

SHORT COMMUNICATIONS

CALCULATION OF PARTIAL MOLAR VOLUME CHANGES AT HIGH PRESSURES*

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Buchanan and Hamann (1953) and Hamann and Strauss (1955, 1956) have suggested that the increase in ionization of weak electrolytes with increasing pressure is caused by a lowering of the solvation-free energy of their ions. This change can be theoretically estimated (Hamann and Strauss 1955) from the Born equation for solvation energy (Born 1920), which expresses the free energy of solvation $\Delta\bar{G}$ as a function of two quantities which vary with pressure; the dielectric constant of the solvent D_p , and the radius of the ions r_p . For a mole of singly charged ions at the pressure p , $\Delta\bar{G}$ is given by

$$\Delta\bar{G} = -\frac{N\varepsilon^2}{2r_p} \left(1 - \frac{1}{D_p}\right), \quad \dots\dots\dots (1)$$

where N is Avogadro's number and ε is the electronic charge.

In the present paper the calculations are extended to the changes in volume which accompany the development of ionic charges in solutions at high pressures. The theoretical partial molar volume change for the solvation of a mole of ions can be calculated by differentiating the Born equation with respect to pressure:

$$\begin{aligned} \Delta\bar{V} &= \left(\frac{\partial\Delta\bar{G}}{\partial p}\right)_T \\ &= -\frac{N\varepsilon^2}{2} \left(1 - \frac{1}{D_p}\right) \frac{1}{r_p^2} \left(\frac{\partial r_p}{\partial p}\right)_T - \frac{N\varepsilon^2}{2r_p} \frac{1}{D_p^2} \left(\frac{\partial D_p}{\partial p}\right)_T \quad \dots\dots\dots (2) \end{aligned}$$

In applying this formula at high pressures, D_p and $(\partial D_p/\partial p)_T$ have been obtained from an empirical equation which Owen and Brinkley (1943) found satisfactory for a number of polar liquids to 12000 kg/cm². The values of r_p and $(\partial r_p/\partial p)_T$ have been estimated from the compressions of some alkali halide crystals (determined experimentally by Bridgman (1931)) assuming that the positive and negative ions are equally compressible.

Table 1 gives the calculated values of the partial molar volume of solvation of a typical ion pair $\text{Cs}^+ + \text{F}^-$ in a number of liquids. The results for other

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TABLE I
THEORETICAL MOLAR VOLUME CHANGES FOR THE SOLVATION OF THE ION PAIR $\text{Cs}^+ + \text{F}^-$ IN VARIOUS MEDIA AT 30 °C

Medium ($\text{cm}^3 \text{mole}^{-1}$)	Pressure (kg/cm^2)				
	1	100	250	500	1500
Water	-19.7	-19.5	-19.1	-18.6	-17.0
Methanol	-42.1	-39.8	-36.9	-33.2	-25.3
Ethanol	-53.8	-50.8	-47.0	-42.1	-31.2
Acetone	-74.8	-67.7	-59.6	-50.4	-33.5
Bromobenzene	-118.2	-110.9	-101.5	-89.3	-61.7
	2500	4000	8000	12000	
Water	-15.9	-14.6	-12.3	-10.5	
Methanol	-21.5	-18.3	-14.1	-11.6	
Ethanol	-25.9	-21.5	-16.0	-12.9	
Acetone	-26.7	-21.6	-15.8	-12.7	
Bromobenzene	-48.3	-37.3	-24.7	-18.9	

alkali halides are substantially the same. The theoretical volumes of solvation in water and methanol listed in Table 1 are compared with the experimental

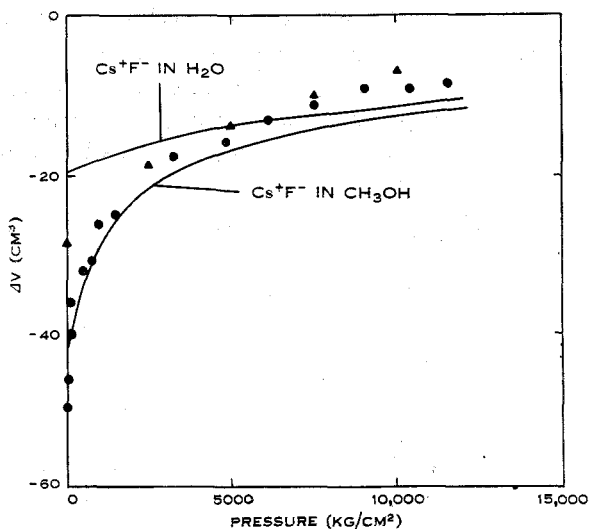


Fig. 1.—Comparison of theoretical and experimental partial molar volume changes in water and methanol to pressures of 12,000 kg/cm^2 .

▲ NH_3 in H_2O . ● Piperidine in CH_3OH .

partial molar volume changes for the ionization of ammonia in water (Hamann and Strauss 1955) and of piperidine in methanol (Hamann and Strauss 1956); see Figure 1. The good agreement of the trends of the calculated and experi-

mental changes shows that the behaviour of the partial molar volume changes in the two solvents can be explained by the effect of pressure on the radii of the ions and the dielectric constants of the media.

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