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IONIZATION OF PIPERIDINE IN METHANOL TO 12,000 ATM

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By S. D. Hamann and W. Strauss
C.S.I.R.O. Division of Industrial Chemistry, High Pressure Laboratory,
Sydney University, Australia

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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

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

where κ is the specific conductance in ohm^{-1} cm, corrected for the contribution of the solvent, and c is the concentraton of electrolyte in mole kg^{-1}.

TABLE 1.—MOLAL CONDUCTANCES IN METHANOL AT 25° C

electrolyte :	sodium bromide	sodium methoxide	piperidinium bromide	piperidine
conc/mole kg^{-1} :	0·00137	0·000756	0·00106	0·0348
press./atm				
1	71·5	74·5	82·3	1·12
1000	59·0	61·5	66·7	1·66
2000	51·5	53·8	56·3	2·32
3000	44·8	47·8	48·9	3·05

TABLE 2.—MOLAL CONDUCTANCES IN METHANOL AT 45° C

electrolyte :	sodium bromide	sodium methoxide	piperidinium bromide	piperidine
conc/mole kg^{-1} :	0·00930	0·0140	0·0110	0·3967
press./atm				
1	80·5	80·8	86·0	0·344
1100	67·9	70·2	75·3	0·520
2500	56·4	58·3	62·7	0·84
4000	46·7	51·4	52·5	1·25
5400	42·6	46·3	44·3	1·73
6800	38·0	43·8	39·0	2·34
8200	31·7	37·9	30·5	2·68
9600	26·5	32·7	25·8	3·18
11000	23·1	28·0	22·5	3·56
12000	19·9	24·0	20·0	3·79

TABLE 3.—CHANGE OF MOLAL CONDUCTANCE WITH CONCENTRATION IN METHANOL AT 45° C

electrolyte	pressure/atm.	Λ'		
sodium bromide	conc/mole kg^{-1} :	0·00075	0·00137	0·00269
	1	74·3	71·5	69·6
	3000	45·4	44·8	44·2
sodium methoxide	conc/mole kg^{-1} :	0·00609	0·0140	0·0312
	1	70·5	64·1	58·7
	3000	45·9	44·4	43·7
piperidinium bromide	conc/mole kg^{-1} :	0·000532	0·00216	0·00415
	1	84·9	78·4	75·2
	3000	48·6	47·5	46·1
piperidine	conc/mole kg^{-1} :	0·0348	0·1283	0·4548
	1	1·118	0·620	0·328
	3000	3·05	1·78	0·858

IONIZATION CONSTANTS

The ionization of piperidine in methanol is represented by the formula

$$C_5H_{11}N + CH_3OH \rightleftharpoons C_5H_{11}NH^+ + CH_3O^-,$$

and the basic ionization constant K is defined as

$$K = (a_{C_5H_{11}NH^+})\,(a_{CH_3O^-})/a_{C_5H_{11}N}\ ,$$

the a's being molal activities. Tables 4 and 5 list values of K calculated from our experimental results by the method described previously.[1]

TABLE 4.—IONIZATION CONSTANT OF PIPERIDINE IN METHANOL AT 25° C

pressure/atm.	$10^6\,K$/mole kg^{-1}	pressure/atm.	$10^6\,K$/mole kg^{-1}
1	6·1	1000	21·9
100	7·2	2000	56
250	8·6	3000	126
500	14·6		

TABLE 5.—IONIZATION CONSTANT OF PIPERIDINE IN METHANOL AT 45° C

pressure/atm.	$10^6\,K$/mole kg^{-1}	pressure/atm.	$10^6\,K$/mole kg^{-1}
1	2·8	6800	480
1100	8·6	8200	860
2500	38	9600	1400
4000	103	11000	2300
5400	240	12000	3100

DISCUSSION

CONDUCTANCES

There are two marked differences between the high pressure behaviour of Λ' for strong salts in methanol and in water. In methanol, Λ' for a particular concentration is reduced much more by pressure than it is in water. Also, the concentration dependence of Λ' which is almost unaffected by pressure in water, is greatly reduced at high pressures in methanol. These changes can be judged from the effect of pressure upon the quantities Λ_0' and B' in the Kohlrausch relation,

$$\Lambda' = \Lambda_0' - B'c^{\frac{1}{2}},$$

where c is the molal concentration of the salt and Λ_0' is its molal conductance at infinite dilution. Table 6 lists some values of Λ_0' and B' for the two solvents.

TABLE 6.—THE QUANTITIES Λ_0' AND B' AT 25° C

	electrolyte	pressure/atm.	Λ_0'	B'expt.	B'calc.
(i) water as solvent:	KCl*	1	149	90	94
		3000	158	75	85
	$KOCOCH_3$ †	1	113	80	85
		3000	117	87	75
(ii) methanol as solvent:	NaBr ‡	1	79	190	171
		3000	46	44	83
	$C_5H_{11}NHBr$ ‡	1	89	225	179
		3000	50	60	85

* ref. (1).
† measurements made as part of some earlier work (ref. (2)).
‡ this work.

In water at 3000 atm, Λ_0' is slightly greater than it is at 1 atm; at higher pressures it decreases. In methanol, however, it shows a steady and much larger decrease over the whole range to 12,000 atm. This difference in behaviour is probably due to the greater relative increase in the viscosity[4] of methanol at high pressures.

