\circ$, ranged from 1.96 to 0.489 cm^{-1} .

The precision (reproducibility) of the high-temperature ($200\text{--}800^\circ$), high-pressure measurements for each experimental run was about $\pm 0.7\%$ at the lowest temperatures to $\pm 1\text{--}2\%$ at 800° , with an estimated overall accuracy of $\pm 2\%$ or better. The precision of the measurements for each run at $0\text{--}120^\circ$ was better than $\pm 0.5\%$; however, the accuracy may not be better than $\pm 1\text{--}2\%$. Therefore, for comparison at intersection points of these values with more accurate values obtained by refined techniques, a normalization or adjustment of the present values can be made to obtain greater accuracy.

Results

The experimental conductances were converted into specific conductances by the methods described earlier.^{10d} A graphical example of a complete set of these specific conductances, each curve corresponding to a constant temperature and plotted as a function of pressure, is shown in Figure 1 for 0.01000 demal (0.745263 g of KCl/1000 g of solution) KCl solutions. Corresponding curves for 0.01000 *m* solutions of the other 1-1 salts conform closely to those shown in Figure 1, as do those presented previously for NaCl and NaBr.^{10d,e} The curves for the different salts therefore show only quantitative differences in specific conductances. Approximately the same number of experimental points (an average of 22, with extremes of 15 and 30) at each temperature were obtained for each 0.01000 *m* salt solution with no difference in precision of measurement. The values of specific conductances for the 12 salts studied, smoothed with respect to pressure but not with tem-

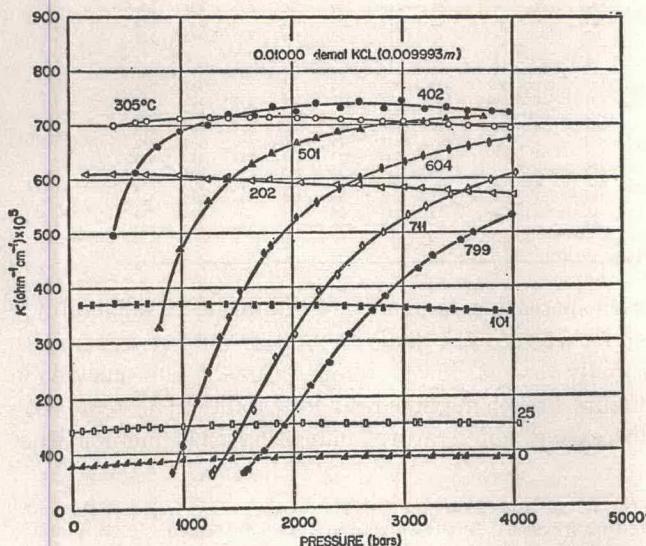


Figure 1. Specific conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of pressure at several temperatures.

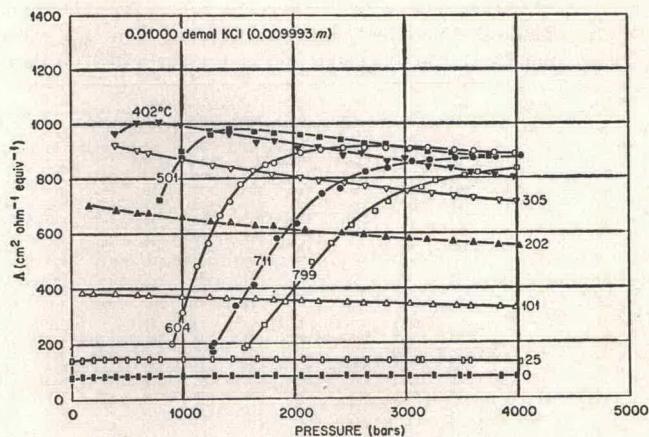


Figure 2. Equivalent conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of pressure at several temperatures.

perature, are presented in Table I and represent the data within the precision and qualifications stated in the Experimental Section. They therefore can be treated as equivalent to the "raw" data. Included also in Table I are those similarly smoothed values for 0.01000 *m* NaCl and NaBr presented elsewhere in graphical form.^{10d,e}

Specific conductances were selected as the basis for intercomparison of these electrolytes. However, the behavior observed when equivalent conductances are plotted as a function of pressure and density is shown in Figures 2 and 3 for 0.01 demal KCl solutions. Figure 4 compares specific conductances *vs.* density for the same solution. The corresponding graphs for the other univalent salts are similar to those for KCl.

