

Preferential solvation in two- and in three-component systems

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Abstract - The concepts of local compositions around a solute and preferential solvation of a solute are defined in terms of the Kirkwood-Buff integrals. The difference between the local and the bulk composition is a measure of the preferential solvation of a solute with respect to the various components of the solvent.

A statistical mechanical theory is developed that leads to simple relationships between local compositions and experimentally measurable quantities. These are applied to both two- and three-component systems.

INTRODUCTION

The problem of preferential solvation (PS) arises almost in any physical chemical study of solutes in mixed solvents. The study could be thermodynamic, spectroscopic, or kinetic (ref. 1). However, in order to understand how the solvent composition affects the solute behavior, we need to know the composition that the solute "sees," i.e., the composition in its immediate vicinity. This is, in general, different from the bulk composition of the mixed solvent.

The simplest approach to answer the question of how to measure PS is to follow some property of a solute in a mixed solvent. For example, if δ_A is the NMR chemical shift (or other spectroscopic quantity) characteristic of the solute \underline{S} in pure solvent A and δ_B the corresponding quantity for pure solvent B, then one might relate the observed chemical shift of \underline{S} in a mixture of A and B, $\delta_{A,B}$, to δ_A and δ_B by the equation

$$\delta_{A,B} = x_A(\text{local}) \delta_A + [1-x_A(\text{local})] \delta_B \quad [1.1]$$

where $x_A(\text{local})$ defined in Eq. 1.1. is a measure of the local composition of the solution near the solute. This may, or may not, be different from the bulk composition x_A of the solvent mixture, x_A being the mole fraction of the component A in the mixture.

Although Eq. 1.1. can serve as an operational definition of $x_A(\text{local})$, it does not really tell us what is the local composition in the vicinity of the solute \underline{S} . We should not be surprised to find that different properties of \underline{S} , used in Eq. 1.1., will result in different values of $x_A(\text{local})$. The reason is that there is no theoretical support to the assumption that $\delta_{A,B}$ is an average of δ_A and δ_B as implied in Eq. 1.1. Therefore, the approximation involved in using Eq. 1.1 will, in general, be different for different properties of \underline{S} in mixtures of A and B.

What we need is an unambiguous definition, and a method of measuring, of the local composition of the solvent, which is independent of a specific property of \underline{S} .

Perhaps the first thermodynamic treatment of the problem of PS was presented by Grunwald et al. (ref. 2), who were interested in the solvation of ions in mixtures of water and dioxane. This approach was further developed by Covington and Newman (ref. 3). However, the ambiguity in the very definition of the local composition has not been removed.

In this paper an attempt is made to define the concept of PS unambiguously and independently of any modelistic assumptions on the system. The definition of the local composition is presented in the next section. This is then applied to three and two-component systems. Some illustrative results are also presented.

THE FORMULATION OF THE PROBLEM OF PS IN THREE-COMPONENT SYSTEMS

Consider a mixture of two components, N_A molecules of A and N_B molecules of B, at some temperature T and pressure P . In such a system the composition measured by the mole fraction $x_A = N_A/(N_A + N_B)$ will be the same at any point R_0 within the system.

We shall refer to x_A as the bulk composition of the system. Next consider a very dilute solution of a solute \underline{S} in our two-component solvent mixture.

Qualitatively, the question we would like to ask is quite simple. What is the composition of the liquid in the immediate vicinity around the solute \underline{S} ? Clearly, since the affinity of \underline{S} toward A might be different from its affinity towards B, we should expect that the composition near the solute \underline{S} will differ from the bulk composition x_A .

The main question is how to define the local region in the vicinity of \underline{S} in which the composition is expected to be affected by the presence of \underline{S} .

Consider first a simple spherical solute, say argon, in a two-component solvent, say water and ethanol. Let $dR' = dx'dy'dz'$ be an element of volume at a distance R' from the center of \underline{S} . The average number densities of A and B in this element of volume will be

$$\rho_A(R') = \rho_A(\text{bulk})g_{AS}(R') \quad [2.1]$$

$$\rho_B(R') = \rho_B(\text{bulk})g_{BS}(R') \quad [2.2]$$

where $\rho_A(\text{bulk})$ and $\rho_B(\text{bulk})$ are the bulk densities of A and B, respectively, and $g_{AS}(R')$ and $g_{BS}(R')$ are the radial distribution functions for the pair of species A,S and B,S, respectively.

