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PHYSICAL CHEMISTRY 2021

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CONTRIBUTION OF DIFFERENT INTERACTIONS TO THE EXCESS GIBBS ENERGY OF MIXING IN AQUEOUS ELECTROLYTE SOLUTIONS

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ABSTRACT

The thermodynamic properties of the mixed electrolyte solutions are conveniently described in terms of excess quantities. The excess Gibbs energy of mixing, presents the difference between the excess free energy of a mixed electrolyte solution and free energies of the individual binary electrolyte solutions at the same temperature, pressure and total ionic strength. In this paper the excess Gibbs energy of mixing is calculated for series of mixed electrolyte solutions and possible pairs, triplets, quads or even higher order multiplets were discussed in respect to Scatchard's mixing parameter values.

INTRODUCTION

In thermodynamics of electrolyte solutions, for aqueous mixture of two electrolytes the excess free energy can be expressed as the sum of the contributions of single electrolyte solutions at the same ionic strength as the mixed one, plus excess free energy of mixing given as an expansion in the ionic strength fractions of electrolyte. The main contribution to the excess free energy of mixing appears due to interactions of pairs and triplets of ions. The contribution of triplet interactions are often considered negligible compared to binary ones. If a solution contains an electrolyte which tends to form complexes or has strong hydrophobic character, the contribution of higher-order multiplets to the excess free energy of mixing must be taken into account, in addition to the contributions due to pairs or pairs and triplets.

THEORY AND MODEL

The model used in calculations is Scatchard's neutral-electrolyte model [1], generally capable of representing osmotic coefficients of mixed electrolyte solutions accurately, given enough mixing parameters. This approach treats all electrolytes present formally as if they were completely dissociated. In the case of mixtures of strong electrolytes, the binary-solution mixing approximation can sometimes provide a fairly reliable estimate of the osmotic coefficients of the ternary solutions. The excess free energy of mixing for the mixed solution of A and B electrolytes, in terms of the Scatchard parameters is given by:

$$\frac{\Delta G_m^{\text{ex}}}{RT} = I y_A y_B \left[B_{AB}^{(0)} + (y_A - y_B) B_{AB}^{(1)} + (y_A - y_B)^2 B_{AB}^{(2)} + \dots + (y_A - y_B)^n B_{AB}^{(n)} \right] \quad (1)$$

where terms B_{AB} represent:

$$B_{AB}^{(n)} = \sum_{k=n+1}^{k'} \frac{I^k}{k} b_{AB}^{(n,k)} \quad \text{for } n \geq 0 \quad (2)$$

In previous relations, y is the ionic strength fraction of electrolyte A or B, I is the ionic strength of the mixed solution and b_{AB} are Scatchard's mixing parameters. The b_{AB} parameters are found by least squares method applied to either the osmotic coefficients or the activity coefficient data for the mixed systems containing A and B electrolytes. If we rearrange the terms in excess free energy of mixing through possible pairs, triplets, quads or even higher order multiplets (HOM), we obtain:

$$\frac{\Delta G_m^{ex}}{RT} = \left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{pairs}} + \left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{triplets}} + \left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{quads}} + \dots + \left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{HOM}} \quad (3)$$

where:

$$\left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{pairs}} = I^2 y_A y_B b_{AB}^{(0,1)} \quad (4a)$$

$$\left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{triplets}} = \left(I^3/2\right) y_A y_B \left[b_{AB}^{(0,2)} + (y_A - y_B) b_{AB}^{(1,2)} \right] \quad (4b)$$

$$\left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{quads}} = \left(I^4/3\right) y_A y_B \left[b_{AB}^{(0,3)} + (y_A - y_B) b_{AB}^{(1,3)} + (y_A - y_B)^2 b_{AB}^{(2,3)} \right] \quad (4c)$$

$$\left(\frac{\Delta G_m^{ex}}{RT}\right)_{\text{HOM}} = \left(I^{n+2}/n+1\right) y_A y_B \left[b_{AB}^{(0,n+1)} + (y_A - y_B) b_{AB}^{(1,n+1)} + \dots + (y_A - y_B)^n b_{AB}^{(n,n+1)} \right] \quad (4d)$$

RESULTS AND DISCUSSION

Excess Gibbs energy of mixing (Figure 1) was calculated by relation (1), for series of mixed electrolyte solutions at temperature 298.15 K. Scatchard's parameters (Table 1.) for each mixed solution were taken from our previous work on osmotic coefficients treatment[2-7].

Table 1. Scatchard's mixing parameters for different electrolyte systems, standard deviation of fitting the osmotic coefficient data for the system, s.d. (ϕ), the solution ionic strength interval, for which the parameters are valid (m^0 stands for standard molality, $1 \text{ mol} \cdot \text{kg}^{-1}$).

