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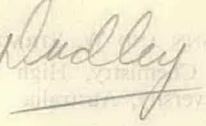

IONIZATION OF PIPERIDINE IN METHANOL TO 12,000 ATM

IONIZATION OF PIPERIDINE IN METHANOL TO 12,000 ATM

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This paper reports the first measurements of the effect of pressure on the ionization of a weak electrolyte in a non-aqueous solvent. The electrical conductances of methanolic solutions of piperidine, piperidinium bromide, sodium bromide and sodium methoxide have been measured to 3000 atm at 25° C, and to 12,000 atm at 45° C.

The results show that the basic ionization constant of piperidine in methanol at 45° C increases from $2{\cdot}8 \times 10^{-6}$ mole kg^{-1} at 1 atm, to 3100×10^{-6} mole kg^{-1} at 12,000 atm. This is a greater pressure effect than has been found in aqueous solutions of weak bases; it can be ascribed to the proportionally greater increase in the dielectric constant of methanol at high pressures.

In earlier papers [1, 2] we showed that pressure causes a large increase in the ionization of weak acids and bases in water, and that the increase arises from the enhanced solvation of the free ions at high pressures.

We have now extended our measurements to solutions of a weak base in methanol, to see how the pressure effect depends upon the nature of the ionizing solvent. The base was piperidine. It would have been preferable to use one of the methylamines whose ionization constants had previously been measured in water to high pressures,[1, 2] but unfortunately they are too little ionized in methanol to give significant ionization constants by the conductance method.

EXPERIMENTAL

Method.—The experimental procedure was the same as in the earlier work.[1, 2] The conductance measurements to 3000 atm at 25° C were made in a glass cell described previously;[1] those to 12,000 atm at 45° C were made in a Teflon cell.[2] Great care was taken to keep moisture from the reagents and the conductance cells.

Materials.—Analytical grade methanol was refluxed with fresh quicklime, then distilled from magnesium activated by iodine. It was finally distilled several times from anhydrous copper sulphate. The product had a specific conductance of $1{\cdot}1 \times 10^{-6}$ ohm^{-1} cm at 45° C. The sodium bromide, sodium methoxide, piperidine and piperidinium bromide were specimens which had been used in earlier work.[3]

RESULTS

ACCURACY

The sources and magnitudes of inaccuracies were the same as in the earlier measurements.[2]

CONDUCTANCES

The conductance of each electrolyte was measured for a range of concentrations and pressures: some typical results are given in tables 1 to 3. Tables 1 and 2 illustrate how the conductances change with pressure for particular concentrations. Table 3 shows how they change with concentration for particular pressures. The quantities listed are *molal* conductances Λ', calculated from the relation

$$\Lambda' = 1000\,\kappa/c,$$