

686. *The Effect of Pressure on the Electrical Conductivity of Aqueous, Mixed Electrolyte Solutions.*

By R. A. HORNE and R. A. COURANT.

The electrical conductivities of aqueous, mixed electrolytic solutions of KCl-HCl and SrCl₂-HCl of total concentration 0.10m have been measured at 25°C as functions of the relative concentrations of the constituent electrolytes and of hydrostatic pressure over the pressure range 1 to 6700 bars. Conductance equations, such as the Onsager-Fuoss relationship, based on considerations of the electrophoretic and relaxation effects, are not applicable to protonic conduction; therefore the several trends exhibited by the observed "mixture effects" are discussed qualitatively. Of these trends the most interesting is a reversal of the effect at about 1300 bars.

WE earlier reported the results of measurements of the electrical conductivity of sea water as a function of salinity, temperature, and hydrostatic pressure.¹ Sea water is roughly 0.48, 0.54, 0.05, and 0.03m in Na⁺, Cl⁻, Mg²⁺, and SO₄²⁻, respectively; it is thus a moderately concentrated mixed electrolyte solution. Pressures obtaining at the bottom of the oceans may be as great as 1000 bars. Little is known concerning the conductive properties of mixed electrolyte solutions under pressure, and the present studies were undertaken as a step toward understanding the behaviour of sea water under pressure. The systems hydrogen chloride-potassium chloride and hydrogen chloride-strontium chloride, although not of oceanographic significance, were chosen because, owing to the widely different mobilities of the cations, a large "mixture effect" or departure from the Kohlrausch principle of independent ionic mobilities was expected.

¹ Horne and Frysinger, *J. Geophys. Res.*, 1963, **68**, 1967.

EXPERIMENTAL

The high-pressure equipment, the conductivity bridge, the thermostatic bath, the construction of the conductivity cell, and the measuring techniques have been described previously.¹ A glass capillary-type conductivity cell with platinized platinum electrodes was used. The electrolytic solutions of the desired concentrations were prepared from chemically pure reagents and, in addition, were analysed by standard procedures.

RESULTS AND DISCUSSION

Fig. 1 shows the results of a typical experiment. The resistance of the solution goes through a minimum as the pressure is increased, corresponding to a maximum in the curve of specific conductance against pressure. The variation of the specific conductance of KCl-HCl and SrCl₂-HCl solutions under pressure is shown in Tables 1 and 2 and Figs. 2 and 3. At a given pressure, the molal conductance was calculated by using the specific conductance of the 0.1m-hydrogen chloride, 0.1m-potassium chloride, and 0.05m-strontium chloride solutions at that pressure and assuming that the conductive contributions of the two constituents of the mixed electrolyte solutions are purely additive. Tables 3 and 4 summarize values of the ratio of the observed conductance to the conductance thus calculated at different electrolyte compositions and different pressures.

The present results for the HCl-KCl systems at one atmosphere are in agreement with the earlier results of Longworth² who found that the conductance of H⁺ in a H⁺-K⁺ mixture of $m_{\text{H}^+}/m_{\text{H}^++\text{K}^+} = 0.2$ is 1.8% lower than that of H⁺ in H⁺ alone (present value 1.5%) and 0.8% lower (present value 0.8%) when $m_{\text{H}^+}/m_{\text{H}^++\text{K}^+} = 0.4$. Longworth² was able to show that in mixtures of the present type the common anion, Cl⁻, is not responsible for the "mixture effect."

The equivalent conductance of an ion in the presence of a mixture of ions is given by³

$$\lambda_j = \lambda_j^\circ - \left[\frac{1.981 \times 10^6}{(D_0 T)^{3/2}} \lambda_j^\circ Z_j \sum_0^\infty C_n r_j^{(n)} + \frac{29.16 Z_j}{\eta_0 (DT)^{1/2}} \right] \sqrt{\Gamma} \quad (1)$$

where the symbols are those as defined by Harned and Owen.⁴ This expression contains a number of pressure-dependent parameters including the limiting conductance, the dielectric constant, and viscosity of the medium, and terms which are functions of the concentration of the ions. A summary of the pressure-dependence of some of these parameters is given in Table 5.

