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

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The Electrical Conductances of Some Alkali Metal Halides in Aqueous Solutions from 0 to 800° and at Pressures to 4000 Bars[1]

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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 structure[3] 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 coworkers[7] who measured the conductances of several electrolytes to 306° at saturation vapor pressure. Fifty years later, Fogo, Benson, and Copeland[8] 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 K_2SO_4,[10a] $KHSO_4$,[10b] H_2SO_4,[10c] NaCl,[10d] NaBr,[10e] HBr,[10f] and NH_3[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.[10d]

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 CsCl, 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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(5) E. U. Franck and K. Roth, *Discussions Faraday Soc.*, **43**, 108 (1967).

(6) G. E. Walrafen, *J. Chem. Phys.*, **47**, 114 (1967).

(7) A. A. Noyes, *et al.*, "The Electrical Conductivity of Aqueous Solutions," Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907.

(8) J. K. Fogo, S. W. Benson, and C. S. Copeland, *J. Chem. Phys.*, **22**, 212 (1954).

(9) E. U. Franck, (a) *Z. Phys. Chem.* (Frankfurt am Main), **8**, 92, 107, 192 (1956); (b) *Angew. Chem.*, **73**, 309 (1961).

(10) (a) A. S. Quist, *et al.*, *J. Phys. Chem.*, **67**, 2453 (1963); (b) *ibid.*, **70**, 3714 (1966); (c) *ibid.*, **69**, 2726 (1965); (d) *ibid.*, **72**, 684 (1968); (e) *ibid.*, **72**, 2100 (1968); (f) *ibid.*, **72**, 1545 (1968); (g) *ibid.*, **72**, 3122 (1968).

(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 ± 0.01°, ranged from 1.96 to 0.489 cm^{-1}.

The precision (reproducibility) of the high-temperature (200–800°), high-pressure measurements for each experimental run was about ±0.7% at the lowest temperatures to ±1–2% at 800°, with an estimated overall accuracy of ±2% or better. The precision of the measurements for each run at 0–120° was better than ±0.5%; however, the accuracy may not be better than ±1–2%. 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.

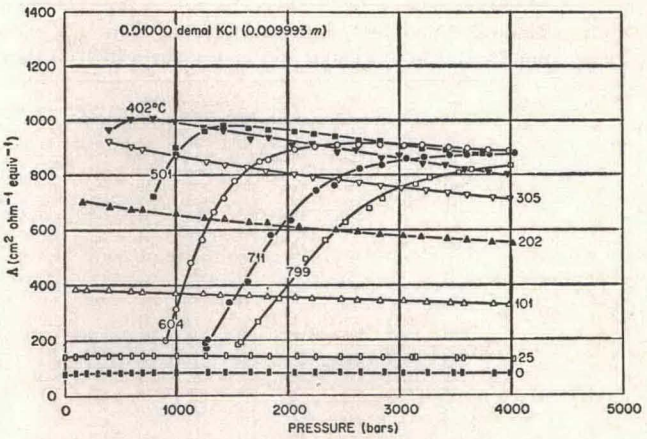

Figure 2. Equivalent conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of pressure at several temperatures.

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 temperature, 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 uni-univalent salts are similar to those for KCl.

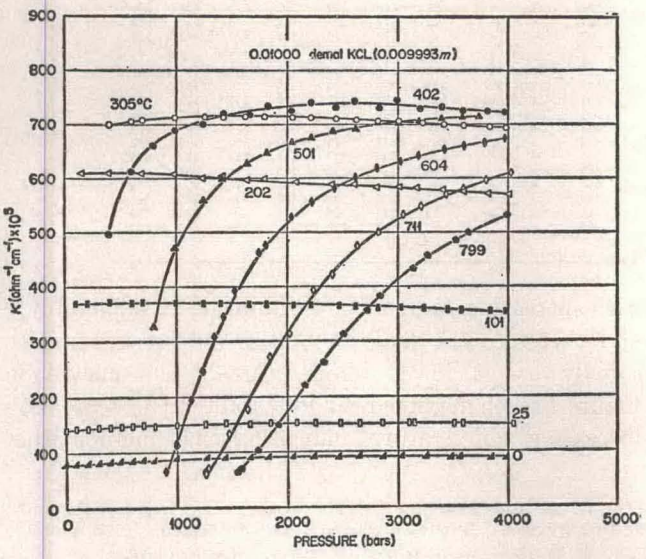

Figure 1. Specific conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of pressure at several temperatures.

