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Short Communications

Thermodynamics in Solvent Mixtures. 1. A Simple Deviation Function for Summarizing Thermodynamic Data in Mixed Solvents

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When dissolving a molecule in a solvent mixture (A + B) the probability that it will only have A molecules as nearest neighbours will be proportional to the fraction of A present, *i.e.* the mol fraction, x_A, and similarly for B. The probability for having both A and B as nearest neighbours will be proportional to the product $x_A x_B$. A thermodynamic quantity studied could then be considered to be made up of three terms, eqn. (1), where Y is the quantity studied, y_A and y_B its value in the pure solvents and B related to mixed solvates.

$$Y = y_A x_A + B x_A x_B + y_B x_B \qquad (1)$$

One can regard function (1) as a deviation function. For $B = 0$ the properties of the mixtures can be predicted from those of the pure solvents and the system behaves ideally.

The quantity B can either be constant or a function of x. In the latter case certain solvates may have a great influence on Y.

The function (1) has found much use in the study of excess thermodynamic quantities of mixing (here y_A and y_B are zero) both in organic and molten salt mixtures.[1] For B = constant the mixture can form regular solutions.[2] Eqn. (1) does not seem to have been applied to solute behaviour in solvent mixtures before. Below it is used on some rather different chemical reactions in mixed solvents.

I *The ionic product of water in methanol–water mixtures.* Rochester[3] studied the ionic product of water in water–methanol mixtures. Measurements were made up to 90 % (w/w) of MeOH. For the ionic product in pure methanol the value 16.7 was chosen.[4] Knowning Y, y_A and y_B, B can be computed. Linear regression gave eqn. (2), where x is the mol

$$B = -1.15 - 3.39x \qquad (2)$$

fraction of MeOH. In Table 1 experimental and computed log K-values are compared. As seen, most of the data fit to within a few hundreds in log K, except for the last point. This is not unreasonable in view of the greater uncertainty at high methanol concentrations. It is possible to improve the fit by using second degree polynomials, *etc.*

Table 1. Experimental and computed log K-values for MeOH – H_2O mixtures.[3] log K (H_2O) = 13.997; log K (MeOH) = 16.7; $B = -1.15 - 3.39x$.

$x = x_{MeOH}$	log K exp.	log K calc.
0.0588	14.091	14.082
0.1232	14.156	14.161
0.1831	14.219	14.228
0.3599	14.416	14.425
0.4575	14.529	14.565
0.5675	14.768	14.778
0.6922	15.158	15.125
0.8350	15.938	15.706

Table 2. Experimental and computed stability constants for the system Hg^{2+}-SCN^- in DMF – NMA mixtures at 40 °C.[5] For K_1 $B = -5.4 \pm 0.6$; For β_4 $B = -8.38 - 4.44x$.

$x = x_{NMA}$	log K_1 exp.	log K_1 calc.	log β_4 exp.	log β_4 calc.
0	17.7	–	25.2	–
0.20	16.2	16.2	22.7	22.8
0.40	15.2	15.0	21.1	20.9
0.60	14.7	14.7	19.65	19.73
0.80	14.4	14.4	19.52	19.53
1.00	14.6	–	20.5	–

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II. *The complex formation between Hg^{2+} and SCN^- in DMF–NMA mixtures.* Tremillon and coworkers[5] studied polarographically at 40 °C the complex formation between Hg^{2+} and SCN^- in mixtures of DMF (dimethylformamide) and NMA(n-methylacetamide). By treating their data in the manner outlined above, it was found that for K_1 (formation of $HgSCN^+$) B was practically constant, while a straight line was needed for the formation of $Hg(SCN)_4^{2-}$(β_4). The results are given in Table 2, where experimental and computed stability constants are compared. As seen, the fit is excellent.

III. *The acidity constant of NH_4^+ in MeOH–H_2O mixtures.* MacKellar and Rorabacher[6] studied the acidity constant of the ammonium ion in mixtures of methanol and water using 0.1 M $(NH_4)ClO_4$ as ionic medium at 25 °C. Although the measurements were made up to 99 % by weight of MeOH the value in pure MeOH is somewhat uncertain. After some trial calculations the following value was chosen

$$\log K(\text{MeOH}) = 10.06$$

Also here B could to a first approximation be fitted with a straight line. Fig. 1 gives the plot $\log K(x_{\text{MeOH}})$. As seen, agreement between experiment and computation is good.

