

Solubility and solvation in mixed solvent systems

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Abstract - The solubility of solutes in mixed solvents depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. Complications may arise if different crystal solvates are formed or if solute-solute interactions are appreciable. In their absence the standard molar Gibbs energies of solution measure the corresponding quantities of solvation, $\Delta_{\text{solv}}G^\circ$, or transfer, $\Delta_{\text{tr}}G^\circ$. The preferential solvation of solutes is described by the composition dependence of $\Delta_{\text{tr}}G^\circ$ and is analyzed in terms of the quasi-lattice quasi-chemical (QLQC) or the inverse Kirkwood-Buff integral (IKBI) methods. These relate $\Delta_{\text{tr}}G^\circ$ to the solvation in the two neat solvents, and in turn to certain properties (polarity, hydrogen-bonding ability, size) of the solvents. These considerations are illustrated by several cases, involving salts and non-electrolytes.

INTRODUCTION

The solubility of solutes of all kinds in mixed solvents is of great practical importance, since many industrial process as well as laboratory procedures call for the use of solvent mixtures, or such mixtures are used by default. The reasons for the preference for the use of solvent mixtures are manifold, including the amelioration of certain physical properties, such as the density, viscosity, volatility, etc., or of their chemical properties, such as stability, inflammability, and not least, their ability to dissolve certain substances. Default, rather than intentional use of solvent mixtures occurs, for instance, in solvent extraction, where the solutes distribute between mutually saturated solvent phases. The organic phases employed often contain appreciable amounts of water, with mole fractions near 0.5 in certain cases (e.g., tri-*n*-butyl phosphate or 3-methyl-1-butanol).

When the solubility of a solute in a solvent or a solvent mixture is appreciable, then solute-solute interactions are significant and must be taken into account in any interpretation of the solubility data. Unfortunately, theoretical considerations pertaining to solute-solute interactions can be employed essentially only for rather dilute solutions. This is true for both ionic and non-electrolyte solutes. For the former, the extended Debye-Hückel expression can be employed for solvents with relative permittivities $\epsilon_r > 20$, approximately, and ionic strengths of the order of 0.2 mol dm⁻³. For the latter some variation of the regular solution or solubility parameter theory can be employed, although these may include also solute-solvent interactions that should be dealt with separately. The solute-solute interactions in concentrated solutions, i.e., when the solubility is very large, cannot be handled by such expressions and systems where such solubilities are encountered are outside the scope of the following considerations.

Another complication that is met with in the case of solid solutes is the formation of crystal solvates. When non-solvated crystals or crystals with one given solvating solvent are in equilibrium with a solution in a mixed solvent then the solvent-composition dependence of the standard molar Gibbs energy of solution, $\Delta_{\text{soln}}G^\circ$, is directly related to that of the standard molar Gibbs energy of solvation, $\Delta_{\text{solv}}G^\circ$. If, however, different crystal solvates can be formed and are in equilibrium with different compositions of the solution, then additional Gibbs energy terms must be added, pertaining to the conversion of one crystal solvate to another. Such cases, again, are outside the scope of the following considerations. Similar complications occur when the solute is a liquid, unless the solubility of the (components of the mixed) solvent in this liquid is entirely

negligible, since only then can its activity in the equilibrium system be equated with that of the pure liquid solute.

The solubility data that are dealt with here yield directly values of the $\Delta_{\text{soln}}G^\circ$. For non-electrolyte solutes:

$$\Delta_{\text{soln}}G^\circ = -RT \ln (s_x f) \approx -RT \ln s_x \quad (1)$$

where s_x is the solubility on the mole fraction scale and f is the rational activity coefficient, and the approximation on the rhs is valid when the solubilities are very low so that $f \approx 1$. For (1:1) ionic solutes:

$$\Delta_{\text{soln}}G^\circ = -RT \ln (s_m \gamma_{\pm})^2 \approx -2 RT \ln s_m \quad (2)$$

where s_m is the solubility on the molal scale and γ_{\pm} is the mean molal activity coefficient, and the approximation on the rhs is valid for poorly soluble salts, so that $\gamma_{\pm} \approx 1$. For other types of electrolytes the 2nd power and the coefficient 2 on the rhs must be modified to take into account the relevant stoichiometries.

