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THE PARTIAL MOLAL VOLUMES OF POTASSIUM
SALTS OF CERTAIN ORGANIC ACIDS
AT 25°C

IRWIN H. PARRILL

This paper is a brief resume of a part of the work performed under the direction of Dr. J. N. Pearce¹ in an attempt to determine from density measurements the partial molal volumes of the potassium salts of various organic acids at various concentrations. It was hoped that some indication might be found as to the influence upon the partial molal volumes of the nature and position of substituent groups in the anion.

Densities have been determined for solutions of the potassium salts of salicylic, monoacetyl salicylic, monoacetylanthranilic, cinnamic, o-nitrocinnamic, m-nitrocinnamic and p-chlorobenzoic acids at several concentrations. Densities as determined by Pumpplin² for solutions of potassium salts of benzoic acids, o-, m-, and p-nitrobenzoic acids, and p-hydroxybenzoic acids as well as results obtained by Ware³ for a large number of potassium salts of the aliphatic acids have been considered. All the data of the latter investigations were carefully recalculated.

The partial molal volume of a solute in a given concentration is the increase in volume which will be produced if one mole of the solute is added to an infinitely large volume of the solution of the given concentration.

For a non-ionizing solute the volume V of the solution is given by the relation

$$V = N_1 \bar{V}_1 + N_2 \bar{V}_2$$

where N_1 , N_2 and \bar{V}_1 , \bar{V}_2 are the numbers of moles and the partial molal volumes of the solvent and solute, respectively. If the solute and solvent form a "perfect solution," that is, one in which the solution process is not accompanied by volume change, the partial molal volumes of the components will be equal to their molal volumes in the pure state. Consider now a binary salt which dissociates completely into two ions. If these ions behave as "perfect solutes," the sum of the partial molal volumes of the two ions should be equal to the partial molal volume of the solute. The

¹ Parrill, Master's Thesis, Iowa, (1933). Library, State University of Iowa.

² Pumpplin, Senior Thesis, Iowa, (1932). Library, State University of Iowa.

³ Ware, Master's Thesis, Iowa, (1924). Library, State University of Iowa.

volume of the "perfect solution" formed under these conditions would be

$$V = N_1 \bar{V}_1 + N_2 \bar{V}_2 = N_1 \bar{V}_1 + N_2 (\bar{V}_+ + \bar{V}_-)$$

Rarely if ever do solutions exhibit this perfect behavior. In general, the solution process is accompanied either by an increase or decrease in volume, that is, the volume of the solution is greater or less than the sum of the volumes of the components of the solution.

The volume of a solution as a function of its molal concentration, m , is accurately given by the linear relation,

$$V = \alpha + \beta m + \gamma m^2$$

where α , β , and γ are specific constants for a given salt solution.

The differentiation of this equation with respect to the molality, m , gives immediately an expression by means of which the partial molal volume of the potassium salt can be calculated for any concentration, namely:

$$dV/dm = \bar{V}_2 = \beta + 2\gamma m$$

The values of the three constants were determined by the method of Least Squares. All calculations were made by means of a Monroe Calculator. It is evident from the equation that α is the volume of 1000 grams of pure water at the concentration $m = 0$. Likewise, β is the partial molal volume of the potassium salt in an infinitely dilute solution.

The partial molal volumes at 25° were calculated for each salt at infinite dilution, 0.1 molal and 1.0 molal concentrations. Having found the partial molal volumes of the dissolved salts, one is prompted to make some attempt at a determination of the partial ionic volumes of the organic anions. With these we can best observe the effect of substituent and configuration upon the solution volume of the ions. If one only knew the volume of a single ion, one could determine the partial molal volume of the salt at any desired concentration and then by subtracting the known ionic volume of the given ion determine the partial ion volume of the second ion.

Unfortunately, the solution volume of no single ion is definitely known. The potassium and chlorine atoms have nearly the same atomic weight; their ions have practically the same ionic mobility and degree of hydration; their transference numbers are nearly equal. It has been found also that in a given concentration of potassium chloride the activities and the activity coefficients of the two ions are almost equal. Therefore, the assumption seems logical that, while the partial ion volumes of the potassium and chloride

ions in any given solution may vary with the concentration, their partial ion volumes will be nearly the same in any given solution of the salt. The partial ion volume of the potassium ion in any solution may then be taken as equal to one-half the partial molal volume of potassium chloride at that concentration. From the density data of Baxter and Wallace⁴ the partial molal volume of potassium chloride at the three concentrations were calculated and are given in Table I.