The experimental values of B' in table 6 are subject to fairly large uncertainties, possibly as much as ± 20 units at 3000 atm. Nevertheless they show clearly that pressure causes a much larger decrease in B' for methanol solutions than for aqueous solutions. This can be understood on the basis of the Debye-Onsager theory of electrolytic conduction. Onsager calculated B in the relation

$$\Lambda = \Lambda_0 - Bx^{\frac{1}{2}}$$

where the Λ's are *molar* conductances and x is the concentration in mole l.$^{-1}$. For a 1 : 1-electrolyte his theory gives [5]

$$B = \frac{8{\cdot}15 \times 10^5 \Lambda_0}{(DT)^{\frac{3}{2}}} + \frac{81{\cdot}9}{(DT)^{\frac{1}{2}}\eta},$$

where D is the dielectric constant of the solvent, η is its viscosity in poises, and T is the temperature (°K). Changing to molal units,

$$B' = \frac{8{\cdot}15 \times 10^5 \Lambda_0' \rho^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}} + \frac{81{\cdot}9 \rho^{\frac{3}{2}}}{(DT)^{\frac{1}{2}}\eta},$$

where ρ is the specific gravity of the solution. The quantities ρ, η, D and Λ_0' are all pressure dependent. Bridgman [4, 6, 7] has measured ρ and η for methanol and water at high pressures, and Kyropoulos [8] has measured D. Some values of Λ_0' are given in table 6. From these data it is possible to calculate B': the results are shown in the last column of table 6.

Clearly the Onsager values of B' change with pressure in much the same way as the experimental values. For methanol the numerical agreement is not good, but it is known that, even at atmospheric pressure, the Onsager formula applies only approximately to methanol solutions.[9] The decrease of B' in methanol at high pressures is caused principally by the large increase in viscosity of the solvent, which reduces the electrophoretic effect.

IONIZATION CONSTANTS

At 45° C the ionization constant K of piperidine in methanol increases from $2{\cdot}8 \times 10^{-6}$ mole kg^{-1} at 1 atm to $3{\cdot}1 \times 10^{-3}$ mole kg^{-1} at 12,000 atm. The value of K for piperidine in water at atmospheric pressure and 45° C is $1{\cdot}2 \times 10^{-3}$ mole kg^{-1}.[10] From this it might be said that methanol at 12,000 atm is a better " ionizing " solvent than water at 1 atm. But it should be emphasized that the change of ionization with pressure arises only partly from the changed properties of the solvent; at least half of the pressure effect is due to the compression of the ions (the factor (*a*) below). This was not appreciated by Kritschewsky,[11] who attributed the whole of the pressure effect to the change in dielectric constant of the medium, and was thereby forced to adopt unrealistic values for ionic radii.

In fig. 1 we compare the effects of high pressures on the ionization of ammonia in water and of piperidine in methanol, The quantity $\Delta\overline{G}_p^\circ - \Delta\overline{G}_1^\circ$ is the difference between the standard free energy of ionization at the pressure p atm and the corresponding value at 1 atm. It is defined by

$$\Delta\overline{G}_p^\circ - \Delta\overline{G}_1^\circ = -RT \ln (K_p/K_1).$$

Some density measurements in this laboratory [3] have shown that $\partial\Delta\overline{G}^\circ/\partial p$ for the ionization of piperidine in water at 1 atm is less negative than it is for the ionization of ammonia in the same solvent. We can safely conclude from this that the plot of $\Delta\overline{G}_p^\circ - \Delta\overline{G}_1^\circ$ against pressure for the piperidine + water system would lie above the curve for the ammonia + water system. The difference between the two experimental curves in fig. 1 must therefore be ascribed to the change of solvent.

In previous papers [1, 2] we have suggested that the increase in ionization of a weak electrolyte at high pressures is caused by the lowering of the free energy of solvation of its ions. This can be estimated by calculating the Born solvation energy[12] of a pair of ions of about the same size as those of the weak electrolyte, and allowing for (*a*) the change in the mean radius of the ions with pressure, and (*b*) the change in the dielectric constant of the solvent with pressure. We have given[2] the results of this calculation for the ions $Cs^+ + F^-$ in water. We have now made similar calculations for the same pair of ions in methanol. The factor (*a*) is, of course, unaltered by the change of solvent but the factor (*b*) is more important for methanol than for water because of the larger percentage increase in the dielectric constant of methanol at high pressures.[8] Fig. 1 shows that the change from water to methanol shifts the predicted solvation energies in the same direction as it does the experimental free energies of ionization.

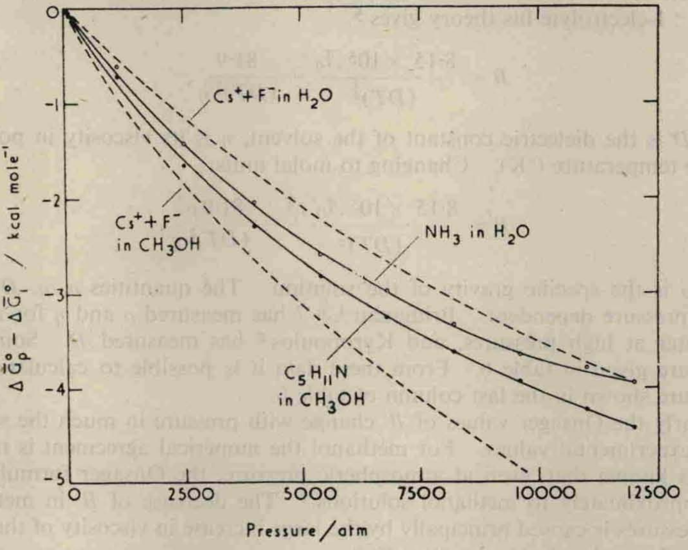

FIG. 1.—Full curves: the ionization free energies of weak bases; dotted curves: the theoretical solvation energies of the ions $Cs^+ + F^-$. All the data are for 45° C.

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