

TABLE 12. Comparison of pressure effects in water and alcohol solvents.

P (atm.)	500	1000	2000	3000
Ratios $\Lambda^P \rho / \Lambda^1$ at 25°.				
0.001m-HCl in water ⁴	1.050	1.087	1.151	1.191
0.0011m-HCl in ethanol-water	0.990	0.980	0.959	0.938
0.0028m-HBr in methanol ⁷	—	0.909	0.844	0.791
0.01m-KCl in water ⁴	1.031	1.052	1.068	1.058
0.011m-NaCl in ethanol-water	0.938	0.876	0.775	0.700
0.0092m-NaCl in methanol ⁷	—	0.846	0.747	0.665
Viscosity ratios η^1/η^P at 30°.				
Water ⁹	0.975	0.947	0.882	0.808
Methanol ⁹	—	0.675	0.510	0.402
Ethanol ⁹	—	0.625	0.440	0.316

is a consequence mainly of their large increase in viscosity with pressure. It was later suggested ⁴ that the concentration dependence of the pressure effects for conductance in aqueous solution as predicted by the Debye-Hückel-Onsager equation may be opposed by the lower structural temperature of water at increased pressures. This would explain the fact that the concentration effects observed for water were even less than those calculated.

Hamann ² has also shown that the excess of conductance of the H_3O^+ and OH^- ions in water, *i.e.*, the amount by which the conductance of these ions exceeds that of similarly-sized ions which move by normal diffusion in an electric field, is increased with pressure but at a decreasing rate. He adopted Bell's ¹⁰ model for proton transfer and suggested that pressure assists proton exchange by providing some of the repulsion energy necessary to bring the oxygen atom close enough for a proton switch to occur. In the model of proton transfer by Conway, Bockris, and Linton ¹¹ the rate-determining step is the rotation of water molecules into the hydration sheath of the H_3O^+ ions as protons are transferred through solution. In water, increased pressure increases the co-ordination number of the H_3O^+ ions by breaking down the open tetrahedral water structure and hence increases the excess of conductance owing to proton transfer ($\lambda_{H^+} - \lambda_{Na^+}$).

In the simple alcohol series the excess of proton conductance decreases with the length of the carbon chain,¹¹ and pressure decreases it slightly ⁷ owing, probably, to the higher viscosity's slowing the rotation of alcohol molecules.

At 1 atm. $\lambda_{H^+} - \lambda_{Na^+}$ in ethanol-water is slightly less than in methanol and much smaller than in water. Pressure has only a small effect. As soon as there is more than a trace of water present in ethanol, equilibrium data show that nearly all protons form H_3O^+ ions in preference to $EtOH_2^+$ ions.¹¹ Normal transfers between H_3O^+ and H_2O are rare at low concentrations of water, so that H_3O^+ entities are more permanent than in water and consequently diffuse in the applied field rather in the manner of salt ions. With increasing water content exchanges between H_3O^+ and H_2O occur more frequently and the anomalous conductance becomes predominant.

Ionization of Weak Electrolytes.—Table 13 gives a comparison of the values for K_a from Series A with those usually accepted. The present experiments were designed to show changes with pressure rather than give highly accurate values at 1 atm. No previous

TABLE 13. Dissociation constants at 25°.

Acid	$10^5 K_a$ (Mean)	Accepted value $10^5 K_a$	Source
Benzoic	6.2	6.29	Harned and Owen ¹³
<i>o</i> -Nitrobenzoic	610	671	Dippy ¹²
<i>m</i> -Nitrobenzoic	31	32.1	"
<i>p</i> -Nitrobenzoic	33	37.6	"
3,5-Dimethyl-4-nitrobenzoic	7.5 *	—	—
Salicylic	101	106	Dippy ¹²

* In 10% v/v ethanol-water.

values for benzoic acids in ethanol-water were found but values are reported¹² for benzoic acid in 50% methanol-water (5.1×10^{-6}) and in 25% ethanol-water (2.3×10^{-5}).

It is now established that pressure causes a large increase in the dissociation of weak acids and bases, and that this increase arises largely from the enhanced solvation of the free ions at high pressures.² For acids and bases of the hydrated gas type, increases in the apparent dissociation constants may be also due partly to the greater concentration of true acid or base molecules at high pressures (*e.g.*, the $\text{CO}_2\text{--H}_2\text{CO}_3$ equilibrium⁴). As the increase in ionization is continuous to the highest pressures measured all weak electrolytes become "strong" under sufficient pressure.²

Tables 2-7 and 9-11 include values for the volume change ΔV which accompanies the ionization as calculated from the slope of the plot of $\log K_a^P/K_a^1$ against pressure. The value of ΔV is given at 3000 atm. (ΔV^{3000}) and also its limiting value at 1 atm. (ΔV^1). The average value of ΔK , the change in compressibility on ionization, was obtained approximately from the difference between ΔV^1 and ΔV^{3000} .

$$\left(\frac{\partial(\ln K_a)}{\partial P}\right)_{T,m} = \frac{-\Delta V}{RT}; \quad -\left(\frac{\partial \Delta V}{\partial P}\right)_{T,m} = \Delta K \approx \frac{\Delta V^{3000} - \Delta V^1}{3000}$$

The values of ΔV^1 and ΔK for the two solvents are compared in Table 14 for benzoic and salicylic acids.

TABLE 14.

	Acid	Ethanol-water		Water	
		ΔV^1	ΔK	ΔV^1	ΔK
Benzoic		-16.1	-0.0013	-10.6	-0.0011
Salicylic		-12.7	-0.0011	-7.2	-0.0005

It is known that the solvent in the immediate neighbourhood of an ion is in a state of compression,¹⁴ and one might therefore expect that the volume decrease accompanying the introduction of ions into a liquid should vary with the compressibility of the liquid. Hamann and Lim¹⁵ have shown that there is a linear relation between the compressibility of several solvents ($-\partial V/V, \partial P$) and the difference between the volume change on ionization in these solvents and the volume change in water ($\Delta V^\circ_{\text{solvent}} - \Delta V^\circ_{\text{water}}$). They list the figure $-14 \text{ cm}^3 \text{ mole}^{-1}$ as the value of $\Delta V^\circ (\text{ethanol}) - \Delta V^\circ (\text{water})$. From Table 14, for both benzoic and salicylic acids, a value of $-5.5 \text{ cm}^3 \text{ mole}^{-1}$ is obtained for $\Delta V^\circ (50:50 \text{ w/w ethanol-water}) - \Delta V^\circ (\text{water})$. This figure seems to be in reasonable agreement with that obtained by Hamann.

The effect of pressure on the hydration free energies of singly charged ions can be calculated by means of the Born equation

$$\Delta G_h = \frac{Ne^2}{2r} \left(1 - \frac{1}{D}\right)$$

where ΔG_h is the free energy of hydration of a mole of ions at infinite dilution, r is the radius of the ion, and D the dielectric constant of the solvent. The increase in the true dissociation constant of a weak acid with pressure can be correlated with the increased free energy of hydration of the ions if it is assumed that the free energy of hydration of the acid molecule is small and that pressure has little effect on the H-A bond dissociation energy, the ionization potential of H, and the electron affinity of A.²

The change in radius of the unsolvated ion with pressure is not affected by varying the solvent. The change in dielectric constant however is much more important for methanol and ethanol solutions than for water. The greater value of $\log K_a^P/K_a^1$ for a given pressure and acid in ethanol-water than in water is associated with the lower and more pressure-susceptible dielectric constant of the former medium. This observation has also been made for the weak base piperidine in methanol and in water.⁸