Solvation is the process of bringing a particle of the solute from a fixed position in the ideal gaseous state to a fixed position in the solution at a given temperature and pressure (ref. 1). The standard molar $\Delta_{\text{soln}}G^\circ$ pertains to the introduction of the solute to make an infinitely dilute solution. In this case, only solute-solvent interactions need to be taken into account, although these reflect the changes in the solvent-solvent interactions that take place on the introduction of the solute. In order to relate $\Delta_{\text{soln}}G^\circ$ to $\Delta_{\text{soln}}G^\circ$ it is necessary to consider also the standard molar Gibbs energy of sublimation or vaporization of the solute (if it is a solid or a liquid). If this quantity is symbolized by $\Delta_{\text{vap}}G^\circ$, then

$$\Delta_{\text{soln}}G^\circ = \Delta_{\text{soln}}G^\circ - \Delta_{\text{vap}}G^\circ \quad (3)$$

Work must be invested in order to vaporize the solute, hence $\Delta_{\text{vap}}G^\circ$ is positive, whereas $\Delta_{\text{soln}}G^\circ$ is generally negative, and the balance between these quantities determines whether $\Delta_{\text{soln}}G^\circ$ is positive or negative, i.e., whether the dissolution process is thermodynamically favorable or not.

Rather than to deal with $\Delta_{\text{soln}}G^\circ$, it is often convenient to subtract from this quantity the $\Delta_{\text{soln}}G^\circ$ to some reference solvent, W, and then to deal with the standard molar Gibbs energies of transfer of the solute from W into the solvent or solvent mixture of interest, $\Delta_{\text{tr}}G^\circ$. If the reference solvent is W = water, then $\Delta_{\text{soln}}G^\circ(W) = \Delta_{\text{hydr}}G^\circ$, for which an extensive amount of data is available (see ref. 2 for $\Delta_{\text{hydr}}G^\circ$ of ions). The convenience of using $\Delta_{\text{tr}}G^\circ$ is brought home in the many cases where $\Delta_{\text{vap}}G^\circ$ is not known, since then:

$$\Delta_{\text{tr}}G^\circ(W \rightarrow S) = \Delta_{\text{soln}}G^\circ(S) - \Delta_{\text{soln}}G^\circ(W) \quad (4)$$

where S symbolizes the solvent or solvent mixture of interest. Again, an extensive amount of data on $\Delta_{\text{soln}}G^\circ(W)$ is available for solubilities in water (see, e.g., ref. 3), from which the $\Delta_{\text{tr}}G^\circ$ can be evaluated from the solubilities by means of eq. (1) or (2) and (4).

PREFERENTIAL SOLVATION

The values of $\Delta_{\text{tr}}G^\circ$ and its dependence on the composition of the solvent mixture can be interpreted in terms of the solvation of the solute by the neat solvents and its preferential solvation by the individual components of the mixture. The solvation by the neat solvents can be described in terms of the linear solvation energy relationships (LSER) of Taft and Kamlet and their coworkers (refs. 3-5) and in the case of non-electrolyte solutes and of Marcus, Kamlet and Taft (ref. 6) in the case of ionic solutes. These relationships are of the form:

$$\Delta_{\text{tr}}G^\circ = \sum A_{ij} P_{iX} (P_{jS} - P_{jW}) \quad (5)$$

where the summation extends over all the i properties P of the solute X and the j properties P of the solvent S relative to those of the reference solvent W. The solvent properties include generally its polarity/polarizability, as measured in a combined form by its Taft-Kamlet parameter π (ref. 4) or individually by its dipole moment μ and its polarizability α_P (or molar refractivity, R_D), its cohesive energy density, given by the square of its Hildebrand solubility parameter, δ_H^2 , its hydrogen bond donation α and acceptance β abilities (ref. 4), and its softness μ_s (ref. 7). The properties of ionic solutes include their charge z , their size (ionic radius) r_1 , their softness σ (or polarizability α_P or molar

refractivity R_D), or combinations thereof, such as the field strength z/r_1 .

