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IONIC DISSOCIATION CONSTANT OF TRIETHYLAMINE IN METHANOL UNDER HIGH PRESSURE AT 25°C

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The ionic dissociation constant of the ionization of triethylamine in methanol have been determined from the measurements of electrical conductivities at high pressures up to 2000 kg/cm^2 at 25°C. The observed dissociation constant increased from 0.50×10^{-6} mol/kg at 1 atm to 5.78×10^{-6} mol/kg at 2000 kg/cm^2, and its pressure dependence was quantitatively explained by the change of intrinsic volume and electrostrictive volume with pressure.

For the study of the high pressure kinetics of some weak-base-catalyzed reactions in organic solvents, the knowledge of the pressure effects on the ionization equilibrium of the base is primarily required. In the course of the study of the reaction of phenylacetonitrile in triethylamine-methanol at high pressure, the authors faced to the elucidation of the pressure effects on the following ionization equilibrium,

$$N(Et)_3 \quad + \quad MeOH \quad \overset{K}{\rightleftharpoons} \quad HN(Et)_3^+ \quad + \quad MeO^-. \qquad (1)$$

Usually the ionization equilibrium of neutral molecules largely depends on pressure. If the solvation free energies of ions are mainly controlled by the solvent dielectric constant, the organic solvents are expected to exhibit greater pressure effect on equilibrium constant than water, because the electrostrictive volume change is larger negative due to the larger value of $D^{-2}(\partial D/\partial P)_T$ as found in Eq.(6).

A formula of the ionic dissociation as a function of pressure can be derived from the pressure dependence of the intrinsic volume and electrostrictive one, and can validly explain the dissociation constant of triethylamine in methanol determined by the electrical conductivity measurements up to 2000 kg/cm^2 at 25°C.

The limiting equivalent conductivities at high pressures have been determined for potassium chloride(KCl), triethylammonium chloride(HN(Et)$_3$Cl), and potassium methoxide(MeOK) in methanol with the aid of the Fuoss-Onsager equation:1)

$$\Lambda = \Lambda^\circ - SC^{1/2} + EC\log C + JC, \qquad (2)$$

where Λ and Λ° are the equivalent conductivity and the limiting equivalent conductivity, respectively, C the molar concentration, S and E the functions of the limiting equivalent conductivity, the dielectric constant, and the viscosity, and J an adjustable parameter.

In Eq.(2), the concentrations of solutions were corrected for the volume contraction of methanol at high pressures by using the Tait equation,$^{2)}$ and the dielectric constants of methanol at high pressures were calculated by means of the Owen-Brinkley expression:$^{3)}$

$$1 - \frac{D^{(1)}}{D^{(p)}} = A \ln \frac{B + P}{B + 1}\,, \qquad (3)$$

where $D^{(1)}$ and $D^{(p)}$ are the dielectric constants at 1 atm and P kg/cm^2, respectively, and A and B the empirical constants.$^{4)}$ And the viscosities of methanol up to 2000 kg/cm^2 were obtained from Bridgman's high pressure data by the graphical interpolation.$^{5)}$

The limiting equivalent conductivity of triethylammonium methoxide is calculated from Kohlrausch's law of the independent migration of ions.

$$\Lambda°(HN(Et)_3OMe) = \Lambda°(HN(Et)_3Cl) + \Lambda°(MeOK) - \Lambda°(KCl) \qquad (4)$$

Triethylamine exhibits the positive pressure dependence of the equivalent conductivity as shown in Fig. 1, in contrast to the general trend for a strong electrolytes in methanol.(Figs. 2 and 3)