Discussion

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

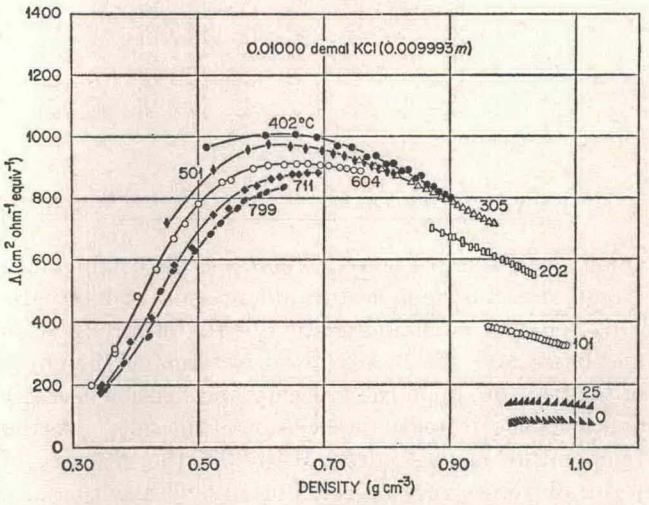

Figure 3. Equivalent conductances of 0.01000 demal (0.009993 *m*) KCl solutions as a function of density at several temperatures.

Table I: Specific Conductances (ohm^{-1} cm^{-1}) × 10^5 of 0.01000 *m* Alkali Metal Halide Solutions from 0 to 800° and at Pressures to 4000 Bars[a]

