THE PARTIAL MOLAL VOLUME OF SODIUM MONOFLUOROPHOSPHATE IN AQUEOUS SOLUTION AT 25°C

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ABSTRACT.—The density of aqueous solutions of sodium monofluorophosphate has been measured at 25°C over the concentration range 0.4 to 2.0 molal. The partial molal volume is a linear function of the square-root of the molality and is defined by the equation

$$\overline{V}_2 = 15.6 + 17.5\sqrt{m}.$$

Similarities between monofluorophosphates and sulfates (Lange, 1950) have been unjustifiably interpreted to mean that the sulfate and monofluorophosphate ions behave similarly in aqueous solution (Devonshire and Rowley, 1962). We have measured the densities of aqueous solutions of sodium monofluorophosphate, Na_2PO_3F, from which the apparent molal volume of the salt is calculated and the partial molal volume ultimately determined.

Using the data for partial molal volumes we are able to compare these isoelectronic and isomorphic anions, sulfate and monofluorophosphate, and qualitatively compare their relative hydration in aqueous solution.

Procedures

Density measurements were made in Sprengel-type pycnometers at 25.00 ± 0.01° C on analyzed samples of sodium monofluorophosphate of 97.0% purity. Pycnometer weighings were made with calibrated weights corrected for the buoyancy of air. A counter-balance was constructed from glass to have approximately the same volume and surface area as the pycnometer to compensate for the buoyancy of the pycnometer.

Results

Table 1 lists the densities, d, and apparent molal volumes, ϕ_v, for aqueous solutions of sodium monofluorophosphate at 25° C. The apparent molal volumes were calculated using the equation (Harned and Owen, 1950)

$$\phi_v = \frac{1000\,(d_0 - d)}{m\,d\,d_0} + \frac{M_2}{d} \qquad (1)$$

where m is the molality of sodium monofluorophosphate, M_2 its molecular weight and d and d_0 the densities of solution and solvent respectively. Masson (Harned and Owen, 1950) observed that the apparent molal volume as a function of the square-root molarity could be expressed by the equation

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \qquad (2)$$

TABLE 1.—Densities and apparent molal volumes of aqueous solutions of sodium monofluorophosphate at 25°C.

m, moles per 1000g solvent	density, g/cm³	Apparent molal volume, $\varnothing_v$, CM³/mole
2.1190	1.2182	32.303
1.9218	1.1985	31.601
1.6974	1.1788	31.040
1.3934	1.1504	29.637
1.1974	1.1302	28.738
0.99702	1.1104	26.967
0.80166	1.0890	26.556
0.59457	1.0670	24.428
0.40160	1.0451	22.950
0.38063	1.0438	22.772

for many electrolyte solutions. The relation often extends to concentrated solutions. In their expression $\varnothing_v^0$ is the limiting molal volume and S_v is the slope of the line. A least-squares evaluation of our data, in which we have chosen to express concentration in terms of molality (MacInnes and Dayhoff, 1952), yields the result

$$\varnothing_v = 15.6 + 11.7\sqrt{m} \qquad (3)$$

where the value of the limiting molal volume of sodium monofluorophosphate is 15.6 ± 0.9 cm³/mole.

The partial molal volume of the solute may be expressed (MacInnes and Dayhoff, 1952) by

$$\overline{V}_2 = \frac{\partial V}{\partial m} = \varnothing_v + m\frac{\partial \varnothing_v}{\partial m} \qquad (4)$$

so that from our data

$$\overline{V}_2 = 15.6 + 17.5\sqrt{m} \qquad (5)$$

for aqueous solutions of sodium monofluorophosphate over the concentration range 0.4 to 2.0 molal at 25°C.

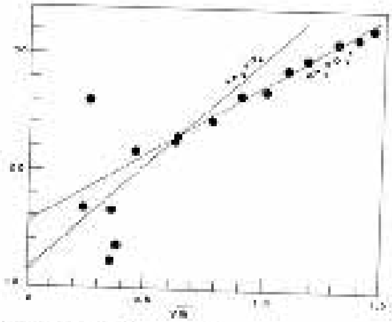

FIGURE 1.—Masson Plot for sodium monofluorophosphate and sodium sulfate at 25°C.

Figure 1 represents the Masson plot of our data with the least-squares line drawn. Included is the line for sodium sulfate taken from the data of Longsworth (1935).

DISCUSSION

As we interpret the extrapolated value of $\varnothing_v^0$ of sodium monofluorophosphate, it is valid above 0.4 molal and represents the state of the salt in the region for which we have made density measurements. The limiting value, $\varnothing_v^0$, cannot be interpreted as representing the salt at low solution concentrations because hydolysis changes this parameter as was observed for sodium carbonate by Lamb and Lee (1913). Comparison of $\varnothing_v^0$ with that of sodium sulfate verifies the expectation that the monofluorophosphate ion is more extensively hydrated than sulfate. Although both ions are tetrahedral and display crystalline isomorphism, the monofluorophosphate ion is assymmetrical so would be expected to be more extensively hydrated than sulfate in aqueous solution.

The difference in slope of the line for sulfate and monofluorophosphate solutions also reflects the more extensive hydration of monofluorophosphate. At higher concentrations the apparent molal volume of monofluorophosphate is less than sulfate. We might interpret this as a manifestation of the compression of that extra quantity of water which is included in the hydration sphere of the monofluorophosphate ion thus effectively reducing the actual volume occupied by solvent in these solutions.

These simple differences in hydration point out the danger in equating solution properties of sulfate and monofluorophosphate simply because they will form mixed salts and their alkaline-earth salts have similar solubilities. Devonshire and Rowley (1962) have substituted the activity coefficients of sulfuric acid for those of monofluorophosphoric acid, H_2PO_3F, in a study of the hydrolysis of monofluorophosphoric acid. Our observations on molal volumes would indicate the danger in such a rash assumption even without the more obvious inconsistency resulting from wide divergence of the acid dissociation constants themselves. Devonshire (Van Wazer, 1958) has reported approximate values of the dissociation constants of monofluorophosphoric acid which show this acid to be much weaker than sulfuric.

ACKNOWLEDGMENT

The authors are grateful for financial suport from the Cooperative Research Program in Chemistry of the Edwardsville Campus of Southern Illinois University and for the gift of sodium monofluorophosphate from the Ozark-Mahoning Company of Tulsa, Oklahoma.

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Manuscript received December 4, 1964.