

Effect of Pressure on Conductance. IV. Ionic Association and Walden Products in Ethanol¹

by E. L. Cussler and Raymond M. Fuoss

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut (Received June 12, 1967)

The conductance at 30° of sodium bromide in methanol and in ethanol, under pressures up to 500 atm, were measured in the concentration range $3 \leq 10^4 c \leq 20$. Confirming previous results,² the association constant in methanol increases with increasing pressure. In ethanol, the association constant is indistinguishable from zero. Solvation of bromide ions by hydrogen bonds to alcohol molecules is suggested. The conductances of tetramethylammonium bromide and tetrabutylammonium bromide and tetraphenylboride in ethanol were measured over the same range of variables. The net conductance of the three salts decreases with increasing pressure, corresponding to the increase of viscosity (relative viscosity at 5000 atm is 5.2). The association constants decrease with increasing pressure, due to the increase by 27% in dielectric constant. The association constant of $\text{Bu}_4\text{N} \cdot \text{BPh}_4$ (about 300 at 30° and 1 atm) is larger than that of Me_4NBr (about 200), presumably because the excluded volume factor in the association constant is so large for the former.

The conductance of an electrolytic solution is a very complicated function of pressure, because every variable and parameter (except temperature and valence) in the conductance function is an implicit function of pressure. Viscosity usually increases with pressure: limiting mobility and the electrophoretic term therefore decrease. Dielectric constant also increases with pressure: electrostatic association constant and relaxation field decrease, the former exponentially and the latter as $D^{-3/2}$. Even the concentration is pressure dependent; due to compression, the volume concentration of a solution of fixed weight concentration increases with pressure. A collection of $\Lambda(P; c)$ data therefore is not very informative; it is necessary to analyze the isobaric phoreograms in order to isolate the fundamental parameters and then to study their dependence on pressure.

In a previous paper,² we reported the conductance of sodium bromide, tetramethylammonium bromide, tetrabutylammonium bromide, and tetraphenylboride in methanol. As expected, the main effect of increasing pressure was to reduce conductance in such a way that the Walden product remained constant for $\text{Bu}_4\text{N} \cdot \text{BPh}_4$ and increased somewhat for the

other three salts. The association constant K_A of sodium bromide appeared to increase with pressure (contrary to expectation); the effect was small, and on account of the many interpolations involved in the calculations, it was practically impossible to assess the uncertainty in K_A . We have therefore repeated the measurements on the system NaBr-MeOH , using a method which required no interpolations of conductance data. The previous result is confirmed. Furthermore, in ethanol, which has a much lower dielectric constant, the association constant of sodium bromide turns out to be very small; in fact, within our experimental error, $K_A(\text{NaBr, EtOH})$ is indistinguishable from zero. Solvation of bromide ions is suggested as the cause of these effects.

As expected from the lower dielectric constant of ethanol, the association constants of the quarternary salts are found to decrease with increasing pressure, corresponding to the 17% increase in dielectric con-

(1) Grateful acknowledgment is made for the support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-244,63,65.

(2) J. F. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **70**, 1426 (1966).

stant at 5000 atm. Just as in methanol, association at a given pressure was greater for $\text{Bu}_4\text{N} \cdot \text{BPh}_4$ than for the bromide. The association constant is the product of a sequence of factors: one of these is the volume exclusion term which increases as the cube of ionic dimensions, and another is the Boltzmann factor $\exp(\epsilon^2/aDKT)$ which decreases with increasing contact distance a . The function has a minimum for $a_M = \epsilon^2/3DKT$; our results for the tetraphenylboride in methanol and in ethanol suggest that the contact distance for this salt is greater than a_M , and therefore the salt is more highly associated than the bromide, for which the contact distance is less than a_M .

Experimental Section

The salts used have already been described.² Reagent grade ethanol (U. S. Industrial Chemicals) was used as received; periodic checks on random samples with an F and M Model 700 chromatograph always showed less than 0.05% water and 0.01% other impurities. The specific conductance of the ethanol (at the relevant pressure) was subtracted from the observed solution conductance; the correction was always less than 1%. Methanol, which was purified by slow distillation from anhydrous calcium sulfate, had a specific conductance of less than 10^{-7} mho; this correction was negligible. Acetonitrile (used in the cell calibration) was dried in the same way. The specific conductance of the acetonitrile was about 2×10^{-7} ; the maximum correction was 0.3%. Solutions were prepared by weight, using a Model M Mettler microbalance for the solutes. Solutions were assumed to have the solvent density at a given pressure.

The high-pressure generating system and autoclave-thermostat have been described previously.³ The operating temperature was $30.0 \pm 0.4^\circ$. The high-pressure conductance cell described previously, recalibrated with Bu_4NBr in freshly distilled acetonitrile at 25° , had a cell constant of $0.1605 \pm 0.0002 \text{ cm}^{-1}$. (The electrodes had been jarred since their previous calibration.) A similar cell, with $2.0 \times 2.8 \text{ cm}$ electrodes 1 mm apart, was used for the dilute solutions. Its constant was $0.0390 \pm 0.0001 \text{ cm}^{-1}$. The cell constants were assumed independent of pressure and temperature. Butyl rubber O-rings, which had been boiled three times in ethanol, were used to seal the conductance cells.

Measurements were made using the same technique and equipment as before,² with one change. Previously, measurements were made at random pressures between atmospheric and our maximum of about 5000 atm, a procedure which subsequently necessitated interpolation to round values of pressure in order to

simplify calculations of parameters, and which therefore obscured experimental errors by the smoothing thereby involved. In the present work, conductances were measured at round values of pressure gauge readings. These were chosen to give approximately equal increments of conductance; they were 0 (atmospheric pressure), 5000, 10,000, 15,000, 25,000, 40,000, and 70,000 psig. (Our gauges read psi, not metric units.) After measuring at atmospheric pressure, and at the above sequence of increasing pressures, pressure was slowly released, and the conductance at 1 atm was remeasured; the final value usually checked the initial value within 0.5%. Increasing pressure naturally raised the temperature in the autoclave; resistance was measured at intervals after reaching a predetermined pressure, and restoration of the original temperature of 30° was indicated by constancy of the resistance within 0.2% for at least 15 min. Small adjustments were made, of course, to hold the desired pressure as the contents of the autoclave cooled after initial compression.

The properties of ethanol and of methanol are summarized in Table I; they were obtained from literature values⁴⁻⁶ by interpolation at the pressures listed above. Densities were used to convert weight concentrations into volume concentrations at the relevant pressures; viscosities and dielectric constants were used to calcu-

Table I: Properties of Ethanol and Methanol at 30°

$10^3 P$	Ethanol			Methanol		
	ρ	100η	D	ρ	100η	D
0	0.781	1.00	23.2	0.782	0.512	31.7
5	0.807	1.21	24.2	0.808	0.599	33.0
10	0.827	1.41	24.8	0.829	0.681	34.0
15	0.845	1.62	25.3	0.847	0.753	34.9
25	0.875	2.12	26.2	0.876	0.916	36.2
40	0.908	3.04	27.2	0.911	1.167	37.7
70	0.960	5.20	29.4	0.963	1.725	40.1

late the Onsager coefficients. Pressures are given in lb/in.²; "zero" means atmospheric pressure, of course. Conductances are summarized in Table II, where pressures are given at the head of each pair of $10^4 c - \Lambda$ columns. Each line in Table II corresponds to a single run; that is, data were taken at a sequence of pressures for a given initial weight concentration.

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