Once the $\Delta_{soln}G^\circ$ in the neat solvents are known, at least relative to the value in the reference solvent W (i.e., $\Delta_{tr}G^\circ$), then it is necessary to have expressions that describe the preferential solvation in the solvent mixtures. A first step is to obtain values for $\Delta_{tr}G^\circ$ from W to the mixture of S_1 and S_2 . These can be obtained experimentally from the solubilities in the mixture via eq. (1), (2) and (4). Fig. 1 illustrates this with some data [$\ln K_{sp} = 2 \ln (s_m \gamma_{\pm})$] for potassium halides in mixed aprotic solvents (ref. 8).

The values of $\Delta_{tr}G^\circ$ from some reference solvent can also be estimated via the QLC theory (ref. 9) and the following eq. (6). In this theory the solution is regarded as a quasi-lattice, that is characterized by a lattice parameter Z . Only near-neighbor interactions are taken into account, and it is assumed that the interaction energies of a neighboring pair of particles is independent of the natures of the other neighbors they may have. The quasi-chemical expression is applied to the numbers of neighbors of each kind that exist at equilibrium, leading finally to (ref. 9):

$$\Delta_{tr}G^\circ(W \rightarrow S_1 + S_2) = x_1 \Delta_{tr}G^\circ(W \rightarrow S_1) + x_2 \Delta_{tr}G^\circ(W \rightarrow S_2) - \Delta G_{12}^F(x) - Z R T \left\{ x_2 \ln [x_2 + x_1 y \Delta] + x_1 \ln [x_1 + x_2 y^{-1} \Delta^{-1}] \right\} \quad (6)$$

where $\Delta G_{12}^F(x)$ is the Gibbs energy of mixing of S_1 and S_2 , x is the mole fraction, and y and Δ are given by:

$$y(x) = x_2 x_1^{-1} [(x_1 - N_s) / (x_2 - N_s)]^{1/2} \quad (7)$$

$$\Delta = \exp \{ [\Delta_{tr}G^\circ(W \rightarrow S_1) - \Delta_{tr}G^\circ(W \rightarrow S_2)] / Z R T \} \quad (8)$$

$$N_s = \{ 1 - [1 - 4 x_1 x_2 P]^{1/2} \} / 2 P \quad (9)$$

$$P = 1 - 1 / \{ 2 \exp [-2 \Delta G_{12}^F(x = 0.5) / Z R T] - 1 \}^2 \quad (10)$$

In principle, at least, the solubility curve of the solute in the solvent mixture can be calculated without the performance of a single solubility measurement, provided the required independent data are available. These are $\Delta_{tr}G^\circ(W \rightarrow S_1)$ and $\Delta_{tr}G^\circ(W \rightarrow S_2)$, estimated from eq. (5) and independently known properties of the solute and the solvents S_1 and S_2 , $\Delta G_{12}^F(x = 0.5)$ provided from independent mixing data of the two solvents, the aqueous solubility datum $\Delta_{soln}G^\circ(W)$, and the lattice parameter Z , chosen arbitrarily as a fitting parameter. Use is then made of eq. (4) and (1) or (2) to calculate the actual solubilities. In practice, of course, the accumulation of errors due to the approximations inherent in the models and the correlations prevents the calculation of solubilities at any practical accuracy from completely independent data. However, given the solubilities of the solute in S_1 and S_2 , it is possible to use the following eq. (11) (derived from eq. (6)), together with eq. (7) - (10) and an assumed value of Z , to calculate actual solubilities in the mixtures of S_1 and S_2 . [In eq. (8) the difference is replaced by $\Delta_{tr}G^\circ(S_1 \rightarrow S_2)$].

$$\Delta_{tr}G^\circ(S_1 \rightarrow S_1 + S_2) = x_2 \Delta_{tr}G^\circ(S_1 \rightarrow S_2) - \Delta G_{12}^F(x) - Z R T \left\{ x_2 \ln [x_2 + x_1 y \Delta] + x_1 \ln [x_1 + x_2 y^{-1} \Delta^{-1}] \right\} \quad (11)$$

An example of the application of these equations in the case of the solubility of KCl in mixtures of *N,N*-dimethylformamide and acetonitrile (ref. 8) is shown in Fig. 2. The curves are drawn with Z values (from top to bottom) of 1.2, 1.0 and 0.8.

