Chapter 2 Partial Molar Volumes of Biochemical Model Compounds in Aqueous Solution

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Symbols

- $V$: volume of the solution [dm$^3$/mol$^{-1}$]
- $V^*_t$: molar volume of the pure solvent [cm$^3$/mol$^{-1}$]
- $V_2^*$: partial molar volume of solute [cm$^3$/mol$^{-1}$] in a two-component system
- $V_2^\infty$: partial molar volume of solute $x$ at infinite dilution [cm$^3$/mol$^{-1}$]
- $V_{0\text{NaA}}^\infty$: partial molar volumes of sodium carboxylates at infinite dilution [cm$^3$/mol$^{-1}$]
- $V_{0\text{HA}}^\infty$: partial molar volumes of carboxylic acids [cm$^3$/mol$^{-1}$] at infinite dilution
- $V_\phi^\infty$: apparent molar volume [cm$^3$/mol$^{-1}$]
- $V_\phi^\text{BH_2O}$: apparent molar volume of a hypothetical neutral aquoamine complex, BH$_2$O, that can dissociate into the hydrolysis products BH$^+$ and OH$^-$
- $V_w$: van der Waals volume
- $r_w$: van der Waals radius
- $\Delta V^0$: change in molar volume
- $\varrho^*$: density of solvent [g/cm$^3$]
- $\varrho$: density of solute [g/cm$^3$]
- $M_2$: molar mass of solute
- $m$: molality of solute [mol solute/1000 g solvent]
- $\alpha$: degree of hydrolysis

1 Introduction

Partial molar volumes have proved very useful in the study of molecular and ionic interactions in solution. The values at infinite dilution provide information about solute-solvent interactions and the concentration dependence will reflect solute-solute interactions. The present review is aimed at volumes of relatively simple organic molecules that may be looked upon as biochemical model compounds. It is believed that the partial molar volumes of these compounds in water represent a basis for the understanding of complex biochemical systems. With this in mind, it is especially interesting to examine homologous series. Systematic trends, such as additivity relations, are of special importance and will be discussed at the end.

2 Definitions

The partial molar volume of a solute is defined as:

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n_1}.$$  (1)
However, in this form it is practically impossible to determine partial molar volumes. Instead, the apparent molar volume is defined:

$$V_\phi = \frac{V - n_1 V^*_1}{n_2},$$  \hfill (2)

where $n_1$ and $n_2$ are the number of moles of solvent and solute respectively, and $V^*_1$ is the molar volume of pure solvent. Equation (2) can be rearranged to read:

$$V_\phi = \frac{1000(q^* - \varrho)}{m\varrho^*} + \frac{M_2}{\varrho}. \hfill (3)$$

In Eq. (3), $q^*$ and $\varrho$ are the densities of solvent and solution, $m$ is the solute molality, and $M_2$ the solute molar mass. The factor 1000 appears when densities are given in $g \text{ cm}^{-3}$, which is generally the case, instead of $kg \text{ m}^{-3}$.

The relation between apparent and partial molar volume is as follows:

$$V_2 = V_\phi + \frac{m^{1/2}}{2} (\partial V_\phi/\partial m^{1/2}) = V_\phi + m(\partial V_\phi/\partial m). \hfill (4)$$

From Eq. (4) it is seen that the apparent and partial molar volumes become equal at infinite dilution. Otherwise it is possible to equate the two quantities, provided the apparent molar volume is known as a function of molality. Similar equations can be evaluated on the molarity scale.

In order to obtain reliable $V_\phi$ data, it is necessary to measure densities with great precision. This is easily demonstrated by differentiating Eq. (3) with respect to $m$ at constant $\varrho$, or with respect to $\varrho$ at constant $m$. One then obtains:

- Probable error in $V_\phi$: $\left(\frac{M_2}{\varrho} - V_\phi\right) \frac{\delta m}{m}; \hfill (5)$

- Probable error in $V_\phi$: $\left(\frac{1000}{m\varrho^*} + V_\phi\right) \frac{\delta \varrho}{\varrho}. \hfill (6)$

Equations (5) and (6) demonstrate that in dilute solutions $V_\phi$ is not seriously affected by errors in $m$. However, errors in $\varrho$ may cause large errors in $V_\phi$. If, for example, $m$ is 0.01 m, an error in $\varrho$ of magnitude $10^{-5} \text{ g cm}^{-3}$ will cause an error of about $1 \text{ cm}^{-3} \text{ mol}^{-1}$ in $V_\phi$. It is therefore necessary to measure densities with great accuracy. Today’s standard with vibrating tube densitometers is of the order $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. This in turn means that the temperature must be controlled very well, approximately ±0.005 K will do.

### 3 Extrapolation to Infinite Dilution

The functional relationship between apparent molar volume and molality reflects solute-solute interactions. It is thus not surprising when experiments show distinct differences between ionic and nonionic solutes. Concerning nonionics, expe-