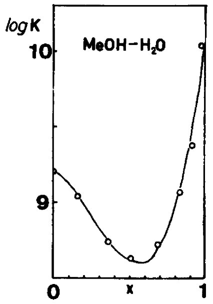

Fig. 1. Log K plotted against x_{MeOH} for the reaction: $NH_3 + H^+ \leftrightharpoons NH_4^+$ at 25 °C in MeOH–H_2O mixtures.[6]
○ Exp. points. —— Curve computed from eqn. (1) and the parameters: $\log K(H_2O) = 9.21$; $\log K(\text{MeOH}) = 10.06$; $B = -(1.34 + 5.56x)$.

Table 3. Experimental and computed $\log K$-values for the reaction: $\text{Coen}_3^{3+} + NH_3 \leftrightharpoons \text{Coen}_3NH_3^{3+}$ in EtOH–H_2O mixtures at 25 °C.[7,8] $\log K$ (H_2O) = -0.77; $\log K$ (EtOH) = -0.2; $B = 2.19 - 3.49x$.

$x = x_{\text{EtOH}}$	$\log K$ exp.	$\log K$ calc.
0.1153	−0.52	−0.52
0.2811	−0.38	−0.37
0.3697	−0.34	−0.35

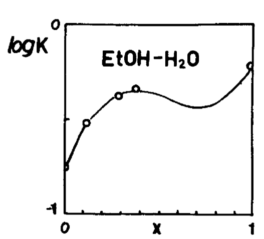

Fig. 2. $\log K$ plotted against x_{EtOH} for the reaction: $\text{Co en}_3^{3+} + NH_3 \leftrightharpoons \text{Co en}_3NH_3^{3+}$ at 25 °C.[7,8]
○ Exp. points. —— Curve computed from eqn. (1) and the parameters given in Table 3.

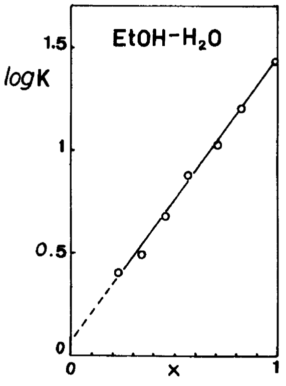

Fig. 3. $\log K$ for formation of LiCl ion-pairs in EtOH–H_2O mixtures at 25 °C plotted against x_{EtOH}[9].
○ Exp. points. —— Curve computed from $\log K = 1.43x + 0.06(1\text{-}x)$.

IV. *The reaction between Coen_3^{3+} and NH_3 in ethanol–water mixtures.* Mironov *et al.*[7,8] studied at 25 °C the reaction (3) in ethanol–water mixtures. Also here B was approximately linear with x_{EtOH}. In Table 3 experimental and computed $\log K$-values are compared. As seen, the agreement is excellent. Fig. 2 gives the plot $\log K(x_{\text{EtOH}})$. Unfortunately, the authors give no data above $x_{\text{EtOH}} = 0.5$. The curve illustrates the capability of function (1) to fit curves of widely different shapes.

$$\text{Co en}_3^{3+} + NH_3 \leftrightharpoons \text{Co en}_3NH_3^{3+} \ (K) \qquad (3)$$

V. *Association of Li^+ and Cl^- in EtOH–H_2O mixtures.* Dill and Popovych[9] measured the conductance of LiCl in mixtures of ethanol and water at 25 °C. In Fig. 3 $\log K$ for formation of the ion-pair is plotted against x_{EtOH}. As seen, a straight line can be fitted to the data, *i.e.* $B = 0$. A least squares treatment gave eqn. (4).

$$\log K = 1.43x + 0.061(1\text{-}x) \qquad (x = x_{\text{EtOH}}) \qquad (4)$$

The extrapolation to pure water has been dashed, in order to emphasize that there is some uncertainty in that procedure. However, if data in several organic solvent–water mixtures extrapolate to the same value in pure water, one should have a fair estimate of the ion-pair formation constant in water.

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