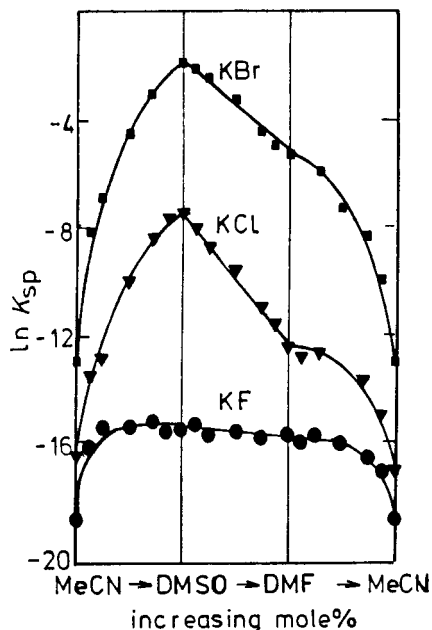


Fig. 1. The solubility products of KBr, KCl and KF in MeCN + DMSO, DMSO + DMF and DMF + MeCN.

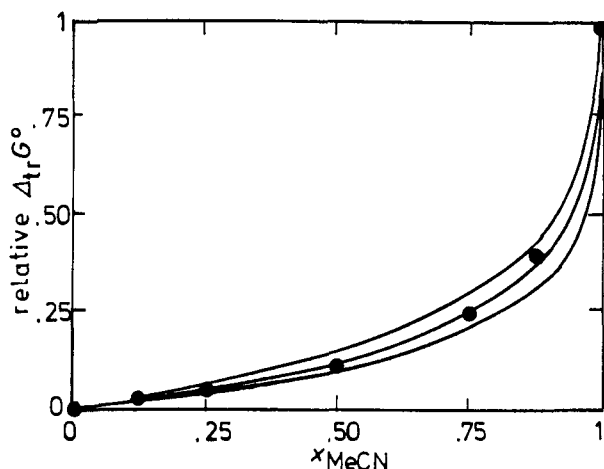


Fig. 2. $\Delta_{tr}G^\circ(W \rightarrow \text{DMF} + \text{MeCN}) / \Delta_{tr}G^\circ(W \rightarrow \text{DMF})$ of KCl. ● experimental (ref. 8), — calculated from eq. (11) with varying Z values.

The QLQC considerations leading to expressions (6) or (11) can now be used for the evaluation of the solvent composition near the solute, i.e., of the preferential solvation that the solute undergoes (ref. 10). A schematic representation of it is shown in Fig. 3.

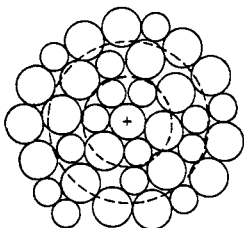


Fig. 3. A two-dimensional representation of the preferential solvation around a cation by a binary mixture of small and large solvents, at $x_{\text{large}} = 2/3$. In the first solvation shell $x_{\text{large}} = 1/3$, hence $\delta x_{\text{large}} = -1/3$ and the smaller solvent is preferred near the cation. (From ref. 10, by permission of the Royal Society of Chemistry.)

The local mole fraction of S_1 near the solute X is given by:

$$x_1^l = N_{1X} / (N_{1X} + N_{2X}) = 1 / [1 + (x_2/x_1) \gamma (\Delta/2)] \quad (12)$$

The preferential solvation can be defined as the excess or deficiency of the local relative to the bulk mole fraction: $\delta x_1 = x_1^l - x_1$. In the case illustrated in Fig. 2, the resulting δx_1 values for $S_1 = \text{DMF}$ are very large (0.11 at $x_2 = 0.2$, 0.22 at $x_2 = 0.4$, 0.30 at $x_2 = 0.6$, 0.31 at $x_2 = 0.8$) up to quite high concentrations of $S_2 = \text{MeCN}$ in the mixtures. It is, however, impossible to specify whether the cation or the anion of the KCl (or both) is preferentially solvated by the DMF without the application of some extrathermodynamic assumption.