Clearly, if we had the full information on these two radial distribution functions, we could have defined the local composition at any distance R' from the center of \underline{S} by

$$x_A(R') = \frac{\rho_A(R')}{\rho_A(R') + \rho_B(R')} \quad [2.3]$$

Furthermore, this local composition will be different at different distances, say R' and R'' (see Fig. 1).

We know from the general theory of liquids that the radial distribution functions normally will tend to unity at distances of the order of magnitude of a few molecular diameters. Thus, at these distances from the center of \underline{S} , all local densities will be identical to the bulk densities.

At short distances, however, large deviation from the bulk densities are expected. A typical form of the radial distribution function for a one-component simple liquid is depicted in Fig. 2.

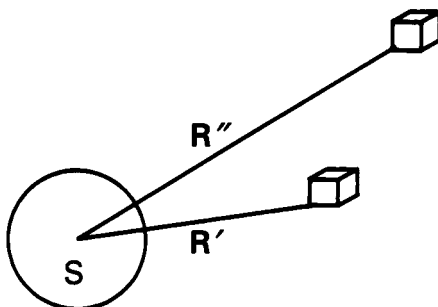


Fig. 1. The average local density of the solvent around a spherical solute \underline{S} depends only on the distance R' and R'' from the center of \underline{S} .

Unfortunately, there is no experimental data on the separate radial distribution functions in two or more component systems. Even if we had such information, it would have been too detailed to be useful for practical purposes. Instead, we are interested in the overall composition in the local neighborhood of the solute, which roughly coincides with the region in which $g(R)$ is significantly different from unity (Fig. 2). Fortunately, this information may be obtained from thermodynamic quantities. The relevant quantities are the so-called Kirkwood-Buff integrals (ref. 4,5). These are defined as follows

$$G_{AB} = \int_0^{\infty} [g_{AB}(R) - 1] 4\pi R^2 dR \quad [2.4]$$

where $g_{AB}(R)$ is the radial distribution function for the pair of species A and B. The integration is extended from zero to infinity. However, in most practical cases $g_{AB}(R)$ differs from unity only at distances of the order of magnitude of a few molecular diameters. Therefore, practically the main contribution to the integral comes from the region in which g_{AB} differs considerably from unity. This region can be conveniently referred to as the correlation region around A (or B, depending on the vicinity of which molecule we are interested in).

The significance of the quantity G_{AB} with respect to the question of preferential solvation is the following. $\rho_A g_{AS}(R) 4\pi R^2 dR$ is the average number of A particles in the element of volume $4\pi R^2 dR$ at the distance R from the center of the solute \underline{S} . On the other hand, $\rho_A 4\pi R^2 dR$ is the average number of A molecules in the same element of volume but taken relative to an arbitrary center in the liquid. Therefore, $\rho_A [g_{AS}(R) - 1] 4\pi R^2 dR$ measures the excess, or deficiency, of A molecules in the spherical shell $4\pi R^2 dR$ around \underline{S} relative to the same spherical shell but an arbitrary location in the liquid. The quantity $\rho_A G_{AS}$, according to the definition [2.4], is simply the overall excess or deficiency of A molecules in the entire volume around \underline{S} .

In the next section we shall use the Kirkwood-Buff theory of solution (ref. 4,5) to relate G_{AB} to thermodynamic quantities. It should be noted that these relationships are derived in an open system (i.e., in the T,V, μ ensemble) where the number of particles in the system are not fixed. The normalization condition for G_{AB} is (ref. 4,5).

$$G_{AB} = \int_0^{\infty} [g_{AB}(R) - 1] 4\pi R^2 dR = V \frac{\overline{N_A N_B} - \overline{N_A} \overline{N_B}}{\overline{N_A} \overline{N_B}} - \frac{\delta_{AB}}{\overline{N_A}} \quad [2.5]$$

where δ_{AB} is the Kronecker delta function.