Discussion

Comparisons of the isobaric specific conductances of most of the alkali metal halides, grouped according to

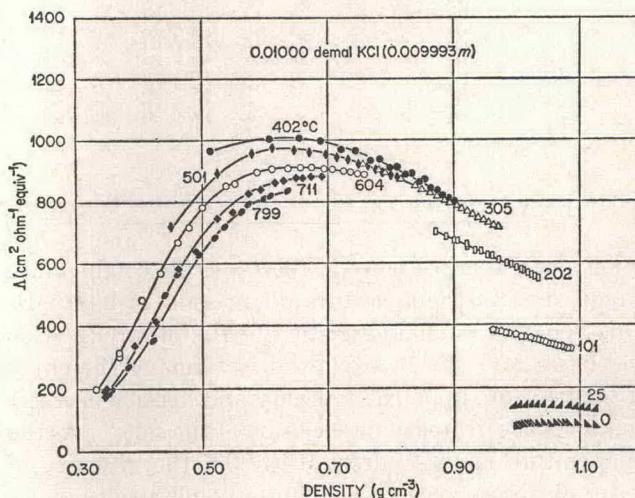


Figure 3. Equivalent conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of density at several temperatures.

Table I: Specific Conductances ($\text{ohm}^{-1} \text{cm}^{-1}$) $\times 10^6$ of 0.01000 *m* Alkali Metal Halide Solutions from 0 to 800° and at Pressures to 4000 Bars^a