In some favorable cases it is possible to apply another theoretical method to the evaluation of preferential solvation from solubility data. The IKBI method is based (ref. 11) on the Kirkwood-Buff integrals:

$$G_{1X} = \int_0^\infty [g_{1X}(r) - 1] 4 \pi r^2 dr \quad (13)$$

where $g_{1X}(r)$ is the pair correlation function for solvent S_1 at distance r , given a particle of solute X at the origin. In the case of ionic solutes there is a complication due to the requirement of electroneutrality. The upper limit of the integral has then to be taken not as ∞ but as R , the distance of a few molecular diameters of the solvents, beyond which the pair correlation practically ceases, i.e., $g_{1X}(r > R) - 1 \approx 0$. The integrals are obtained from thermodynamic data for the solvent mixture and for the solution of the solute. The former are κ_T , the isothermal compressibility of the solvent mixture, which is of secondary importance, and the second derivative of the Gibbs energy of mixing or of the excess Gibbs energy of mixing with respect to the solvent composition, $(\partial^2 G_{12}^E / \partial x_1^2)_{T,P}$. This quantity is one major reason for the difficulty to apply the method, since it is hard to obtain it with good accuracy. The data required for the solute are its standard partial molar volume in the solvent mixtures, \bar{V}_X° , and the derivative of its Gibbs energy of transfer with respect to the composition, $(\partial \Delta_{tr}G(W \rightarrow S_1 + S_2) / \partial x_1)_{T,P}$. This quantity, obtained from

the solubility data, is again of low accuracy and may limit the applicability of the method. If the required thermodynamic data are available, then the preferential solvation is obtainable from:

$$\delta x_{1X} = x_1 x_2 (G_{1X} - G_{2X}) / [x_1 G_{1X} + x_2 G_{2X} + (4\pi/3)R^3] \quad (14)$$

This quantity is seen to be directly proportional to the difference in the Kirkwood-Buff integrals and to depend inversely on the correlation distance R . The larger this quantity is, i.e., the more concentric solvent shells around a solute particle are taken, the smaller is the effect of the solute on this enlarged environment and the smaller is δx_{1X} . For the first shell R may be taken as the sum of the solute and mean solvent radii. This is seen in Fig. 3, where x_{large} increases from 0.33 in the first solvation shell to $x_{\text{large}} = 0.43$ when the first two shells are taken together, so that the preference for the smaller solvent decreases from 0.33 to 0.24. As farther solvation shells are taken into account, this preference diminishes still further. The two-dimensional representation already shows what becomes even more pronounced in three dimensions that the packing of the solvents in the solvation shells permits some penetration of outer molecules into inner shells, so that R is no longer simply related to the radii of the solvents.

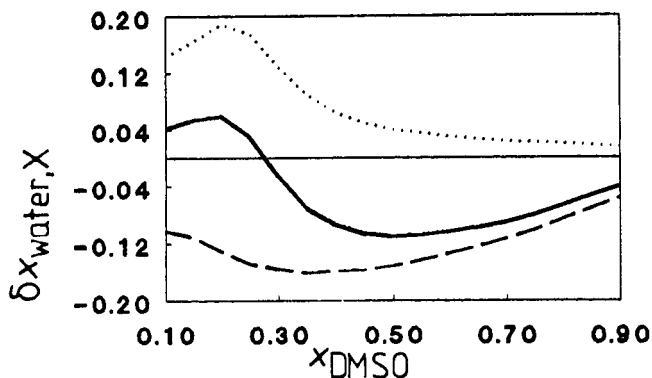


Fig. 4. The preferential solvation, $\delta x_{\text{water},X}$ of AgI and its ions in aqueous DMSO. I^- , ——— AgI, - - - Ag $^+$.