Salt	Temp., °C	Pressure, Bars: 1	500	1000	1500	2000	2500	3000	3500	4000
LiCl	0	54.0	59.0	62.5	64.9	66.0	66.5	66.0	65.5	64.5
	25	107.7	112.5	115.4	117.4	118.2	118.5	118.3	117.5	116.5
	102	(300)	300	300	300	300	297	295	293	291
	207	(518)	516	512	509	504	500	493	489	483
	301	(585)	605	610	610	608	605	600	595	587
	401	-	528	618	643	652	652	648	645	640
	442	-	280	568	620	645	650	655	657	657
	494	-	-	420	542	595	622	635	646	650
	547	-	-	230	450	545	590	615	628	638
	594	-	-	88	325	470	540	580	605	622
	692	-	-	-	100	260	390	470	525	560
	795	-	-	-	23	95	205	308	390	450
NaCl	0	69.5	71.1	74.8	77.0	78.1	78.1	77.5	76.3	74.9
	25	121.2	126.0	129.1	131.0	131.7	131.5	130.7	129.3	127.5
	106,108	(341)	341	340	338	336	333	330	327	323
	203	(556)	551	544	538	533	528	523	518	513
	309	(622)	651	660	664	664	662	659	653	648
	318	(617)	655	670	675	676	675	673	669	664
	404,405	-	512	632	670	682	688	690	690	690
	455,458	-	145	540	620	655	677	685	690	695
	506,507	-	-	395	553	615	655	665	675	685
	515	-	-	350	518	585	620	640	655	665
	554,555	-	-	210	445	542	595	628	650	665
	594	-	-	100	355	490	565	610	640	655
	606	-	-	80	320	468	545	590	620	635
	708,710	-	-	15	108	263	395	480	540	575
	812	-	-	-	30	110	222	327	415	477
NaBr	0	65.5	69.8	72.5	73.8	73.9	73.2	72.0	70.2	68.5
	25	120.6	124.1	126.2	127.0	126.6	125.5	124.0	122.0	119.8
	100	339	340	338	337	332	328	324	321	317
	205	(540)	537	533	528	522	516	510	503	497
	300	(620)	637	641	641	638	634	628	622	616
	399	-	550	643	667	675	680	678	677	675
	441	-	325	585	637	660	670	675	677	677
	501	-	-	445	575	622	645	655	657	660
	557	-	-	240	470	565	605	632	645	655
	600	-	-	132	390	515	582	620	640	653
	698	-	-	20	153	325	440	510	555	585
	809	-	-	-	40	135	258	360	435	487
NaI	0	63.8	67.5	69.5	70.0	69.4	68.2	66.7	64.7	62.5
	25	118.0	121.0	121.7	121.4	120.1	118.0	115.9	113.4	110.6
	101	(320)	318	315	310	305	300	296	291	287
	207	(552)	548	541	533	524	517	508	500	493
	306	(610)	624	625	623	622	619	614	610	603
	406	-	540	623	646	650	652	650	648	640
	457	-	235	573	625	643	650	653	653	652
	508	-	-	460	570	612	632	640	645	647
	605	-	-	152	412	527	580	605	626	633
	702	-	-	22	190	368	472	530	568	590
	796	-	-	-	68	208	338	425	485	522
KCl	0	78.2	84.4	88.4	90.7	91.7	91.6	90.9	89.5	87.7
	25	141.5	147.0	150.3	152.0	152.6	152.4	151.5	149.9	147.6
	101	(369)	369	368	367	365	362	358	354	349
	202	(610)	609	606	602	596	590	583	577	572
	305	(684)	703	714	715	714	711	706	700	693
	402	-	575	687	720	733	737	737	733	725
	501	-	-	470	612	665	690	705	713	715
	604	-	-	115	385	518	590	630	657	675
	711	-	-	-	135	312	442	522	575	610
	799	-	-	-	52	170	308	410	485	532
KBr	0	79.0	85.3	89.0	90.8	91.6	91.2	90.0	88.3	86.2
	25	143.0	147.6	150.8	152.2	152.2	151.3	149.6	147.4	144.6
	110	(397)	396	394	392	387	382	377	372	367
	211	(612)	611	606	600	594	587	580	572	564
	310	-	690	694	695	695	694	692	689	682
	402	-	560	662	690	700	703	705	705	703
	447	-	300	597	648	673	688	698	700	700
	503	-	-	455	590	642	667	683	692	695
	596	-	-	150	405	525	577	617	636	648
	692	-	-	24	185	360	467	528	567	595
	798	-	-	-	62	195	328	420	485	530
KI	0	80.0	85.0	88.2	89.2	89.4	88.4	87.0	85.0	82.5
	25	143.2	146.8	148.7	149.0	148.3	146.7	144.5	142.2	139.2
	110	(399)	398	396	390	383	377	372	366	357
	210	(600)	596	589	581	573	565	557	548	540
	308	(660)	685	690	686	681	673	666	660	651
	404	-	565	652	680	683	686	685	682	677
	446	-	325	595	645	663	670	673	673	670
	503	-	-	472	590	627	646	660	670	672
	543	-	-	360	537	600	628	643	650	655
	647	-	-	78	315	463	535	575	600	615
	711	-	-	25	192	355	465	527	568	595
	744	-	-	-	145	317	432	497	542	568
	803	-	-	-	80	225	355	440	500	543
RbF	0	67.4	72.4	75.4	77.4	78.2	78.3	78.0	77.2	75.8
