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Standard partial molar volumes of 1:1 salts in aqueous mixtures of ethanol (EtOH), dimethyl sulfoxide (DMSO) and acetonitrile (MeCN) at 298.15 K were obtained from the literature. In such mixtures there is evidence that preferential solvation occurs in the solvent shell around the ion where electrostriction takes place. Specifically, the anions are better solvated by the water whereas the cations are generally solvated by both the water and the nonaqueous component of the mixtures to various extents. There are no clear-cut criteria for how the measured volumes are to be apportioned between the ions in such mixtures. Various solvation models were used to estimate the volumes of the salts by calculation of the electrostriction around the ions. Only the taking into account of the preferential solvation of the ions in the solvation shell yielded calculated results of the standard partial molar volumes of the salts in agreement with the experimental data.

KEY WORDS: Partial molar volume; preferential solvation; modeling; electrostriction; aqueous solution; nonaqueous solution; mixtures.

1. INTRODUCTION

In previous papers it was shown that for hydrophilic univalent ions in neat solvents and certain solvent mixtures, the standard partial molar volume of an ion in solution, $V^\circ$ (ion), can indeed be described by the widely accepted expression:

$$V^\circ \text{ (ion)} = V_{\text{intr}} + V_{\text{el}}$$

provided, in the case of solvent mixtures, that no or little preferential solvation takes place. Here $V_{\text{intr}}$ is the intrinsic, solvent-independent volume of the ion and $V_{\text{el}}$ is the decrease in volume caused by electrostriction of the solvent in the surroundings.
of the ion. The shell-by-shell calculation of the (negative) electrostriction volume for an ion in a solvent according to Marcus and Hefter\(^{(3)}\) together with the intrinsic volume of the ion according to Marcus et al.\(^{(4)}\) yielded calculated values of the standard partial molar volumes of hydrophilic univalent ions \( (i.e., \text{with } z = \pm 1) \) that agreed with the experimental data. This means that the measured salt data can be reproduced within reasonable limits of error by summing the calculated \( V^\circ \) (ion) values for cations and anions in neat solvents and in mixtures without preferential solvation.

The shell-by-shell calculation procedure for electrostriction was described in detail in the previous publications in this series.\(^{(1,2)}\) For the relevant quantities in the \( j \)th shell of solvent around the ion, at the distance \( r(j) \) from its center, it employs the coupled expressions

\[
\varepsilon(j) - \varepsilon(0) = \beta E(j)^2 \tag{2}
\]

\[
E(j, \varepsilon, r) = \frac{ze}{4\pi\varepsilon_0} \left[ \varepsilon(0) + \beta E(j, \varepsilon, r)^2 \right] r(j)^2 \tag{3}
\]

where \( \varepsilon(0) \) is the relative permittivity of the bulk solvent \( \text{[shorthand for } \varepsilon(E = 0) \text{ or } \varepsilon(\infty)] \), \( ze \) the charge of the ion, \( \varepsilon_0 \) the permittivity of vacuum, and \( \beta \) the nonlinear dielectric effect (NDE), relating the relative permittivity \( \varepsilon \) and the electric field strength \( E \). These quantities, calculated iteratively, are needed to obtain the electrostriction volume.

\[
V_{el} = -(8\pi^2 N_A \varepsilon_0) \sum_j \left[ r(j)^3 - r(j-1)^3 \right] \times \left\{ \varepsilon(j) \left[ (\partial \ln \varepsilon / \partial P)_T - \kappa_T \right] + \kappa_T \right\} E(j)^2 \tag{4}
\]

The summation is carried out up to the shell \( j \) at the distance \( r(j) \), where \( \varepsilon(j) \approx \varepsilon(0), \text{i.e., the field strength is negligible. For its application, the isothermal compressibility } \kappa_T, \text{ the NDE } \beta, \text{ the relative permittivity } \varepsilon, \text{ and the pressure derivative of the latter } (\partial \varepsilon / \partial P)_T \text{ are needed for the solvent surrounding the ion.}

It is to be expected that in binary solvent mixtures preferential solvation of the ions generally takes place, so that their near environment, where the solvent is electrostricted, differs in composition from the bulk. In extreme cases of selective solvation the ions of either sign may be exclusively surrounded by one of the components of the solvent mixture. Then the solvent properties of the surroundings of the ions, \( \kappa_T, \beta, \varepsilon, \text{ and } (\partial \varepsilon / \partial P)_T \), to be used in the calculation of the electrostriction are those of this solvating solvent. In such cases the electrostriction can again be estimated by the shell-by-shell calculation. If the preferential solvation is only partial, then the required solvent properties should be the appropriately weighted means of those of the two solvent components. The problem remains of how to estimate the weighting factors.

The consequences of preferential solvation as regards the standard partial molar volumes of salts are here explored for three aqueous mixtures: those of water