Application of the IKBI method to the solubility of AgI in aqueous DMSO is shown in Fig. 4. In fact, rather than use the solubility data directly, independent $\Delta_{\text{tr}}G^\circ$ data for Ag^+ and I^- , based on an extrathermodynamic assumption, were employed (ref. 11-13). However, their combination to give the value for the complete electrolyte makes the choice of the assumption immaterial. The continuous curve in Fig. 4 pertains to the mean excess or deficiency of water in the first solvation shell of the ions of AgI. However, if the individual ions are considered, it is seen that I^- prefers solvation by water, having positive $\delta x_{\text{water},I}$ values, and Ag^+ avoids water in favor of DMSO, having negative $\delta x_{\text{water},\text{Ag}}$ values. Up to a mole fraction of DMSO of 0.28, the complete electrolyte also prefers water, the effect of the iodide ion predominating, but at higher DMSO contents it is the solvation of the silver ions that predominates, and DMSO is preferred.

A prerequisite for the application of the IKBI method, in addition to the availability of very accurate $\Delta_{\text{mix}}G^\circ$ data, is the availability of very accurate $\Delta_{\text{tr}}G^\circ$ data for the solute of interest. The standard condition places the additional constraint of having adequate theoretical expressions to correct from the actual concentration in the saturated solution to infinite dilution. This is possible for very sparingly soluble solutes, if the solubility of the solute is the quantity that is being measured. Then, of course, the effects of impurities becomes more pronounced, if they preferentially solvate the solute or its ions, if it is an electrolyte. To explore the effect of such impurities, some experiments were made with very carefully dried potassium chloride in equimolar mixtures of aprotic solvents at 298.15 K once in the strict absence of water and once in the presence of 0.6 mole % of water. The results (ref. 8 and unpublished results) are shown in Table 1.

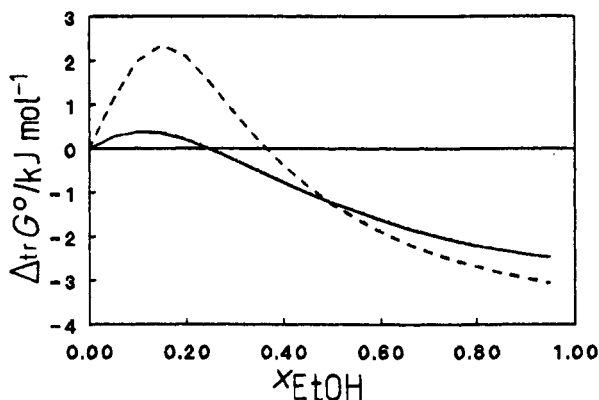
Table 1. Solubilities of KCl, in g/100 g solvent in equimolar mixed aprotic solvents at 298.15 K.

Solvents	MeCN + DMSO	DMSO + DMF	DMF + MeCN
No water	0.053	0.066	0.0098
0.6% water	0.078	0.070	0.0124

Table 1 shows that in the systems involving acetonitrile, where the preferential solvation of the cations by DMSO or DMF prevails, the effect of the presence of 1:170 of the protic solvent water increases the solubility appreciably, due to the preferred solvation of the chloride anion by the water. In the DMSO + DMF system, where no pronounced preferred solvation takes place (see the straight lines in the middle panel of Fig. 1), the effect of added water is smaller but still measurable.

The behavior of non-electrolyte solutes, as regards their solubility and solvation in mixed solvents, is also of interest. As an example, consider the solubility of carbon dioxide in mixtures of S_1 = water and S_2 = ethanol (ref. 14). The results are similar to those for argon in this mixed solvent (ref. 15), so that no specific interaction of the solute with the solvents needs to be taken into account in the present case. The solubility data (Ostwald coefficients), converted into $\Delta_{tr}G^\circ(S_1 \rightarrow S_1 + S_2)$, are shown in Fig. 5 for two temperatures, 288.15 and 308.15 K. A large temperature effect is noted, and both $\Delta_{tr}H^\circ$ and $T \Delta_{tr}S^\circ$ are an order of magnitude (in absolute values) larger than $\Delta_{tr}G^\circ$.

Fig. 5. The values of $\Delta_{tr}G^\circ/\text{kJ mol}^{-1}$ for the transfer of CO_2 from water to water + ethanol at 288.15 K (—) and at 308.15 K (---) (ref. 14).