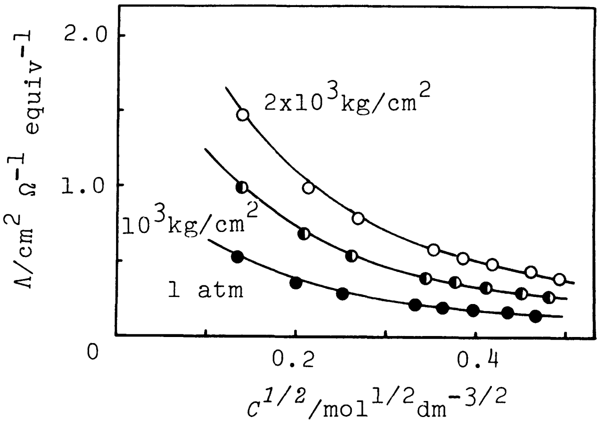

Fig. 1. Λ of $N(Et)_3$ in MeOH *vs.* $c^{1/2}$ at 25°C

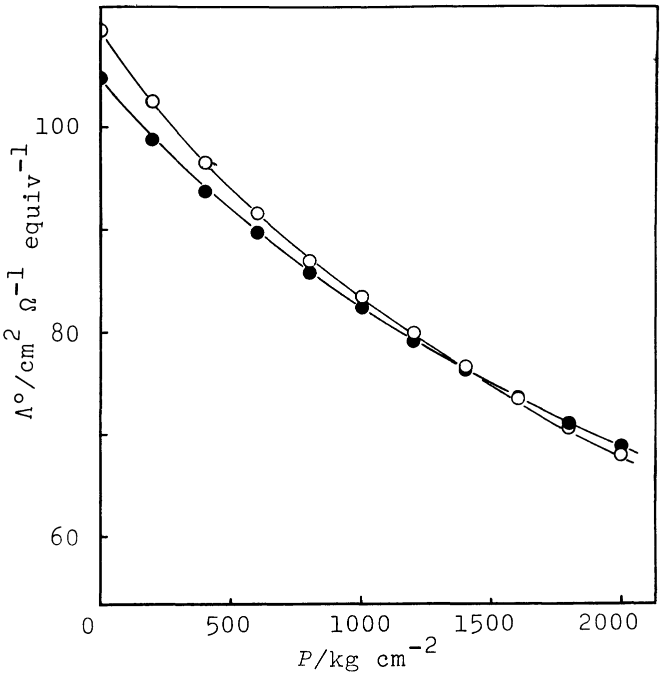

Fig. 2. Pressure dependence of $\Lambda°$ in MeOH at 25°C

○: $HN(Et)_3Cl$, ●: KCl

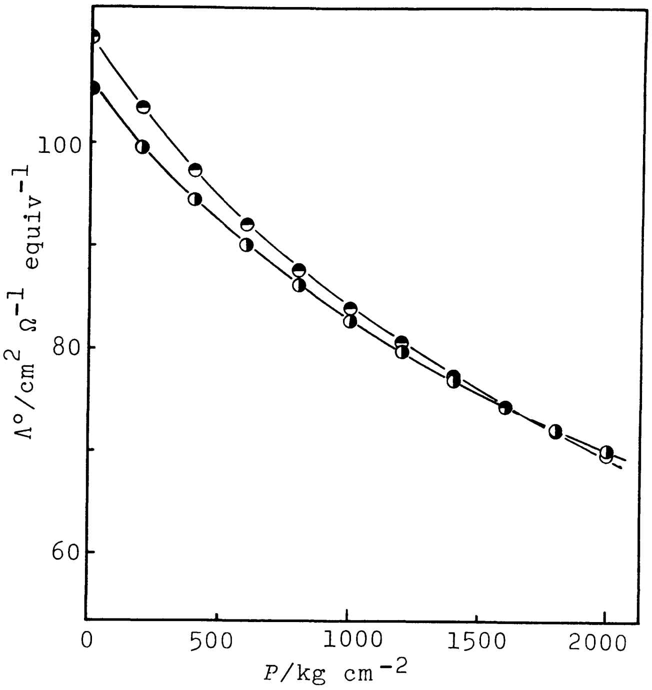

Fig. 3. Pressure dependence of $\Lambda°$ in MeOH at 25°C

◑: MeOK, ⊖: $HN(Et)_3OMe$

This fact is easily understood taking into account that the increase of the number of ionized speices at higher pressures overcomes the decrease of the conductivity of free ions due to the enhancement of the viscosity of the medium.
In order to obtain the ionic dissociation constant from the equivalent conductivity of triethylamine and the limiting equivalent conductivity of triethylammonium methoxide, Shedlovsky's method was used.[6] The results show that the ionic dissociation constant in methanol at 25°C increases from 0.50×10^{-6} mol/kg at 1 atm to 5.78×10^{-6} mol/kg at 2000 kg/cm^2.

If the difference in the partial molal volumes of the product and reactant can be expressed as an explicit function of pressure, the pressure dependence of equilibrium constant can be calculated by the integral of the thermodynamic relationship,

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta\bar{V}^o = -\Delta\bar{V}^o_{int} - \Delta\bar{V}^o_{elect} \;, \tag{5}$$

where $\Delta\bar{V}^o_{int}$ and $\Delta\bar{V}^o_{elect}$ refer to the intrinsic volume change and electrostrictive one, respectively. $\Delta\bar{V}^o_{elect}$ can be expressed as follows:

$$\Delta\bar{V}^o_{elect} = -\frac{Nz^2e^2}{2}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\frac{1}{D^2}\left(\frac{\partial D}{\partial P}\right)_T \;, \tag{6}$$

where N, z, e, and r are Avogadro's number, electronic charge, the valence number, and ionic radius, respectively. The integration of Eq.(5) assuming $\Delta\bar{V}^o_{int}$ is pressure-independent, gives Eq.(7),

$$RT\ \ln\frac{K^{(p)}}{K^{(1)}} = -\Delta\bar{V}^o_{int}(P - 1) - \int_1^P \Delta\bar{V}^o_{elect}\, dP \;. \tag{7}$$

According to Nakahara's derivation, in which Born s solvation model and the invariance of the ionic radii are assumed, Eqs.(8) and (9) are obtained.[7]

$$\int_1^P \Delta\bar{V}^o_{elect}\, dP = \Delta\bar{V}^{o(1)}_{elect}\ (B + 1)\ \ln\frac{B + P}{B + 1} \tag{8}$$

$$\frac{-RT}{P-1}\ \ln\frac{K^{(p)}}{K^{(1)}} = \Delta\bar{V}^{o(1)}_{int} + \Delta\bar{V}^{o(1)}_{elect}\ \frac{B + 1}{P - 1}\ \ln\frac{B + P}{B + 1} \tag{9}$$