Salt	Temp., °C	Pressure, Bars								Salt	Temp., °C	Pressure, Bars								
		1	500	1000	1500	2000	2500	3000	3500			4000	1	500	1000	1500	2000	2500	3000	3500
LiCl	0	54.0	59.0	62.5	64.9	66.0	66.5	66.0	65.5	64.5	0	67.4	72.4	75.4	77.4	78.2	78.3	78.0	77.2	75.8
	25	107.7	112.5	115.4	117.4	118.2	118.5	118.3	117.5	116.5	25	125.0	128.5	131.2	132.8	133.5	133.4	132.8	132.0	130.4
	102	(300)	300	300	300	300	297	295	293	291	100	332	330	328	325	323	321	318	316	315
	207	(518)	516	512	509	504	500	493	489	483	203	(570)	568	566	562	560	555	551	545	540
	301	(585)	605	610	610	608	605	600	595	587	303	(605)	623	620	633	645	650	655	656	655
	401	-	528	618	643	652	652	648	645	640	356	-	585	603	630	650	655	660	663	657
	442	-	280	568	620	645	650	655	657	657	RbF	400	-	515	603	635	650	655	660	663
	494	-	-	420	542	595	622	635	646	650	460	-	156	507	580	615	630	642	650	655
	547	-	-	230	450	545	590	615	628	638	502	-	-	403	523	570	597	610	620	630
	594	-	-	88	325	470	540	580	605	622	606	-	-	110	333	455	520	555	580	600
692	-	-	-	100	260	390	470	525	560	718	-	-	-	136	287	398	467	510	537	
795	-	-	-	23	95	205	308	390	450	801	-	-	-	58	175	295	380	437	475	
NaCl	0	69.5	71.1	74.8	77.0	78.1	78.1	77.5	76.3	74.9	0	80.5	86.8	90.8	92.7	93.3	93.0	92.2	90.6	88.6
	25	121.2	126.0	129.1	131.0	131.7	131.5	130.7	129.3	127.5	25	145.0	150.0	153.0	154.6	154.7	154.5	153.2	151.0	148.4
	106,108	(341)	341	340	338	336	333	330	327	323	102	(369)	370	368	367	363	360	357	353	348
	203	(558)	551	544	538	533	528	523	518	513	201	(628)	620	613	608	602	595	590	583	577
	309	(622)	651	660	664	664	662	659	653	648	302	(687)	709	717	717	715	713	709	706	702
	318	(617)	655	670	675	676	675	673	669	664	352	(585)	680	710	720	722	720	718	715	707
	404,405	-	512	632	670	682	688	690	690	690	409	-	525	660	695	722	715	722	720	718
	455,458	-	145	540	620	655	677	685	690	695	448	-	290	600	665	695	716	725	730	730
	506,507	-	-	395	553	615	655	665	675	685	547	-	-	290	507	595	640	665	677	683
	515	-	-	350	518	585	620	640	655	665	602	-	-	135	392	520	592	635	660	678
554,555	-	-	210	445	542	595	628	650	665	697	-	-	17	161	336	450	517	558	585	
594	-	-	100	355	490	565	610	640	655	793	-	-	-	62	187	327	425	490	530	
594	-	-	80	320	468	545	590	620	635	0	81.8	87.6	91.0	92.7	93.0	92.2	91.0	89.0	86.5	
606	-	-	90	320	468	545	590	620	635	25	146.0	150.5	153.0	154.0	154.0	152.6	151.0	148.4	145.5	
708,710	-	-	108	263	395	480	540	575	575	102	(374)	372	370	367	362	357	352	348	342	
812	-	-	30	110	222	327	415	477	477	202	(617)	613	608	601	594	586	578	570	562	
NaBr	0	65.5	69.8	72.5	73.8	73.9	73.2	72.0	70.2	68.5	0	81.2	86.2	88.4	89.3	88.7	87.5	85.7	83.5	80.8
	25	120.6	124.1	126.2	127.0	126.6	125.5	124.0	122.0	119.8	25	145.0	148.2	149.5	149.3	148.0	146.0	143.4	140.2	137.0
	100	339	340	338	337	332	328	324	321	317	100	357	357	353	349	343	337	331	325	318
	205	(540)	537	533	528	522	516	510	503	497	202	(690)	713	720	718	713	708	702	697	690
	300	(620)	637	641	641	638	634	628	622	616	352	(562)	665	674	682	682	682	680	675	670
	399	-	550	643	667	675	680	678	677	675	401	-	566	675	709	712	710	712	715	717
	441	-	325	585	637	660	670	675	677	677	454	-	265	600	663	690	707	715	720	720
	501	-	-	445	575	622	645	655	657	660	494	-	-	500	610	655	675	685	690	692
	557	-	-	240	470	565	605	632	645	655	546	-	-	310	515	594	630	650	660	665
	600	-	-	132	390	515	582	620	640	653	617	-	-	115	367	503	575	617	640	650
698	-	-	20	153	325	440	510	535	545	650	-	-	30	290	440	527	575	607	625	
809	-	-	40	135	258	360	435	487	487	709	-	-	30	175	345	460	528	570	595	
NaI	0	63.8	67.5	69.5	70.0	69.4	68.2	66.7	64.7	62.5	0	81.2	86.2	88.4	89.3	88.7	87.5	85.7	83.5	80.8
	25	118.0	121.0	121.7	121.4	120.1	118.0	115.9	113.4	110.6	25	145.0	148.2	149.5	149.3	148.0	146.0	143.4	140.2	137.0
	101	(320)	318	315	310	305	300	296	291	287	100	357	357	353	349	343	337	331	325	318
	207	(552)	548	541	533	524	517	508	500	493	199	(590)	583	576	567	558	550	540	530	522
	306	(610)	624	625	623	622	619	614	610	603	300	(656)	674	675	672	668	665	658	652	642
	406	-	540	623	646	650	652	650	648	640	348	(610)	660	682	688	688	682	675	667	662
	457	-	235	573	625	643	650	653	653	652	401	-	570	657	676	684	682	680	675	670
	508	-	-	460	570	612	632	640	645	647	447	-	300	597	645	665	670	672	673	672
	605	-	-	152	412	527	580	605	626	633	503	-	-	500	615	650	665	670	674	675
	702	-	-	22	190	368	472	530	568	590	547	-	-	360	543	610	640	655	665	668
796	-	-	68	208	338	425	485	522	522	598	-	-	183	435	538	588	613	630	638	
KCl	0	78.2	84.4	88.4	90.7	91.7	91.6	90.9	89.5	87.7	0	81.2	86.2	88.4	89.3	88.7	87.5	85.7	83.5	80.8
	25	141.5	147.0	150.3	152.0	152.6	152.4	151.5	149.9	147.6	25	145.0	148.2	149.5	149.3	148.0	146.0	143.4	140.2	137.0
	101	(369)	369	368	367	365	362	358	354	349	100	357	357	353	349	343	337	331	325	318
	202	(610)	609	606	602	596	590	583	577	573	202	(645)	662	660	657	653	650	646	642	634
	305	(684)	703	714	715	714	711	706	700	693	300	(615)	612	607	600	593	583	577	569	560
	402	-	575	687	720	733	737	737	733	725	303	(664)	687	692	690	685	681	675	669	660
	501	-	-	470	612	665	690	705	713	715	400	-	585	680	703	710	710	710	706	703
	604	-	-	115	385	518	590	630	657	675	447	-	305	600	665	692	705	707	707	707
	711	-	-	135	312	442	522	575	610	610	512	-	-	445	600	656	685	700	703	705
	799	-	-	52	170	308	410	485	532	532	599	-	-	140	400	525	587	620	643	655
KBr	0	79.0	85.3	89.0	90.8	91.6	91.2	90.0	88.3	86.2	0	81.7	87.5	90.8	92.5	92.6	91.6	90.0	88.0	85.5
	25	143.0	147.6	150.8	152.2	152.2	151.3	149.6	147.4	144.6	25	144.5	148.3	150.6	151.2	150.6	148.6	146.3	143.5	140.5
	110	(397)	396	394</																