	25	125.0	128.5	131.2	132.8	133.5	133.4	132.8	132.0	130.4
	100	332	330	328	325	323	321	318	316	315
	203	(570)	568	566	562	560	555	551	545	540
	303	(605)	623	636	642	645	647	647	643	638
	356	-	585	620	633	645	650	655	656	655
	400	-	515	603	635	650	655	660	663	657
	460	-	156	507	580	615	630	642	650	655
	502	-	-	403	523	570	597	610	620	630
	606	-	-	110	333	455	520	555	580	600
	718	-	-	-	136	287	398	467	510	537
	801	-	-	-	58	175	295	380	437	475
RbCl	0	80.5	86.8	90.8	92.7	93.3	93.0	92.2	90.6	88.6
	25	145.0	150.0	153.0	154.6	154.7	154.5	153.2	151.0	148.4
	102	(369)	370	368	367	363	360	357	353	348
	201	(628)	620	613	608	602	595	590	583	577
	302	(687)	709	717	717	715	713	709	706	702
	350	(585)	680	710	720	722	720	718	715	707
	409	-	525	660	695	712	715	722	720	718
	448	-	290	600	665	695	716	725	730	730
	547	-	-	290	507	595	640	665	677	683
	602	-	-	135	392	520	592	635	660	678
	697	-	-	17	161	336	450	517	558	585
	793	-	-	-	62	187	327	425	490	530
RbBr	0	81.8	87.6	91.0	92.7	93.0	92.2	91.0	89.0	86.5
	25	146.0	150.5	153.0	154.0	154.0	152.6	151.0	148.4	145.5
	102	(374)	372	370	367	362	357	352	348	342
	202	(617)	613	608	601	594	586	578	570	562
	302	(690)	713	720	718	713	708	702	697	690
	352	(562)	645	674	682	682	682	680	675	670
	401	-	566	675	709	718	722	725	720	715
	454	-	265	600	663	690	707	715	720	720
	494	-	-	500	610	655	675	685	690	692
	546	-	-	310	515	594	630	650	660	665
	617	-	-	115	367	503	575	617	640	650
	650	-	-	60	290	440	527	575	607	625
	709	-	-	30	175	345	460	528	570	595
	742	-	-	-	120	285	405	485	533	572
	809	-	-	-	67	198	320	415	480	520
RbI	0	81.2	86.2	88.4	89.3	88.7	87.5	85.7	83.5	80.8
	25	145.0	148.2	149.5	149.3	148.0	146.0	143.4	140.2	137.0
	100	357	357	353	349	343	337	331	325	318
	199	(590)	583	576	567	558	550	540	530	522
	300	(656)	674	675	672	668	665	658	652	642
	348	(610)	660	682	688	688	682	675	667	662
	401	-	570	657	676	684	682	680	675	670
	447	-	300	597	645	665	670	672	673	672
	503	-	-	500	615	650	665	670	674	675
	547	-	-	360	543	610	640	655	665	668
	598	-	-	183	435	538	588	613	630	638
	641	-	-	105	355	495	565	600	622	632
	700	-	-	-	230	410	510	566	605	620
	802	-	-	-	95	245	380	465	518	552
CsCl	0	80.8	86.7	90.1	91.9	92.0	91.6	90.6	88.6	86.3
	25	144.5	149.3	151.7	152.5	152.5	151.4	149.5	147.4	144.5
	102	(363)	362	360	357	353	350	346	340	334
	201	(615)	612	607	600	593	583	577	569	560
	303	(664)	687	692	690	685	681	675	669	660
	400	-	585	680	703	710	710	710	706	703
	447	-	305	600	665	692	705	707	707	707
	512	-	-	445	600	656	685	700	703	705
	599	-	-	140	400	525	587	620	643	655
	648	-	-	50	275	440	525	575	605	623
	700	-	-	25	180	370	485	553	592	618
	796	-	-	-	70	205	335	425	485	525
CsBr	0	81.7	87.5	90.8	92.5	92.6	91.6	90.0	88.0	85.5
	25	144.5	148.3	150.6	151.2	150.6	148.6	146.3	143.5	140.5
	120	(420)	417	412	407	401	395	388	382	375
	220	(625)	622	614	605	597	587	577	568	558
	314	(660)	685	692	688	683	677	670	665	650
	414	-	515	645	675	690	690	690	685	680
	462	-	175	575	640	668	680	682	681	680
	509	-	20	450	587	640	665	675	680	680
	632	-	-	95	340	482	550	593	627	630
	712	-	-	25	177	350	460	523	570	592
	813	-	-	-	72	203	330	425	492	535
CsI	0	80.0	84.5	86.7	87.0	86.4	85.0	83.0	80.5	77.8
	25	142.5	145.3	146.0	145.4	144.0	141.1	138.5	135.0	131.6
	105	(397)	392	387	380	373	366	358	351	343
	206	(610)	600	590	578	568	558	547	536	525
	303	(684)	697	695	687	678	669	658	649	638
	401	-	580	660	675	680	680	675	665	655
	448	-	323	595	657	675	680	680	677	672
	503	-	-	480	600	633	650	658	662	665
	607	-	-	160	418	532	588	618	632	638
	661	-	-	70	300	450	530	574	600	613
	708	-	-	35	200	370	470	530	565	584
	762	-	-	15	135	300	413	488	535	565
	798	-	-	-	100	250	370	450	503	543