The very asymmetric manner of $\Delta_{tr}G^\circ$ in this case indicates the breakdown of the assumptions that underlie the QLQC method, so that this approach cannot be used for the interpretation of the results. Neither can (ref. 14) the theory of Pierotti (ref. 16), involving terms in cavity formation in the solvent and dipole-induced dipole interactions but not hydrogen bonding. It

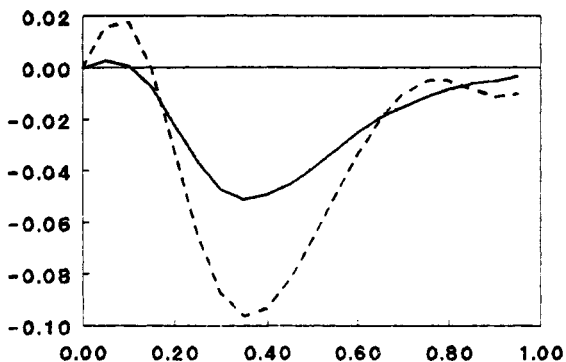
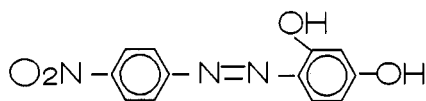


Fig. 6 The values of $\delta x(\text{H}_2\text{O}, \text{CO}_2)$ for solvation of CO_2 in water + ethanol at 288.15 K (—) and at 308.15 K (---).

is noteworthy that at low x_{EtOH} the solubility of CO_2 is lower than in water ($\Delta_{tr}G^\circ$ goes to a positive maximum) but increases beyond that value at higher x_{EtOH} . Application of the IKBI method to the data shows that CO_2 is preferentially solvated by ethanol in these mixtures (i.e., $\delta x(\text{H}_2\text{O}, \text{CO}_2)$ is negative) over almost the entire composition range, and the more so, the higher the temperature as is seen Fig. 6.

The solubility of a solid organic, non-electrolytic solute in a mixture of two solvents is illustrated by the solubility of 4-[(4-nitrophenyl-azo)]-1,3-benzenediol (**1**, the colorimetric reagent for magnesium, Magneson I) in mixtures of water and N-methylformamide (ref. 17).



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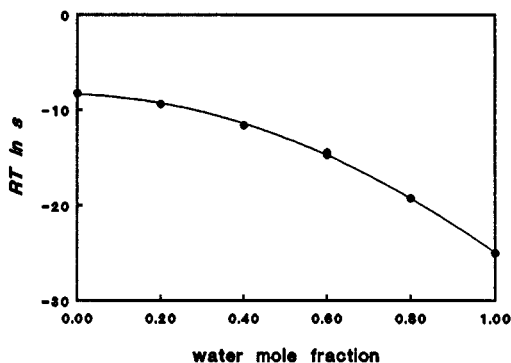


Fig. 7. The solubility of Magneson (**1**) in mixtures of water and N-methylformamide at 298.15 K (s in mol dm⁻³).

The standard molar Gibbs energy of solution is approximated sufficiently well by

$$\Delta_{\text{soln}}G^{\circ} = -RT [\ln (s/\text{mol dm}^{-3}) + \ln (V/\text{dm}^3 \text{ mol}^{-1})] \quad (15)$$

(see eq. (1)), where V is the mean molar volume of the solvent: $V = x_1 (M_1/\rho_1) + x_2 (M_2/\rho_2)$, M and ρ being the molar mass and the density of the indicated solvent, subscript 1 for water, 2 for N-methylformamide, the excess volume on mixing being ignored.

Application of the QLQC method to this case requires in addition to the standard molar Gibbs energies of transfer also the molar excess Gibbs energies of mixing of N-methylformamide and water (ref. 18). Eq. (6) to (12) then yield the results shown in Fig. 8 and 9. The former presents the $\Delta_{\text{tr}}G^{\circ} = \Delta_{\text{soln}}G^{\circ}(X_{\text{H}_2\text{O}}) - \Delta_{\text{soln}}G^{\circ}(\text{HC(O)NHCH}_3)$ data from the experiments and from the QLQC calculations with three assumed values of the lattice parameter Z : 3, 4, and 5. The value $Z = 4$ is seen to fit the data best, but the uncertainty is ± 1 .