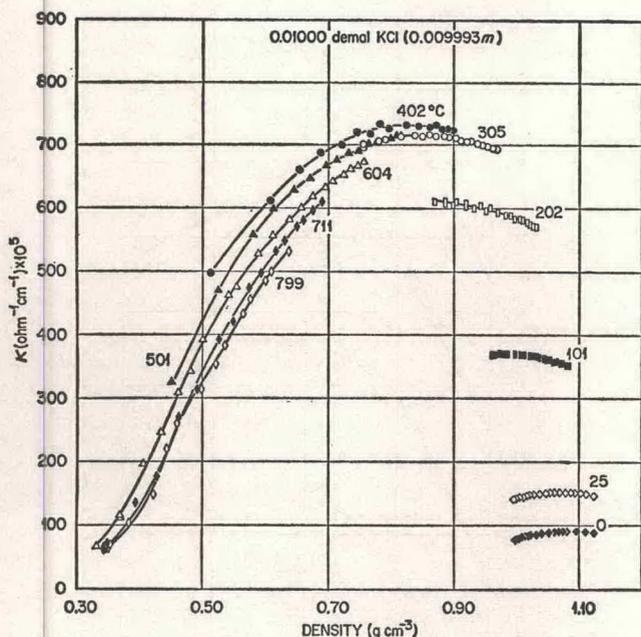


Figure 4. Specific conductances of 0.01000 demol (0.009993 *m*) KCl solutions as a function of density at several temperatures.

than viscosity must be considered at higher temperatures. Because the isobaric density of water decreases with increasing temperature,^{17,18} this effect will reduce the number of ions per unit volume for a solution of constant molality and therefore will cause a decrease in specific conductance. It has also been found^{9,10} that

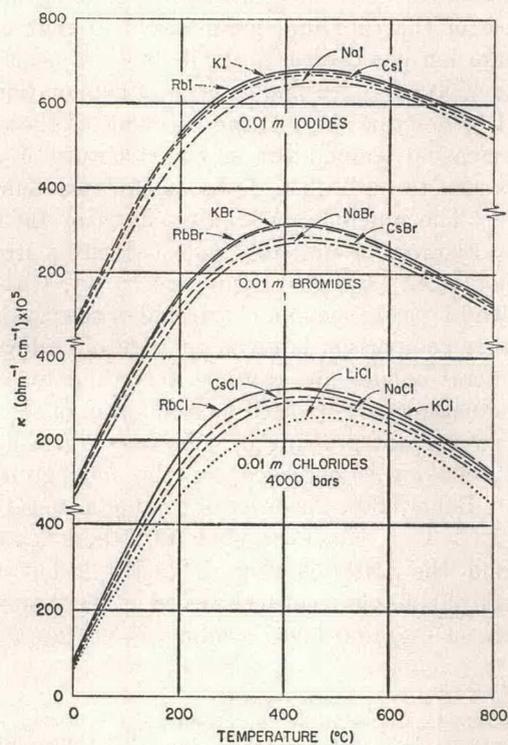


Figure 5. Isobaric specific conductances of 0.01000 *m* aqueous solutions of some alkali metal halides as a function of temperature; pressure = 4000 bars.

ionic association increases with increasing temperature; consequently, this effect will also reduce the number of ions per unit volume and, accordingly, the specific conductance. The maximum in isobaric specific conductance results when the increase in ionic mobility due to the viscosity effect is offset by a decrease in ionic concentration due to density and association effects.