[a] Values in parentheses are those extrapolated to saturation vapor pressure.

anion, are given in Figure 5 where specific conductance is plotted against temperature at a pressure of 4000 bars. This behavior is characteristic of salts of strong acids and bases and can be explained in terms of the effect of temperature upon the viscosity and density of water and upon the degree of dissociation of the salts. As the temperature increases from 0 to 800° the viscosity of water decreases very rapidly initially,[14,15] resulting in a sharp increase in the mobilities of the ions. Above approximately 300° the rate of decrease of viscosity with increasing temperature diminishes considerably,[16] and therefore the ionic mobilities do not increase as rapidly as at lower temperatures. The curves in Figure 5 reach maxima near 400° and then decrease with increasing temperature, indicating that factors other

(14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed (revised), Butterworth and Co. Ltd., London, 1965, p 457.

(15) K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965).

(16) K. H. Dudziak and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **70**, 1120 (1966).

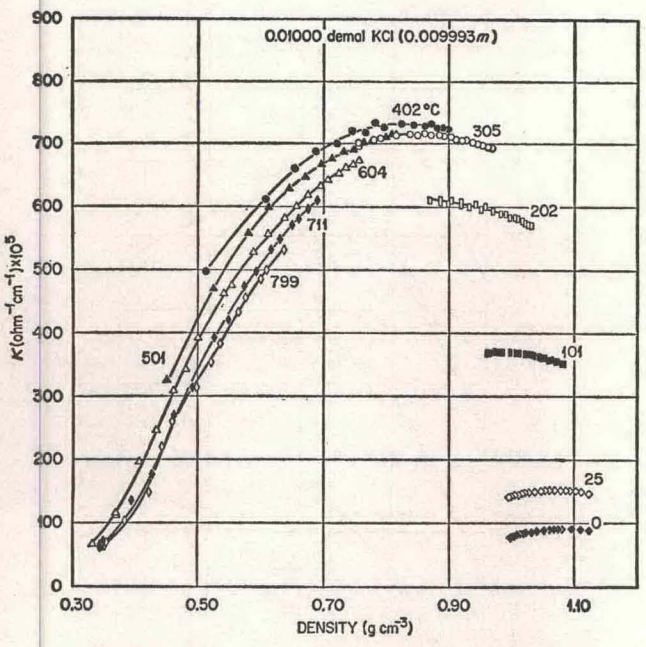

Figure 4. Specific conductances of 0.01000 demal (0.009993 m) KCl solutions as a function of density at several temperatures.

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 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 Rb^+, $K^+ > Cs^+ > Na^+ > Li^+$. 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.