On the basis of the values listed in Table 5 at 25° the term

$$1.98 \times 10^6 / (D_0 T)^{3/2}$$

decreases by 27% over the pressure range 1 to 5360 bars while the term

$$29.16 / \eta_0 (DT)^{1/2}$$

decreases by 39%.

The ratios in Tables 3 and 4 are based on molal concentrations. They are not, therefore, affected by the compression of water. If molar concentrations are used, at a given pressure they must be multiplied by the reciprocal of the relative volume.

Hamann⁵ has calculated limiting molal conductances of some ions in aqueous solution from data by Buchanan and Hamann⁶ and Hamann and Strauss.⁷ Values for KCl and HCl are shown in Table 6. At 25°, $\Lambda^\circ_{\text{KCl}}$ exhibits a maximum between 1 and 2000 bars

² Longworth, *J. Amer. Chem. Soc.*, 1930, **52**, 1897.

³ Onsager and Fuoss, *J. Phys. Chem.*, 1932, **36**, 2689.

⁴ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N.Y., 34d edn., 1958.

⁵ Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publns., London, 1957, p. 123.

⁶ Buchanan and Hamann, *Trans. Faraday Soc.*, 1953, **49**, 1425.

⁷ Hamann and Strauss, *Trans. Faraday Soc.*, 1955, **51**, 1684.

3550 Horne and Courant: Effect of Pressure on the Electrical

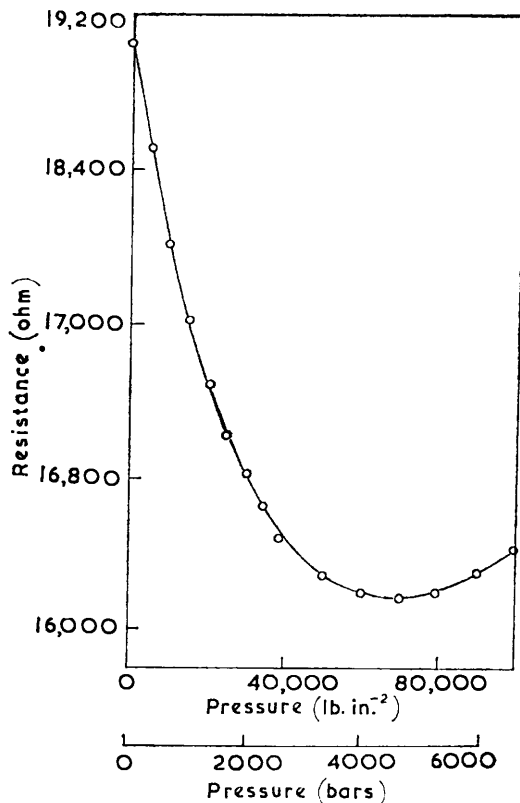


FIG. 1. Variation of the electrical resistance with pressure of a solution of 0.06m-KCl—0.04m-HCl at 25°.

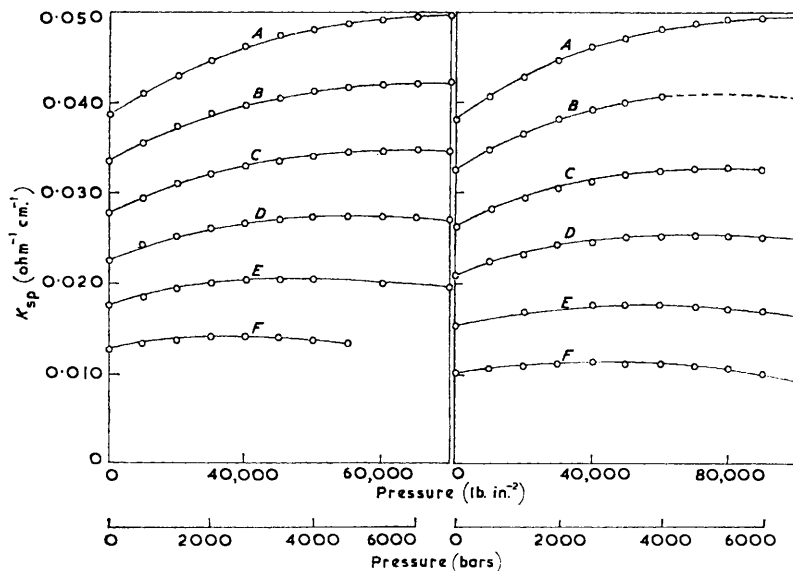


FIG. 2.