If we were in a closed system (i.e., T,V,N ensemble), then $\overline{N_A}$ and $\overline{N_B}$ are fixed quantities and $\overline{N_A N_B} = \overline{N_A} \overline{N_B}$; hence, the corresponding normalization condition is

$$\int_0^{\infty} [g_{AB}(R) - 1] 4\pi R^2 dR = -\delta_{AB} \quad [2.6]$$

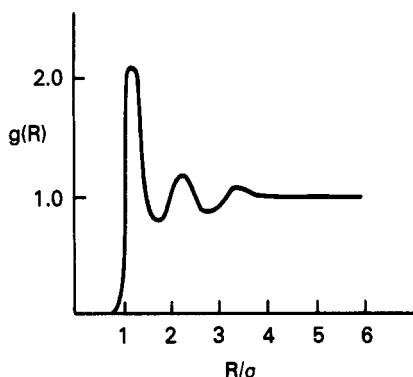


Fig. 2. Schematic form of the pair correlation function $g(R)$ for a pure liquid of simple spherical particles. Note that $g(R)$ is practically unity at distances of a few molecular diameters σ .

Thus, if $A=B$, the integral in [2.6] is -1 as it should be, since the total deficiency of A's around a fixed A is exactly the one particle that we have placed at the center. On the other hand, for $A \neq B$ the integral is zero. Placing of, say, one A at the center does not change the total number of particles in the entire system.

We can now exploit the fact that $g_{AB}(R)$ decays to unity beyond some distance $R \geq R_{AB}$, where R_{AB} may be referred to as the correlation distance for any pair of species in the system. We define the correlation volume as

$$V_{\text{cor}} = (4\pi/3)R_c^3 \quad [2.7]$$

Since all the pair correlation functions are practically equal to unity at $R \geq R_c$, we may write the average number of A particles in the correlation volume around S as

$$\begin{aligned} \bar{N}_{A,S}(R_c) &= \rho_A \int_0^{R_c} [g_{AB}(R) - 1] 4\pi R^2 dR = \\ &= \rho_A \int_0^{\infty} [g_{AS}(R) - 1] 4\pi R^2 dR + \rho_A \int_0^{R_c} 4\pi R^2 dR = \rho_A^G V_{\text{cor}} + \rho_A^V V_{\text{cor}} \end{aligned} \quad [2.8]$$

Eq. [2.8] simply means that the average number of A's in the correlation volume is the sum of the average number of A's in the same region, before placing S at its center, $\rho_A^V V_{\text{cor}}$ plus the change in the number of A's in the same region caused by placing S in the center of this region, $\rho_A^G V_{\text{cor}}$.

Using a similar definition for $\bar{N}_{B,S}(R_c)$

$$\bar{N}_{B,S}(R_c) = \rho_B^G V_{\text{cor}} + \rho_B^V V_{\text{cor}} \quad [2.9]$$

we can define the local composition in the correlation region around S as

$$\begin{aligned} x_{A,S}(\text{local}) &= \frac{\bar{N}_{A,S}(R_c)}{\bar{N}_{A,S}(R_c) + \bar{N}_{B,S}(R_c)} \\ &= \frac{x_A^G V_{\text{cor}} + x_A^V V_{\text{cor}}}{x_A^G V_{\text{cor}} + x_B^G V_{\text{cor}} + V_{\text{cor}}} \end{aligned} \quad [2.10]$$

where x_A is the bulk composition in the system.

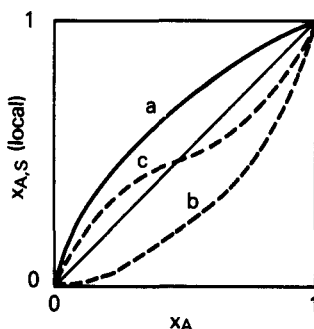


Fig. 3. Schematic dependence of the local composition $x_{A,S}(\text{local})$ as a function of the bulk composition x_A . The diagonal line corresponds to the case when there is no preferential solvation of S. Curves a and b correspond to positive and negative preferential solvation. In curve c the preferential solvation changes sign as x_A changes.