The validity of Eq.(9) is tested by the plots of the left-hand side against $(B + 1)/(P - 1)\ \ln\ (B + P)/(B + 1)$ as shown in Fig. 4, where the experimental points lie well on the calculated straight line of $\Delta\bar{V}^{o(1)}_{elect} = -36.2$ and $\Delta\bar{V}^{o(1)}_{int} = -11.5$ cm^3/mol. Another empirical expression, Eq.(10), was postulated by El'yanov and Hamann:[8]

$$RT\ \ln\frac{K^{(p)}}{K^{(1)}} = -\Delta\bar{V}^{o(1)}\frac{(1 + \beta)(P - 1)}{1 + \beta P} \;, \tag{10}$$

where β is the empirical parameter which is a function of dielectric constant, and $\Delta\bar{V}^{o(1)}$ includes both intrinsic and electrostrictive parts. Its application to the present system, however, failed resulting in the curved plot of $-RT\ \ln K^{(p)}/K^{(1)}$ against $(1 + \beta)(P - 1)/(1 + \beta P)$. Nakahara derived a formula similar to El'yanov and Hamann's empirical formula, in which $\Delta\bar{V}^{o(1)}$ consists of only the electrostrictive part. And his expression can be modified to Eq.(11) when the intrinsic volume is taken into account,

$$\frac{-RT}{P-1}\ln\frac{K^{(p)}}{K^{(1)}} = \Delta\bar{V}^{\circ(1)}_{elect}\frac{1+\beta}{1+\beta P} + \Delta\bar{V}^{\circ(1)}_{int}\ . \qquad (11)$$

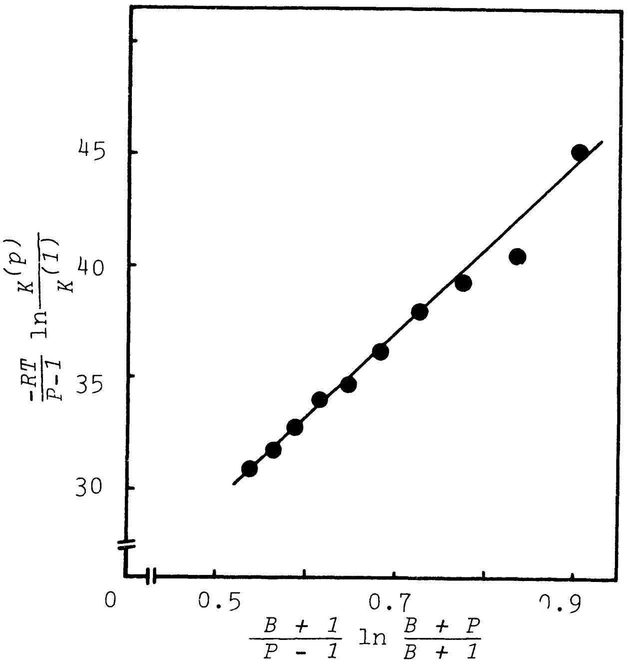

Fig. 4. Pressure dependence of K at 25°C

From Eq.(11) $\Delta\bar{V}^{\circ(1)}_{elect}$ is obtained to be -37.0 cm^3/mol and $\Delta\bar{V}^{\circ(1)}_{int}$ to be -9.4 cm^3/mol.

Almost the same values of the electrostrictive volume and the intrinsic one at 1 atm are obtained in spite of using the different expressions, Eqs.(9) and (11). Thus both the electrostrictive volume and intrinsic one play undoubtly important role in the pressure effect on the dissociation of triethylamine in methanol, though the latter seems to be too large to be caused only by the structural change from neutral molecules to ions. The further detailed consideration on the intrinsic volume change cannot be done at present. According to Born's solvation theory, it is reasonable that $-\Delta\bar{V}^{\circ(1)}_{elect}$ for the present system is larger than those of amines in water which are reported to be around 26–28 cm^3/mol.

References

1) R.M.Fuoss and F.Accascina, "Electrolytic Conductance", Interscience Publishers, Inc., New York (1959).
2) H.S.Harned and B.B.Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York (1958).
3) B.B.Owen and S.R.Brinkley, Phys.Rev.,64,32 (1943).
4) K.R.Srinivasan and R.L.Kay, J.Solution Chem.,4,299 (1975).
5) P.W.Bridgman, Proc.Am.Acad.Arts Sci.,77,117 (1949).
6) T.Shedlovsky and R.L.Kay, J.Phys.Chem.,60,151 (1956).
7) M.Nakahara, Rev.Phys.Chem.Jpn.,44,57 (1974).
8) B.S.El'yanov and S.D.Hamann, Aust.J.Chem.,28,945 (1975).

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