The three sets of curves given in Figure 5 show a nearly consistent behavior, where at all temperatures the order of conductance is $\text{Rb}^+, \text{K}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$. As seen from these curves, the conductances of the rubidium and potassium ions are almost the same in these 0.01 *m* solutions. Below 200° there is practically no difference in the conductances of these two ions. Above 200° the rubidium ion appears to be more mobile in iodide and bromide solutions, but the potassium ion has the higher conductance in chloride solutions. However, at present we cannot find any significance in this change in relative behavior of these two ions since the variations are small and nearly within the limits of the experimental accuracy. Figure 6 compares the specific conductances of the alkali metal chlorides at a pressure of 1000 bars. The general features of this graph are similar to those observed at 4000 bars. Although not shown, the relative behavior at 1000 bars of the bromide and iodide solutions are the same as for the chloride solutions.

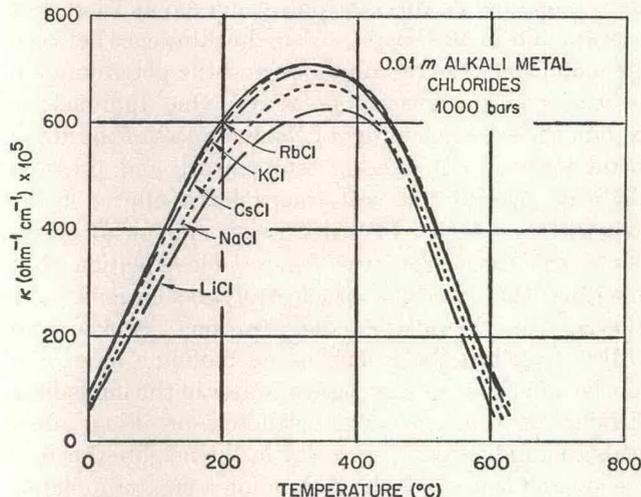


Figure 6. Isobaric specific conductances of 0.01000 *m* aqueous solutions of the alkali metal chlorides as a function of temperature; pressure = 1000 bars.

It is of interest to compare the relative conductances of the alkali metal ions as shown in Figure 5 at high temperatures and pressures with their corresponding behavior at room temperature and atmospheric pres-

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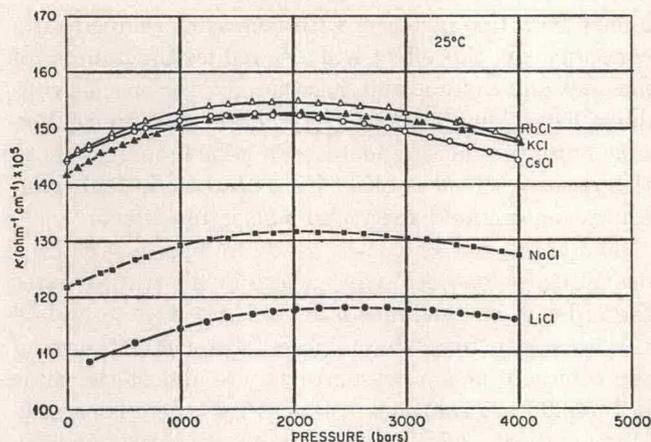


Figure 7. Isothermal specific conductances of 0.01000 *m* alkali metal chloride solutions as a function of pressure at 25°.

