Solute-solute interactions; Pairwise

Analysis of the thermodynamic properties of aqueous solutions was taken a step further by Savage and Wood who envisage two solute molecules A and B in aqueous solution [1]. The total pairwise interaction between these molecules is described in terms of pairwise group-group interaction parameters. Then, for example, the pairwise enthalpic solute-solute interaction parameter $H_{AB}$ is written as the sum of products,

$$ n_i^A \cdot n_j^B \cdot h_{ij} $$

where $n_i^A$ is the number of A-groups in solute molecule $i$ and $n_j^B$ is the number of B-groups in solute molecule $j$ where $h_{ij}$ is a pairwise enthalpic group interaction parameter. A similar analysis is carried out for interaction Gibbs energies leading to pairwise Gibbs energy parameters $g_{ij}$. So, for example, $g$(OH-OH) is negative characteristic of a hydrophilic-hydrophilic interaction. Whereas $g$(OH-CH$_2$) is positive indicating 'repulsion' within hydrophobic-hydrophilic pairs. Interestingly $g$(CH$_2$-CH$_2$) is negative" which is indicative of a hydrophobic-hydrophobic attraction (cf. hydrophobic bonding); the corresponding enthalpic pairwise parameter is positive. Thus it is tempting to speculate that hydrophobic attraction is entropy driven [2]; for further comments see references [3-13].

The general approach is readily extended to a consideration of pairwise interactions between added solutes and both initial and transitions states for given chemical reactions in aqueous solution [14-18].

Footnotes


[13] Small peptides(aq); enthalpies; O. V. Kulikov, A. Zielenkiewicz, W. Zielenkiewicz.


