Gibbs Energies

Salt solutions

Cosphere - Cosphere Interactions

The Debye-Hückel equations form the starting point for detailed analyses of the properties of salt solutions. An interesting method examines excess thermodynamic properties of salt solutions and their dependence on salt molality [1]. For an aqueous solution containing a 1:1 salt in 1 kg of solvent, the excess Gibbs energy $G^E$ is given by equation (a).

$$ G^E = 2 \cdot R \cdot T \cdot m_j \cdot [1 - \phi + \ln \gamma_\pm] $$

(a)

The corresponding excess molar Gibbs energy is given by equation (b).

$$ G_m^E = 2 \cdot R \cdot T \cdot [1 - \phi + \ln \gamma_\pm] $$

(b)

The corresponding excess molar enthalpy $H_m^E$ is obtained from calorimetric data. Hence the molar excess entropy is calculated using equation (c).

$$ G_m^E = H_m^E - T \cdot S_m^E $$

(c)

A common observation is that $H_m^E$ and $T \cdot S_m^E$ are more sensitive to both the molality $m_j$ and the salt than is $G_m^E$. For dilute salt solutions $G_m^E < 0$ as a consequence of charge-charge interactions between the ions leading to a stabilisation. Further $H_m^E$ and $T \cdot S_m^E$ are more sensitive to switching the solvent from $H_2O$ to $D_2O$ than is $G_m^E$.

The dependence of $G_m^E$ on salt at fixed $m_j$ shows that in addition to charge-charge interactions there are further interactions which are characteristic of the ions in a given salt. So the suggestion is that even in the absence of charge-charge interactions the properties of the solution would not be ideal by virtue of cosphere - cosphere interactions along the lines suggested by Gurney. But there are two types of solutes in a simple 1:1 salt solution so we must consider in the analysis of these properties at least $g_{++}$, $g_+$, and $g_-$ pairwise ion-ion Gibbs energy interaction parameters. Consequently the analysis is not straightforward.
An interesting approach examines patterns in $\ln(\gamma_{\pm})$ for a series of 1:1 salts at fixed molality $m_j$, temperature and pressure [2-4]. A most dramatic change is observed for Pr$_4$N$^+$ salts (aq; 0.2 mol kg$^{-1}$). Thus $\ln(\gamma_{\pm}) > (\ln \gamma_{\pm} (\text{DHLL} - \text{calc}))$ for the fluoride salt; i.e. a higher chemical potential than calculated simply on the basis of the DHLL--- a destabilisation. But $\ln(\gamma_{\pm}) < (\ln \gamma_{\pm} (\text{DHLL} - \text{calc}))$ for the corresponding iodide salt; i.e. lower chemical potential than calculated simply on the grounds of the DHLL--- a stabilisation. The dependence of $\ln \gamma_{\pm}$ for K$^+$, Rb$^+$ and Cs$^+$ on the anion F$^-$, Cl$^-$, Br$^-$ and I$^-$ is much more modest. The pattern signals the important role of hydrophobic-hydrophobic, hydrophilic-hydrophobic and hydrophilic-hydrophilic ion-ion interactions. Indeed there is considerable merit in the approach [4]. The pattern emerges in a comparison of salt effects on rates of hydrolysis in aqueous salt solutions [5]. This conclusion is supported by the observation that the dependence of $\ln \gamma_{\pm}$ on $(m_j)^{1/2}$ for (HOCH$_2$CH$_2$)$_4$N$^+$Br$^-$ deviates from the DHLL pattern in a direction indicating a more hydrophilic character for the cation than in the cases of Pr$_4$N$^+$ and Et$_4$N$^+$ [6].

The patterns identified in $\ln \gamma_{\pm}$ signal that the ion-ion pair potential for ions in solution comprises several components. This recognition forms the basis of the treatment developed by Friedman and coworkers. The pair potential $u_{ij}$ for two ions charge $z_i.e$ and $z_j.e$ in a solvent having relative permittivity $\varepsilon_r$ is expressed in the form shown in equation (d) [6].

$$u_{ij}(r) = \left[\frac{(z_i \cdot e) \cdot (z_j \cdot e)}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r}\right] + \text{COR}_{ij} + \text{CAV}_{ij} + \text{GUR}_{ij} \quad (d)$$

The first term takes account of charge-charge interactions; i.e. the Coulombic term, COUL. The term COR$_{ij}$ is a repulsive core potential, being a function of the sizes of the ions i and j. The CAV$_{ij}$ term takes account of a special effect arising from the interactions between ion + solvent cavities. The impact of cosphere overlap is taken into account by the Gurney potential, GUR$_{ij}$. The pair potential is used in conjunction with McMillan-Mayer theory [8]. The GUR$_{ij}$ term includes an adjustable
parameter $A_{ij}$, the change in Helmholtz energy, $F$ when one mole of solvent in the overlap region returns to the bulk solvent. There are therefore three such terms, $A_{++}$, $A_{+-}$, and $A_{--}$ for the three types of overlap. These terms are related to the corresponding volumetric $V_{ij}$, entropy $S_{ij}$ and energy $U_{ij}$ terms. The analysis is slightly complicated by the fact that the derived thermodynamic functions refer to a solution in osmotic equilibrium with the solvent at the standard pressure; the MM state. Conversion is required to thermodynamic parameters for a solution of the same salt at the same molality at the standard pressure.

**Footnotes**


[3] H. S. Frank and A. L. Robinson, J.Chem.Phys.,1940,8,933; this paper concerns the dependence of partial molar entropies on composition of salt solutions; the analysis set the stage for subsequent developments in this subject.