Table I.

m	\bar{V}_{0m}	$\bar{V}_{0.1m}$	$\bar{V}_{1.0m}$
\bar{V}_{KCl} cc.	28.361	28.493	29.685
\bar{V}_{K+}	14.181	14.246	14.842

The values of \bar{V}_{K+} represent the partial molal volumes of the potassium ion at the three reference concentrations. These values subtracted from the values of the partial molal volumes of the organic salts gives the partial ion volumes of the organic anions. The values thus calculated are given in Table II.

A study of Table II at once brings forth a striking conclusion.

Table II — Partial Molal Volumes of Organic Anions at 25°

	\bar{V}_{0m}	$\bar{V}_{0.1m}$	$\bar{V}_{1.0m}$
Formic	22.412	22.701	24.400
Acetic	34.762	35.488	42.022
Monochloroacetic	35.121	35.774	41.642
Dichloroacetic	61.975	62.985	72.076
Trichloroacetic	75.631	76.287	82.186
Bromoacetic	49.851	50.216	53.505
Propionic	49.347	49.849	53.753
Butyric	64.890	65.137	67.354
Iso-butyric	72.790	71.216	57.045
Benzoic	82.724	82.887	84.354
p-Chlorobenzoic	67.337	76.518	159.151
Dinitrobenzoic	112.477	113.135	119.058
m-Aminobenzoic	88.168	88.133	87.824
p-Aminobenzoic	89.855	89.160	82.908
o-Nitrobenzoic	99.933	100.171	102.129
m-Nitrobenzoic	96.506	96.682	98.247
p-Nitrobenzoic	112.987	113.143	114.543
o-Hydroxybenzoic	90.822	90.867	91.375
m-Hydroxybenzoic	88.299	88.420	89.514
p-Hydroxybenzoic	90.974	91.368	94.919
Salicylic	89.357	89.474	90.525
Monoacetylsalicylic	113.525	113.665	114.923
Monoacetylanthranilic	133.984	135.818	152.325
Cinnamic	99.207	103.417	141.305
o-Nitrocinnamic	120.166	124.820	166.705
m-Nitrocinnamic	129.129	129.260	130.442

⁴ Baxter and Wallace, J. Am. Chem. Soc., 38, 70 (1916).

In every case the partial ion volume is a specific characteristic of the individual anion. It does not increase regularly with increasing ion mass. The change in partial ion volume with concentration is equally specific for each ion. Although the partial ion volume is effected measurably by the nature of the substituent present, the substituent does not have the same influence when substituted in different anions.

It has been suggested that as ionic size increases, factors other than the field strength become less important. It is probable then also that as the effective diameter of the ion increases the volume contraction of the solution should decrease; the electrostatic and mass attraction should decrease, and, in accord with Webb's⁵ work, the energy of hydration becomes less. In this observation of partial molal volumes of these comparatively large organic ions this has been approximately true. It might be expected that the more easily deformable ions would exert unusual effects which might be explained by relative deformability.

This leads to the conclusion that substituents have part of their characteristic effect in their ability to flex and conform to a spherical effect as the solvent molecules are compressed or constricted to a central point. If, however, the substituent is less tightly bound and the electrostatic charge distributed over the ion rather than centered as a point charge, one might even think of the ionic atmosphere enlarged by the pull of the water dipoles on the charged substituents of the organic ions. For example, the forked chain ion of iso-butyric acid occupies a larger volume and has a negative compression effect. In all cases the substitution of a radical in the para position had more effect on the partial ionic volume than substituting the same group in the ortho position, and more effect in the ortho position than in the meta position when substituted in benzoic acid.

In conclusion it seems evident that although each individual ion is a unit universe within itself, such a universe must be effected in varying degrees by the complex forces of attraction and repulsion due perhaps in part to the mass and electrostatic charge of the ions themselves and of the solvent molecules. In case of the various organic anions the effects of these complex forces depend also upon the nature and position of the substituents as well as internal deformability of the individual ion.

⁵ T. J. Webb, *J. Am. Chem. Soc.*, 48, 2589 (1926).

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