At 25° and 1 atm, the limiting equivalent conductances of these ions are given by Robinson and Stokes¹⁹ in the order Rb^+ (77.81) > Cs^+ (77.26) > K^+ (73.50) > Na^+ (50.10) > Li^+ (38.68). At 0° and 1 atm, the order is the same except that the conductances of the cesium ion and the rubidium ion are essentially equal. Figure 7 illustrates the effect of pressure on the conductances of the alkali metal chlorides at 25°. This graph shows that the relative order of the conductances of the alkali metal ions changes as the pressure is increased from 1 to 4000 bars. Thus the cesium ion is more mobile than the potassium ion at 1 bar, but is less mobile at 4000 bars. Also, the difference between the mobility of the rubidium ion and the potassium ion decreases with increasing pressure. One approach to explain the change in order of conductances of the alkali metal ions with increasing temperature and pressure might be a correlation with their relative effects on the structure of water. In a discussion of ionic *B* coefficients (obtained from the Jones-Dole equation that describes the viscosity of electrolyte solutions as a function of electrolyte concentration), Stokes and Mills²¹ described the cesium ion as having a large, disruptive effect on the structure of water in the immediate vicinity of the ion. This structure-breaking effect leads to a reduction in viscosity in the neighborhood of the ion and thus gives the cesium ion a greater mobility than it might be expected to have on the basis of ion size. Since increasing the pressure tends to break up the structure present in liquid water, the cesium ion will have less structure to break at high pressures and so its "excess" mobility will be diminished. The potassium ion has only a small effect on the structure of water and therefore the change in its conductance with increasing pressure is close to "normal." Consequently, when the pressure is increased, the conductance of the cesium ion near room temperature will decrease relative to that of the potassium ion. This behavior is observed in Figure 7. The rubidium ion is slightly structure breaking (a *B* coefficient midway between K^+ and Cs^+),

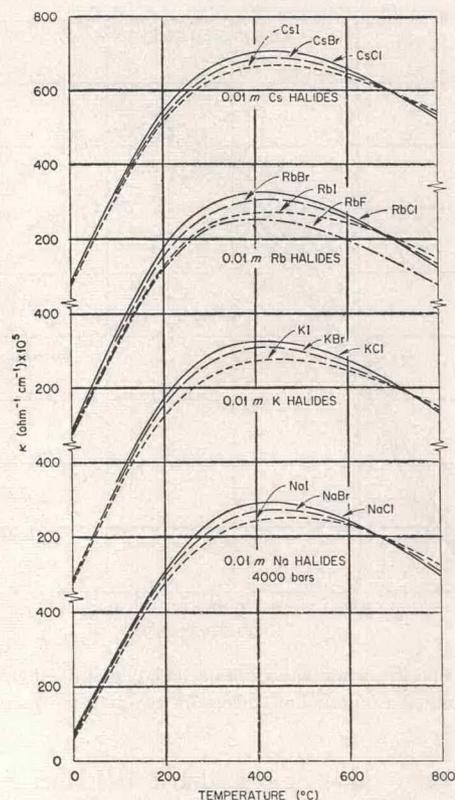


Figure 8. Isobaric specific conductances of 0.01000 *m* aqueous solutions of some alkali metal halides as a function of temperature; pressure = 4000 bars.

and therefore it also loses some of its excess mobility with increasing pressure. As seen in Figure 7, the conductance of the rubidium ion relative to that of the potassium ion has decreased until they are nearly the same at 4000 bars. A similar type of explanation can be used to describe the relative behavior of these ions with increasing temperature as the structure of water appears also to be broken down at elevated temperatures.⁴⁻⁶ The much lower conductances of LiCl and NaCl in Figures 5-7 probably reflect chiefly a stronger hydration of Li^+ and Na^+ compared to K^+ , Rb^+ , and Cs^+ , with Li^+ being the more hydrated of the two ions.²¹

Another comparison is given in Figure 8 where the alkali metal halides are grouped according to cation, and conductances are plotted as a function of temperature at a constant pressure of 4000 bars. Again, consistent behavior is observed for the four groups of curves. Below 600°, the order of conductance is $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{F}^-$. However, near 700°, there is a cross-over, and the order is then $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. This type of behavior is also observed at lower pressures as shown in Figure 9 for the rubidium halides at 1000

(19) See ref 14, p 465.

(20) The effect of pressure on the conductance of a 0.01 *m* KCl solution at 25° agrees well with the results of W. A. Zisman, *Phys. Rev.*, **39**, 151 (1932); A. J. Ellis, *J. Chem. Soc.*, 3689 (1959); and F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).

(21) R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press, Oxford, 1965.