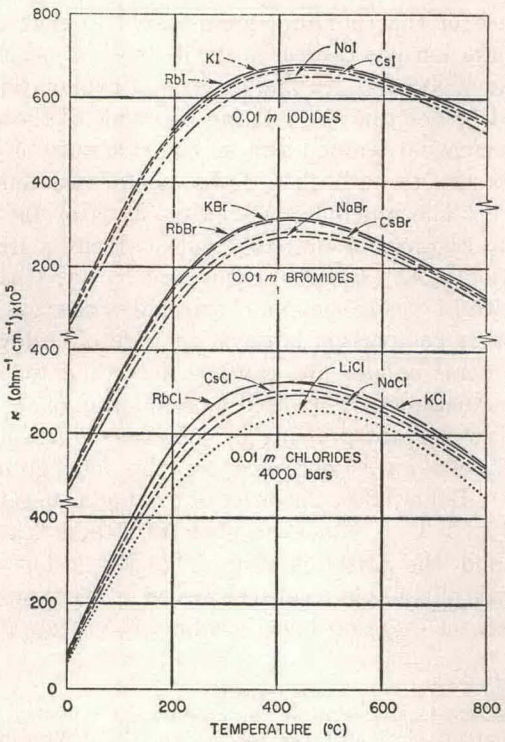

Figure 5. Isobaric specific conductances of 0.01000 m aqueous solutions of some alkali metal halides as a function of temperature; pressure = 4000 bars.

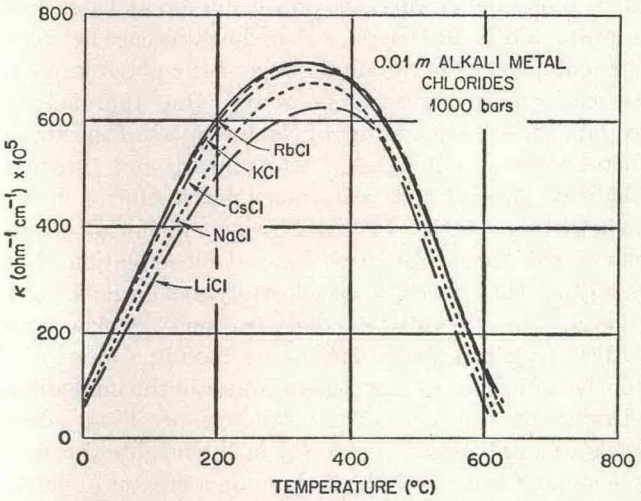

Figure 6. Isobaric specific conductances of 0.01000 m aqueous solutions of the alkali metal chlorides as a function of temperature; pressure = 1000 bars.

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-

(17) W. E. Sharp, "The Thermodynamic Functions for Water in the Range −10 to 1000° and 1 to 250,000 Bars," University of California Radiation Laboratory Report UCRL-7118, 1962.

(18) S. Maier and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **70**, 639 (1966).

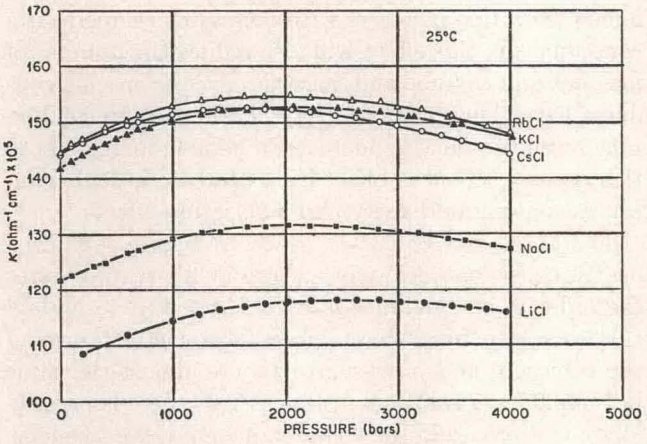

Figure 7. Isothermal specific conductances of 0.01000 *m* alkali metal chloride solutions as a function of pressure at 25°.

sure. At 25° and 1 atm, the *limiting* equivalent conductances of these ions are given by Robinson and Stokes[19] 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°.[20] 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 Mills[21] 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^+),