FIG. 3.

FIG. 2. The effect of pressure on the specific conductance of aqueous KCl-HCl solutions.

A, 0.100m-HCl; B, 0.020m-KCl-0.080m-HCl; C, 0.040m-KCl-0.060m-HCl; D, 0.060m-KCl-0.040m-HCl; E, 0.080m-KCl-0.020m-HCl; F, 0.100m-KCl.

FIG. 3. The effect of pressure on specific conductance of aqueous SrCl₂-HCl solutions. A, 0.100m-HCl; B, 0.010m-SrCl₂-0.080m-HCl; C, 0.020m-SrCl₂-0.060m-HCl; D, 0.030m-SrCl₂-0.04m-HCl; E, 0.040m-SrCl₂-0.020m-HCl; F, 0.050m-SrCl₂.

TABLE 1.

The effect of pressure on the electrical conductivity of HCl-KCl solutions.

Soln. Composition	KCl 0.100m HCl 0.000m	0.080m 0.020m	0.060m 0.040m	0.040m 0.060m	0.020m 0.080m	0.000m 0.100m
Temp. (°C)	24.94 ± 0.005	24.94 ± 0.05	24.90 ± 0.07	25.00 ± 0.02	24.87 ± 0.08	24.96 ± 0.01
Pressure (bars)	Specific conductance (ohm ⁻¹ cm. ⁻¹)					
1	0.01283	0.01763	0.02280	0.02785	0.03309	0.03822
340	—	0.01813	0.02349	0.02869	0.03416	0.03955
670	0.01333	0.01863	0.02415	0.02968	0.03528	0.04079
1000	0.01357	0.01902	0.02472	0.03042	0.03623	0.04193
1340	0.01373	0.01931	0.02520	0.03110	0.03706	0.04294
1680	0.01383	0.01953	0.02558	0.03161	—	—
2000	0.01388	0.01971	0.02591	0.03211	0.03845	0.04463
2350	0.01387	0.01987	0.02619	0.03251	—	—
2690	0.01384	0.01998	0.02645	0.03288	0.03954	0.04594
3000	0.01378	—	—	—	—	—
3350	0.01371	0.02004	0.02679	0.03343	0.04032	0.04698
4000	0.01354	0.02003	0.02698	0.03383	0.04095	0.04776
4360	0.01340	—	—	—	—	—
4700	0.01325	—	0.02703	0.03406	0.04138	0.04837
5360	—	0.01976	0.02702	0.03424	0.04166	0.04884
6040	—	—	0.02688	0.03418	0.04184	0.04916
6700	—	0.01923	0.02672	0.03414	0.04187	0.04935

TABLE 2.

The effect of pressure on the electrical conductivity of HCl-SrCl₂ solutions.

Soln. Composition	SrCl ₂ 0.050m HCl 0.000m	0.040m 0.020m	0.030m 0.040m	0.020m 0.060m	0.010m 0.080m	0.000m 0.100m
Temp. (°C)	25.03 ± 0.01	25.02 ± 0.00	24.98 ± 0.01	24.98 ± 0.01	24.98 ± 0.01	24.96 ± 0.01
Pressure (bars)	Specific conductance (ohm ⁻¹ cm. ⁻¹)					
1	0.01018	0.01526	0.02099	0.02639	0.03266	0.03822
340	0.01067	—	0.02227	0.02808	0.03478	0.04079
670	—	0.01662	—	—	—	—
1280	—	—	—	—	0.03634	—
1340	0.01097	—	0.02326	0.02945	—	0.04294
1680	—	—	—	—	0.03785	—
2000	0.01109	—	0.02397	0.03042	—	0.04463
2620	—	—	—	—	0.03889	—
2690	0.01109	0.01736	0.02447	0.03115	—	0.04594
3290	—	0.01746	—	—	0.03966	—
3350	0.01099	—	0.02480	0.03165	—	0.04698
3960	0.01081	—	—	0.03202	0.04025	—
4000	—	0.01745	0.02496	—	—	0.04776
4700	—	—	0.02506	0.03227	—	0.04837
4770	0.01053	0.01734	—	—	—	—
5300	—	—	0.03237	—	—	—
5360	—	0.01717	0.02504	—	—	0.04884
5430	0.01023	—	—	—	—	—
5900	—	—	—	0.03239	—	—
6040	0.00995	0.01698	0.02494	—	—	0.04916
6440	—	—	0.02483	—	—	—
6530	—	0.01677	—	—	—	—
6700	—	—	—	—	—	0.04935

