APPLICATION OF A NEW METHOD TO REPRODUCE THE ENTHALPIES OF TRANSFER OF NaI FROM WATER TO AQUEOUS METHANOL, ETHANOL AND iPROH SOLVENT SYSTEMS AT 298 K.

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The thermodynamic parameters for transfer of a solute to mixed solvent show a number of different complex variations with the solvent composition[1-6]. In this paper we present enthalpies of transfer for NaI in three aqueous solvent systems. The improved method including variable \( (an + \beta N) \) values, have been used to reproduce the enthalpies transfer data. The agreement between experimental and calculated points via new method is excellent in all present cases and strikingly supports the equation. The enthalpies of transfer, \( \Delta H_t^\theta \), of NaI from water to aqueous methanol, ethanol and isopropanol, iPrOH, systems are reported. The new solvation theory is as follow:

\[
\Delta H_t^\theta = x'_B \Delta H_t^\theta - (an + \beta N)_A \left[ x'_A L_A + x'_B L_B \right] - x'_B \left[ (an + \beta N)_A - (an + \beta N)_B \left[ x'_A L_A + x'_B L_B \right] \right]
\]

\( A \rightarrow B \)

where

\[ x'_A = \frac{1}{x_A + px_B} \quad \text{and} \quad x'_B = \frac{px_B}{x_A + px_B} \]

In equation 1, \( \Delta H_t^\theta \) is the enthalpy of transfer from pure solvent A to pure solvent B, \( L_A \) and \( L_B \) are the relative partial molar. The superscript \( \theta \) refers to the quantities in infinite dilution of the solute. \( (an + \beta N)_A \) and \( (an + \beta N)_B \) are the net effect of the solute on solvent-solvent bonds in water-rich region and alcohol-rich region respectively. Where \( x_A \) and \( x_B \) represent the mole fractions of the components, A and B, of the mixed solvent and \( n_A = N_A \) and \( n_B = N_B \), \( N_A \) and \( N_B \) are the number of A and B components which are the nearest neighbours of the solute. \( p \) is an index of preferential solvation. \( p<1 \) or \( p>1 \) indicate a preference for solvent A or B respectively; \( p=1 \) indicates random solvation.

The enthalpies transfer are considered in terms of the new developed solvation theory including variable \( (an + \beta N) \), the net effect of the solute on the solvent-solvent bonding and is positive if there is a net breaking or weakening of solvent-solvent bonds. The salvation parameters recovered from the analyses indicate that the net affect of NaI on solvent structure is a breaking of solvent-solvent bonds and that NaI is preferentially solvated by water in all aqueous alcohol systems considered. \( (an + \beta N) \) values increase with increasing in the size of the alcohol alkyl residue from methanol to iPrOH.

References