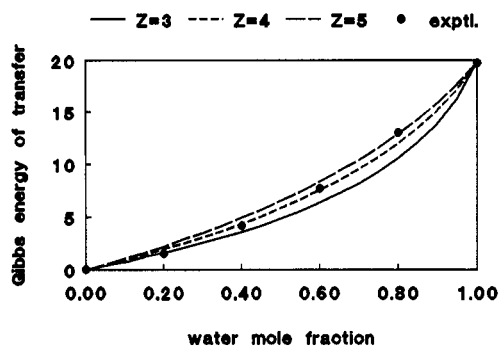


Fig. 8. $\Delta_{\text{tr}}G^{\circ}/\text{kJ mol}^{-1}$ for transfer of Magneson from N-methylformamide to its mixture with water at 298 K.

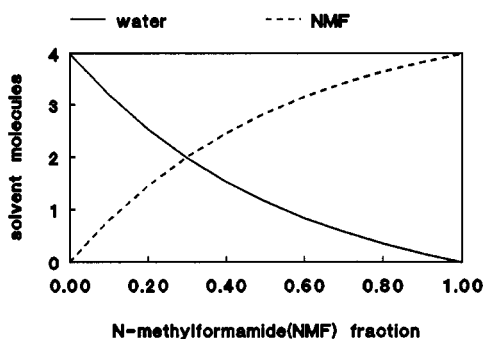


Fig. 9. The number of N-methylformamide and water molecules around a Magneson one (assuming $Z = 4$).

Fig. 9 shows the number of solvent molecules of the two kinds in the first solvation sphere around the solute. It is seen that N-methylformamide is preferred over water near the Magneson solute. The reasons for the preference may be sought in the higher dipole moment of the former, $\mu = 3.86$ D, compared with the latter, $\mu = 1.82$ D ($1 \text{ D} = 3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$) and the expected large dipole-dipole and dipole-induced dipole interactions between the solvents and the particular solvent studied. Such interactions

may, in this case, be more important than hydrogen bonding interactions between the hydroxyl groups of the solute and the basic oxygen atom in each solvent. That such interactions with the components of solvent do take place is indicated by the color changes from red to yellow that occur when the composition of the solvent is changed, Magneson thus acting as a solvatochromic indicator.

CONCLUSIONS

The foregoing illustrates the assertion that solubility measurements of any kind of solute in a mixture of solvents discloses significant information concerning the preferential interactions of the solute with the components of this mixture. This generalization is illustrated by several concrete cases: the solubilities of salts and of non-electrolytes in binary solvent mixtures. Salt solubilities include those of KF, KCl, and KBr in binary mixtures of aprotic solvents: MeCN, DMF, and DMSO and of AgI in aqueous DMSO. Non-electrolyte solubilities include those of CO₂ in aqueous ethanol and of Magneson I in aqueous NMF. Once the precautions have been taken to obtain standard Gibbs energies of solution, $\Delta_{\text{soln}}G^\circ$, readily converted to standard Gibbs energies of transfer, $\Delta_{\text{tr}}G^\circ$, these can be evaluated in terms of the QLQC or the IKBI methods, to yield the local solvent composition, x_1^l . The difference $\delta x_1 = x_1^l - x_1$ is the preferential solvation parameter. The QLQC method also provides an estimate of the number of solvent molecules near the solute, $m_1 = Z \cdot x_1^l$, where the lattice parameter Z is obtained from fitting the $\Delta_{\text{tr}}G^\circ = f(x_1)$ curve. The IKBI method also provides estimates of the rate of decline of the preferential composition of the solvent with the distance from the solute.

Since the solubilities in neat solvents can be described by certain properties of the solutes and the solvents (eq. 5), the QLQC method could, in principle, permit the approximate prediction of the solubility in a binary solvent mixture. However, before this goal is achieved, it is, perhaps, more appropriate to try to describe this solubility in terms of the properties of the solvent mixture itself. The relevant properties (cohesive energy density, polarity/polarizability, hydrogen bond acceptance and donation abilities) of binary solvents are now in the process of being measured in the author's laboratory (ref. 17).

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