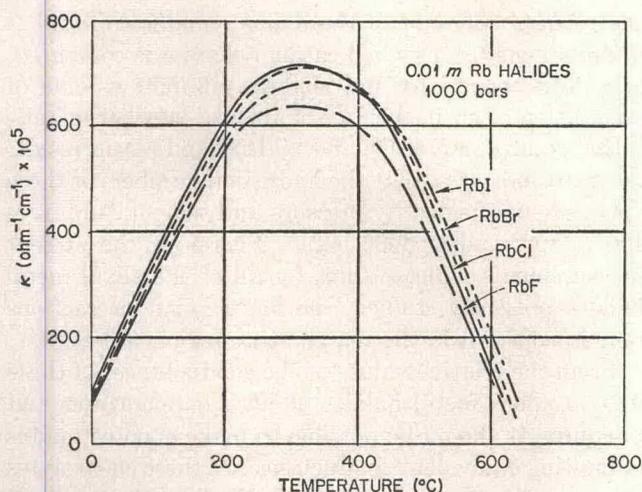


Figure 9. Isobaric specific conductances of 0.01000 *m* aqueous solutions of the rubidium halides as a function of temperature; pressure = 1000 bars.

bars. The change in order of conductance does not appear to be connected with any relative effects of the ions on the structure of water since most of the structure is probably destroyed before temperatures near 700° are reached. A reasonable explanation may relate to the differences in degree of association of these salts at high temperatures. Thus, as the salts become more associated with rising temperature,^{10d,e} the different but increasing quantities of ions lost in the formation of the ion pairs will cause a proportionally greater difference in the respective conductances. This explanation requires that the 0.01 *m* chloride solutions contain more associated species than the corresponding bromide or iodide solutions. Sodium chloride is observed to be a weaker electrolyte than NaBr or NaI in the temperature range 400–800°.^{10d,e,22} This behavior is also in agreement with the results of conductance studies on rubidium halides in water-dioxane mixtures, which indicate that the order of association is $\text{Cl}^- > \text{Br}^- > \text{I}^-$.²³ Therefore it is possible that, although the limiting conductance of the chloride ion may be larger than that of the bromide or iodide ion at 800° and 4000 bars, association effects may cause the conductance of 0.01 *m* chloride solutions to be less than the corresponding bromide or iodide solutions. Since crossovers were not observed (except for the questionable case of K^+ and Rb^+) when isobaric specific conductances *vs.* temperature plots were grouped according to anion (Figure 5), the behavior shown in Figure 8 may indicate that ionic association is more dependent on the anion than on the cation.

The relative conductances of the halide anions at elevated temperatures and pressures may be compared with their relative values near room temperature and atmospheric pressure. Aside from the crossovers near 700° (at 4000 bars) and 450° (at 1000 bars) discussed above, the order of conductance of the halide ions at

elevated temperatures and pressures is $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{F}^-$. The order at 25° and 1 atm is¹⁹ $\text{Br}^- (78.14) > \text{I}^- (76.84) > \text{Cl}^- (76.35) > \text{F}^- (55.4)$, but at 55° it has changed to¹⁹ $\text{Br}^- (127.86) > \text{Cl}^- (126.40) > \text{I}^- (125.44) > \text{F}^-$. Let us assume that the "normal" order, without regard to any influence of the ions on the structure of water, is given by the high-temperature results. Then the order found near 25° may be explained, as was the behavior of the cesium and rubidium ions, in relation to the effect of the bromide and iodide ions on the structure of water. Both of these halide ions have negative *B* coefficients, with that of the iodide ion being more negative than that of the bromide ion.²¹ Thus both of these ions reduce the viscosity in their vicinity, leading to an excess mobility for these ions. The *B* coefficients become more positive with increasing temperature, indicating the diminution of this effect at higher temperatures and an approach to more "normal" behavior. As mentioned earlier, this approach to "normality" occurs because the structure of water is destroyed by increasing temperature, and consequently these ions have less or very little structure to break. Thus the iodide ion, with the larger excess mobility, has reached its normal position in the ranking of the halide ions when a temperature of 55° has been attained, but higher temperatures (and greater disruption of the water structure) are required in order that the mobility of the chloride ion exceeds that of the bromide ion.