System	$b_{AB}^{(0,1)} (m^0)$	$b_{AB}^{(0,2)} (m^0)^2$	s.d. (ϕ) 10^3	Ionic strength interval ($\text{mol} \cdot \text{kg}^{-1}$)
$\{y\text{KCl}+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[2]$	-0.03724	0.047634	7.8	2-12
$\{y\text{KNO}_3+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[3]$	-0.028196	0.081518	4.2	2.5-6.5
$\{y\text{KBr}+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[4]$	-0.020035	0.020422	8.0	3-10
$\{y\text{K}_2\text{SO}_4+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[5]$	-0.010654	0.0062619	8.0	1.2-2
$\{y\text{KH}_2\text{PO}_4+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[6]$	-0.0025	0.0122	1.6	0.4-3.4
$\{y\text{Na}_2\text{HPO}_4+(1-y)\text{K}_2\text{HPO}_4\}(\text{aq})[7]$	0.0084145	0.0	0.9	0.9-1.06

If pairwise interactions are truly the only interactions occurring in a mixed solution, then $b_{AB}^{(0,1)}$ parameter will be the only one required to fit the data, and the total excess free energy of mixing will be equal to $(\Delta G_m^{ex} / RT)_{pairs}$. This is the case with the system $\{y\text{Na}_2\text{HPO}_4 + (1-y)\text{K}_2\text{HPO}_4\}(\text{aq})$ where standard deviation of the fit is of 10^{-4} order even with only one mixing parameter. If the sole use of $b_{AB}^{(0,1)}$ is found to be inadequate in fitting the data, then there must also be triplet interactions in the solution. Therefore, both $b_{AB}^{(0,2)}$ and $b_{AB}^{(1,2)}$ as well as $b_{AB}^{(0,1)}$ must be used in fitting the data, as it is the case for the systems $\{y\text{KCl} + (1-y)\text{K}_2\text{HPO}_4\}(\text{aq})$, $\{y\text{KBr} + (1-y)\text{K}_2\text{HPO}_4\}(\text{aq})$ and $\{y\text{K}_2\text{SO}_4 + (1-y)\text{K}_2\text{HPO}_4\}(\text{aq})$ where the standard deviation of the fit by using just two mixing parameters $b_{AB}^{(0,1)}$ and $b_{AB}^{(0,2)}$ is still relatively high. Gibbs energy of mixing for these systems, specially with $\{y\text{KCl} + (1-y)\text{K}_2\text{HPO}_4\}(\text{aq})$, changes evidently with the increase of solution ionic strength reflecting possible triplet interactions.

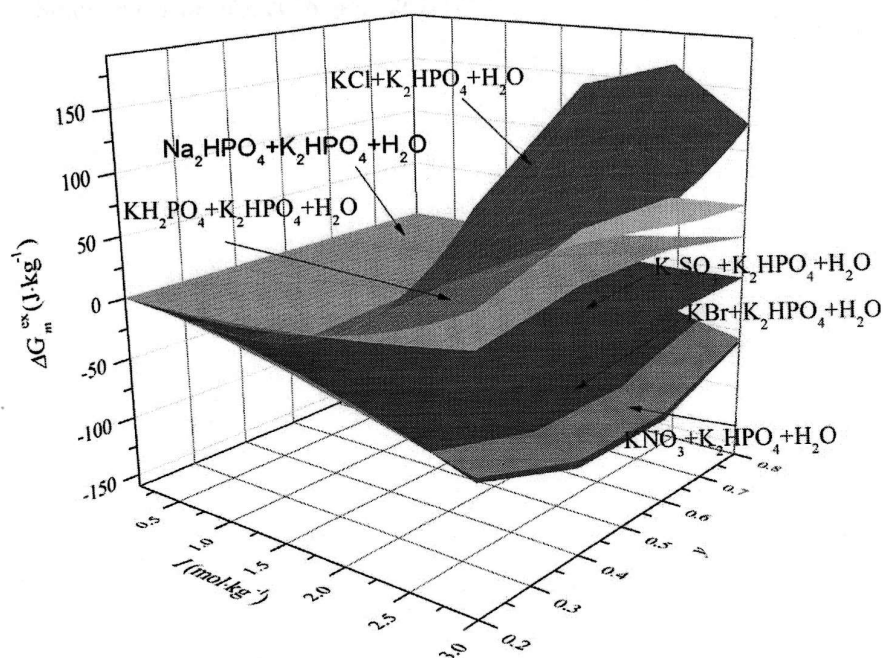


Figure 1.: Excess Gibbs energy of mixing per kilogram of solvent (water) for different mixed electrolyte solutions at $T = 298.15$ K in respect to solution ionic strength, I , and ionic strength fraction, y .

CONCLUSION

By obtaining detailed thermodynamic data on excess Gibbs energy of mixing for the aqueous electrolyte systems, using Scatchard's parameters, significant information regarding specific ion interactions can be obtained.

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