TABLE 3.

Additivity of conductances with pressure for KCl-HCl.

	Value of $K_{m, obs.}/K_{m, calc.}$ at			
	1	1340	2690	4000 bars
0.080m-KCl-0.020m-HCl	0.985 (1.5%)	0.987 (1.3%)	0.986 (1.3%)	0.983 (1.7%)
0.060m-KCl-0.040m-HCl	0.992 (0.8%)	0.991 (0.9%)	0.991 (0.9%)	0.991 (0.9%)
0.040m-KCl-0.060m-HCl	0.993 (0.8%)	0.995 (0.5%)	0.993 (0.7%)	0.993 (0.7%)
0.020m-KCl-0.080m-HCl	0.999 (0.1%)	0.999 (0.1%)	1.000 (0.05%)	1.001 (0.07%)

TABLE 4.
Additivity of conductances with pressure for SrCl₂-HCl.

	1	Value of $K_{m, obs.}/K_{m, calc.}$ at				5360 bars
		1340	2690	4000	5360 bars	
0.040m-SrCl ₂ -0.020m-HCl	0.957	0.981	0.962	0.961	0.957	0.957
0.030m-SrCl ₂ -0.040m-HCl	0.992	0.976	0.976	0.976	0.976	0.978
0.020m-SrCl ₂ -0.060m-HCl	0.978	0.974	0.976	0.973	0.969	0.969
0.010m-SrCl ₂ -0.080m-HCl	1.002	0.996	0.999	0.998	1.005	1.005

TABLE 5.
Variation of solvent dielectric constant (D_0 , at 20°), viscosity (η_0 , at 30°), and relative volume with pressure.

Pressure, P (bars)	D_0 ^a	η_0 ^b (centipoise)	Rel. vol. ^c
1	81.0	0.80	1.00
1340	86.0	0.86	0.96
2680	91.3	0.96	0.91
4020	95.2	1.08	0.89
5360	98.8	1.20	0.86
	(18% increase)	(50% increase)	(14% decrease)

^a Scaife, *Proc. Phys. Soc.*, 1959, **B68**, 790. ^b Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1926, **61**, 57. ^c Bridgman, *ibid.*, 1912, **48**, 309.

whereas $\Lambda^\circ_{\text{HCl}}$ does not, and at 45° $\Lambda^\circ_{\text{HCl}}$ exhibits a maximum but only at much higher pressures (between 4000 and 6000 bars) than $\Lambda^\circ_{\text{KCl}}$. This significant difference in behaviour between KCl and HCl solutions is attributable to different mechanisms of electrical conduction. The conduction of KCl is "normal" and entails translational movement of the hydrated ions through the viscous medium or, considered microscopically, the formation of a "hole" in the solvent followed by the movement of the hydrated ion to fill the "hole." Protons, however, exhibit anomalously large apparent mobilities and conduct by a Grotthuss-type mechanism. Studies of the pressure-dependence of the activation energy of electrical conductance ⁸ have shown that below about 1300 bars the rotation of water molecules is the rate-determining step of this mechanism, as maintained earlier by Hückel ⁹ and Conway, Bockris, and Linton ¹⁰ but that at greater pressures the proton flip becomes rate-determining.

Equation (1) and other related expressions which have been formulated to describe the electrically conductive properties of aqueous solutions are based on consideration of two

TABLE 6.
Effect of pressure on limiting molar conductances.