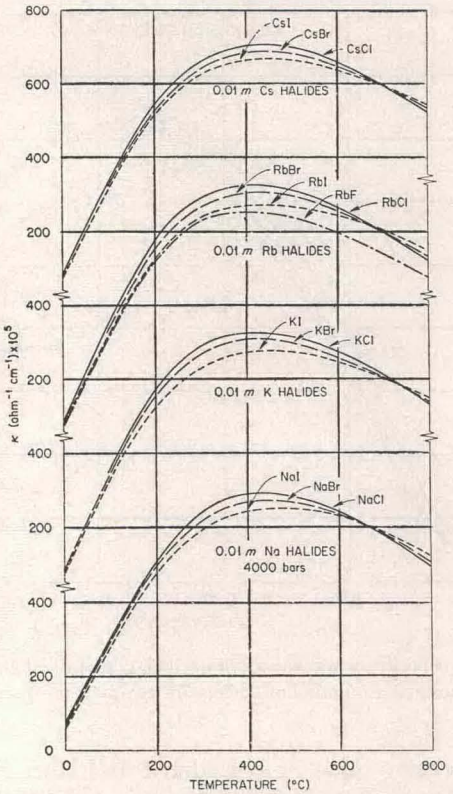

Figure 8. Isobaric specific conductances of 0.01000 *m* aqueous solutions of some alkali metal halides as a function of temperature; pressure = 4000 bars.

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 Cl^- > Br^- > I^- > F^-. However, near 700°, there is a crossover, and the order is then I^- > Br^- > Cl^- > 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.

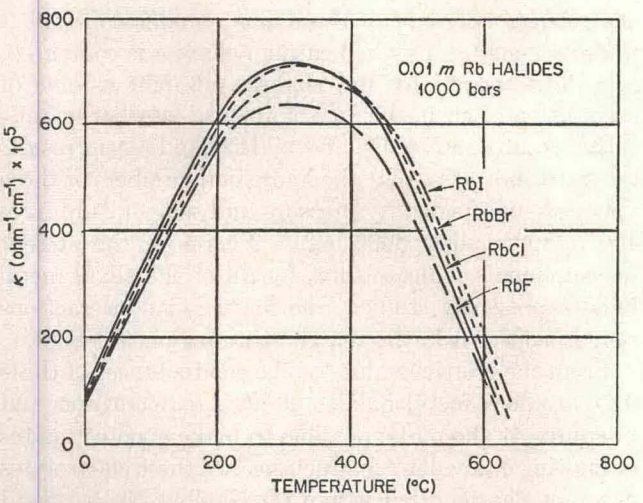

Figure 9. Isobaric specific conductances of 0.01000 *m* aqueous solutions of the rubidium halides as a function of temperature; pressure = 1000 bars.

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 $Cl^- > Br^- > I^-$.[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 $Cl^- > Br^- > I^- > F^-$. The order at 25° and 1 atm is[19] Br^- (78.14) > I^- (76.84) > Cl^- (76.35) > F^- (55.4), but at 55° it has changed to[19] Br^- (127.86) > Cl^- (126.40) > I^- (125.44) > 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.

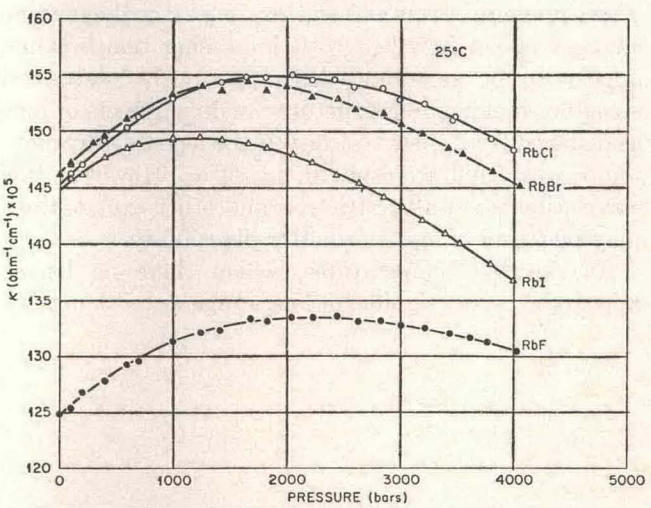

Figure 10. Isothermal specific conductances of 0.01000 *m* aqueous rubidium halide solutions as a function of pressure at 25°.

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 ±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).