The local composition $x_{A,S}(\text{local})$ can now be compared with x_A to determine the preferential solvation of S. If $x_{A,S}(\text{local}) > x_A$, we may say that S is preferentially solvated by A. Thus, we define the preferential solvation of S with respect to A simply by the difference

$$\delta_{A,S} = x_{A,S}(\text{local}) - x_A = \frac{x_A x_B (G_{AS} - G_{BS})}{x_A G_{AS} + x_B G_{BS} + V_{\text{cor}}} \quad [2.11]$$

Clearly, the sign and extent of preferential solvation might depend on the composition of the solvent. Figure 3 depicts a few possible cases where there are positive, negative, or mixed signs of preferential solvation according to whether $x_{A,S}(\text{local})$ is above or below the diagonal line.

Note that in all cases

$$\delta_{A,S} \rightarrow 0 \begin{cases} \text{if } x_A \rightarrow 0 \\ \text{or } x_A \rightarrow 1 \\ \text{or } G_{AS} - G_{BS} \rightarrow 0 \end{cases} \quad [2.12]$$

The quantity which is left ambiguous in [2.11] is V_{cor} . Clearly, if we take a very large correlation volume, we obtain

$$\delta_{A,S} \rightarrow 0 \text{ for } V_{\text{cor}} \rightarrow \infty$$

On the other hand for too small V_{cor} , the approximate equality of $g_{AS}(R) \approx 1$ presumed in [2.8] (for $R > R_c$) will not hold. In practice, we can choose, for each specific system, a reasonable R_c (and hence V_{cor}) according to the behavior of the functions g_{ij} at large distances.

Theoretically, however, we can get rid of V_{cor} by taking the first order term in the expansion of $\delta_{A,S}$ in [2.11] in power series about $\epsilon = V_{\text{cor}}^{-1}$, thus

$$\delta_{A,S} = 0 + \epsilon x_A x_B (G_{AS} - G_{BS}) + \dots \quad [2.13]$$

We define the limiting linear preferential solvation as

$$\delta_{A,S}^0 = \left. \frac{\delta \delta_{A,S}}{\delta \epsilon} \right|_{\epsilon=0} = x_A x_B (G_{AS} - G_{BS}) \quad [2.14]$$

Since $x_A x_B > 0$, the sign of $\delta_{A,S}^0$ is determined by the sign of $G_{AS} - G_{BS}$, and this is, of course, independent of the correlation volume.

Thus, we have defined in [2.14] a quantity that unambiguously measures the preferential solvation of S with respect to a two-component solvent. As noted earlier (5,6), G_{AS} measures the affinity of S toward A. Thus, the difference $G_{AS} - G_{BS}$ measures the difference between the affinities of S toward A and B. We next turn to the question of measurability of the quantity $G_{AS} - G_{BS}$.

RELATIONS BETWEEN PREFERENTIAL SOLVATION AND MEASURABLE QUANTITIES IN THREE- AND TWO-COMPONENT SYSTEMS

In this section we shall present the relationships between preferential solvation and measurable quantities (ref. 7-10). The detailed derivations may be found in previous articles.

For a three-component system in which S is very dilute in a mixture of A and B the result is (ref. 9).

$$\lim_{\rho_S \rightarrow 0} \left(\frac{\delta \Delta G_S^*}{\delta x_A} \right)_{P,T} = \frac{kT(\rho_A + \rho_B)^2}{\eta} (G_{BS} - G_{AS}) \quad [3.1]$$

where $\eta = \rho_A + \rho_B + \rho_A \rho_B (G_{AA} + G_{BB} - 2G_{AB})$ [3.2]

where ΔG_S^* is the solvation free energy of S in our system (ref. 6).

Thus, by measuring the slope of the solvation free energy as a function of x_A , we can extract the difference $G_{AS} - G_{BS}$. As we have seen in section 2, this is a measure of the limiting preferential solvation of S with respect to A. Next we turn to a two-component system of A and B.

Within the realm of the traditional concept of solvation thermodynamics, only very dilute solutions could be treated. Therefore the concept of PS could have been dealt with only for a three- (or more-) component system; a solute and a two-component solvent.