Pressure, P (bars)	Limiting molar conductance (ohm ⁻¹ cm. ² mole ⁻¹)			
	$\Lambda^\circ_{\text{KCl}}, 25^\circ$	$\Lambda^\circ_{\text{KCl}}, 45^\circ$	$\Lambda^\circ_{\text{HCl}}, 25^\circ$	$\Lambda^\circ_{\text{HCl}}, 45^\circ$
1	149	218	427	535
1000	153	—	444	—
2000	149	218	453	591
3000	144	—	454	—
4000	—	205	—	604
6000	—	187	—	604
8000	—	166	—	596
10,000	—	145	—	579

effects which are believed to be responsible for ion-ion interactions in more concentrated solutions—the electrophoretic and the relaxation effects. Both are kinetic effects; the former relates to the movement of an ion in a non-stationary medium, the latter to the

⁸ Horne, Myers, and Frysinger, *J. Chem. Phys.*, 1963, **39**, 2666.

⁹ Hückel, *Z. Elektrochem.*, 1928, **34**, 546.

¹⁰ Conway, Bockris, and Linton, *J. Chem. Phys.*, 1956, **24**, 834.

displacement of an ion in a coulombic field. But the movement of a proton by the Grotthus mechanism is only an *apparent* motion. Therefore, the electrophoretic and relaxation effects, at least in their present form, and thus relation (1) and variations thereof, are not relevant to protonic conduction in aqueous solutions. It might be noted in passing that the rotation of a water molecule in the coulombic field arising from its neighbours entails a relaxation effect but it is not the same effect as treated in the conductance equations. Onsager and Fuoss³ have calculated mixture effects for the system NaCl-HCl at 25° on the basis of equation (1); the agreement with the observed values is poor, especially at higher total concentrations and for smaller NaCl : HCl ratios. This result is not surprising in view of the inapplicability of equation (1) to protonic systems. Equation (1) should be applicable to salt mixtures. Kreiger and Kilpatrick¹¹ have calculated mixture effects for the system LiCl-KCl but they used Shedlovsky's empirical relation rather than equation (1); the mixture effect is much less pronounced because the relative similarity of the mobilities of Li⁺ and K⁺, and the discrepancies between observed and calculated results, are still considerable.

The inapplicability of equation (1) or related expressions to acidic aqueous solutions precludes a quantitative analysis of the pressure-dependence of the mixture effect in the case of the KCl-HCl and SrCl₂-HCl systems at this time. However, several worthwhile qualitative generalizations can be made on the basis of the values in Tables 3 and 4:

(1) The ratio of the observed to the calculated conductance increases or the deviation from unity decreases, as the H⁺ concentration increases. In a solution 0.080m in HCl and 0.020m KCl the former constituent accounts for more than 92% of the total conduction, and hence this solution differs little from a solution of HCl only, and there is little mixture effect.

(2) The mixture effect is greater for SrCl₂-HCl mixtures than for KCl-HCl mixtures. This finding is expected on the basis of the greater charge of Sr²⁺ and the greater dissimilarity of its mobility from that of H⁺ (Λ° 's at 25° for H⁺, K⁺, and Sr²⁺ are 350, 74, and 59 ohm⁻¹ cm.⁻² equiv.⁻¹).

With certain exceptions,

(3) Above about 1300 bars for solutions of greatest H⁺ concentration the ratio of observed to calculated conductance tends to increase, whereas

(4) Above about 1300 bars for solutions of least H⁺ concentration the ratio tends to decrease.

(5) Below about 1300 bars for solutions of greatest H⁺ concentration the ratio tends to decrease, and

(6) Below about 1300 bars for solutions of least H⁺ concentration the ratio tends to increase.

The reversal of the trends at about 1300 bars is of particular interest, for this is the same pressure range in which the activation energy of conduction of "normal" solutions goes through a minimum, and the activation energy of Grotthus conduction exhibits an inflection.⁸

This work was partially supported by the Bureau of Ships, U.S. Department of the Navy.

ARTHUR D. LITTLE, INC., CAMBRIDGE, MASSACHUSETTS.

[Received, November 4th, 1963.]

¹¹ Kreiger and Kilpatrick, *J. Amer. Chem. Soc.*, 1937, **59**, 1878.