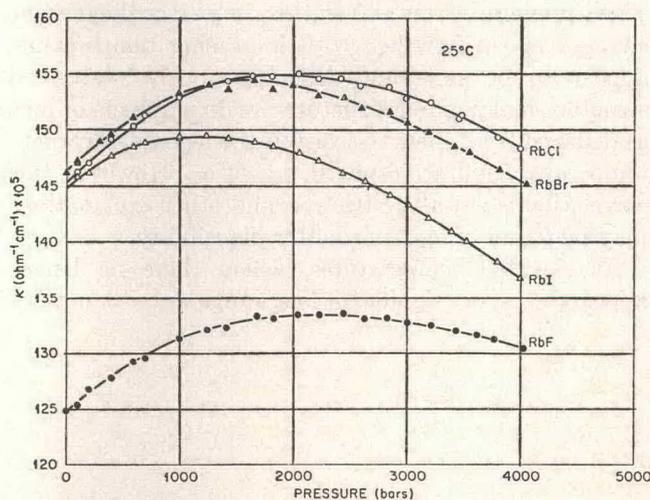


Figure 10. Isothermal specific conductances of 0.01000 *m* aqueous rubidium halide solutions as a function of pressure at 25°.

Figure 10 shows the effect of pressure on the specific conductances of the rubidium halides at 25°. Although the relative values for the conductances of the chloride and iodide ions at 1 bar are slightly different from literature values,¹⁹ these differences are within the

(22) L. A. Dunn and W. L. Marshall, *J. Phys. Chem.*, **73**, 723 (1969).

(23) T. L. Fabry and R. M. Fuoss, *ibid.*, **68**, 974 (1964).

expected accuracy of our measurements. The relative behavior of the halide ions given in Figure 10 is consistent with predictions from a knowledge of the ionic B coefficients. Since increasing the pressure on water at 25° destroys its structure, at high pressures the structure-breaking ions, with little structure to break, will lose their excess mobility and become normal in behavior. Thus at high pressures at 25° the relative conductances of the halide ions change to the order that is observed at high temperatures. By analogy with the behavior of Li^+ and Na^+ (Figure 7), the much lower specific conductances of RbF probably reflect chiefly a stronger hydration of F^- , compared to the other anions, and thus a lower ionic mobility. The effect of pressure on the conductance of aqueous RbF , as shown in Figure 10, is consistent with the structure-making behavior of the fluoride ion as observed from viscosity studies.²⁴ Increasing pressure destroys the solvent structure, counteracting the solvent-ordering properties of the fluoride ion, and, consequently, increasing its conductance relative to the other ions. The relative behavior of LiCl at 25° (Figure 7) can be explained in a similar manner, since solvated Li^+ is considered to be a structure-making ion.

Summary

By comparing the effect of pressure on alkali metal halide conductances at 0 and 25°, it appears that most of the long-range structure of water has been destroyed by the time pressures of 4000 bars have been reached. These pressure effects at 0 and 25°, as well as the relative changes in conductance with increasing temperature, appear to be consistent with previously postulated structure-making and structure-breaking effects of ions as deduced from their viscosity B coefficients near room temperature and atmospheric pressure. However, this correlation is not all-restrictive, and other explanations may be found of equal or better plausibility.

At elevated temperatures, where there no longer appears to be any significant long-range water structure,

the relative behavior of these ions remains constant—under all conditions when cation behavior is compared, and until appreciable but slightly different extents of association occur in the case of anions. Earlier quantitative results on NaCl ^{10d} and NaBr ^{10e} and recent results on NaI ²² indicated that the hydration numbers of these ions were unaffected by pressure and temperature from 400 to 800° and to 4000 bars. Therefore, the present measurements indicate that, for all of the alkali metal halides presently studied, the ion-solvent interactions remain constant in the temperature region 400–800°.

From the relative values of the conductances of these 0.01 m alkali metal halides at high temperatures and pressures, it should be possible to make good estimates of limiting equivalent conductances of these electrolytes based on the reported values for NaCl ,^{10d} NaBr ,^{10e} and NaI .²² With these estimated values for Λ_0 and the conductances of the 0.01 m solutions presented in this paper, it is possible to estimate the degree of dissociation of each electrolyte at these supercritical temperatures and pressures.^{9a} Although it is of interest to make Walden product comparisons for these electrolytes under supercritical conditions, the available viscosity data for water extend only to 560° and 3500 bars, and are reliable only to $\pm 5\%$.¹⁶ Previous work^{10d} has indicated that correlation of the Walden product at high temperatures as a function of density is not as simple nor as useful as the correlation of Λ_0 vs. density.

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(24) E. R. Nightingale and R. F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).