However, the question of PS can also be asked in a two-component system, say of A and B. At any composition x_A , we may focus on one A molecule and ask what is the PS of A with respect to the two components, A and B in its immediate vicinity. Likewise, we may focus on one B-molecule and ask the same, but independent, question of the PS of B with respect to the two components of A and B.

Consider an A molecule, placed at the center of a spherical volume of radius R_c . For an arbitrary radius R_c , the average number of A and B molecules in this sphere is given by

$$\bar{N}_{A,A} = \rho_A \int_0^{R_c} g_{B,A}(R) 4\pi R^2 dR \quad [3.3]$$

$$\bar{N}_{B,A} = \rho_B \int_0^{R_c} g_{B,A}(R) 4\pi R^2 dR \quad [3.4]$$

where ρ_A and ρ_B are the number densities of A and B, respectively, and $g_{\alpha\beta}$ is the angular averaged pair correlation function for the pair of species α and β . In the following treatment we focus on a single A molecule to which we refer to as an A-solvaton (ref. 6). A similar treatment applies to a B-solvaton.

For any radius R_c , we define the local mole fraction of A-molecules around an A-solvaton by

$$x_{A,A}(R_c) = \bar{N}_{A,A}(R_c) / [\bar{N}_{A,A}(R_c) + \bar{N}_{B,A}(R_c)] \quad [3.5]$$

As in the three-component case we define the PS of an A-solvaton with respect to A-molecules simply by the deviation of the local from the bulk composition, i.e.,

$$\delta_{A,A} = x_{A,A}(R_c) - x_A \quad [3.6]$$

Using the same arguments as in section 2 we define

$$\delta_{A,A} = \frac{\bar{N}_{A,A}}{\bar{N}_{A,A} + \bar{N}_{B,A}} - x_A = \frac{x_A x_B (G_{AA} - G_{BA})}{x_A G_{AA} + x_B G_{AB} + V_{cor}} \quad [3.7]$$

similarly for the PS of B in the same system we have

$$\delta_{A,B} = \frac{\bar{N}_{A,B}}{\bar{N}_{A,B} + \bar{N}_{BB}} - x_A = \frac{x_A x_B (G_{AB} - G_{BB})}{x_A G_{AB} + x_B G_{BB} + V_{cor}} \quad [3.8]$$

Note that $G_{AB} = G_{BA}$, and that $\delta_{A,A}$ and $\delta_{A,B}$ are in general independent quantities but $\delta_{A,A} = -\delta_{B,A}$ and $\delta_{B,B} = -\delta_{A,B}$ which follows from the definitions [3.7] and [3.8].

Since all the $G_{\alpha\beta}$ are computable from thermodynamic quantities, using the inversion of the Kirkwood-Buff theory of solution (ref. 8), one can compute $\delta_{A,A}$ and $\delta_{A,B}$ for any choice of V_c .

In particular the linear coefficient of the PS are defined by

$$\delta_{A,A}^0 = x_A x_A (G_{AA} - G_{AB}) \quad [3.9]$$

$$\delta_{A,B}^0 = x_A x_A (G_{AB} - G_{BB}) \quad [3.10]$$

Thus, besides the product $x_A x_B$ the difference $G_{AA} - G_{AB}$ characterizes the linear coefficient of PS of A, and likewise $G_{AB} - G_{BB}$ characterizes the linear coefficient of the PS of B.

SOME REPRESENTATIVE RESULTS

In the following we have used as our main source of data, tables of G_{ij} that were computed by Matteoli and Lepori (ref. 11,12). These tables were obtained by the inversion procedure of the Kirkwood-Buff theory (ref. 8), using experimental data for mixtures of water and an organic liquid, and similar mixtures of carbon tetrachloride with the same organic liquids.

In order to gain some feeling for the order of magnitude of the correlation distance, we took the values of the effective molecular diameters as used in the scaled particle theory (ref. 13). The following values of the diameters were used in our calculations:

water - 2.8\AA , methanol - 3.3\AA , ethanol - 4.2\AA , propanol - 4.6\AA , n-butanol - 5.1\AA . We also define the distance of closest approach between two different molecules as

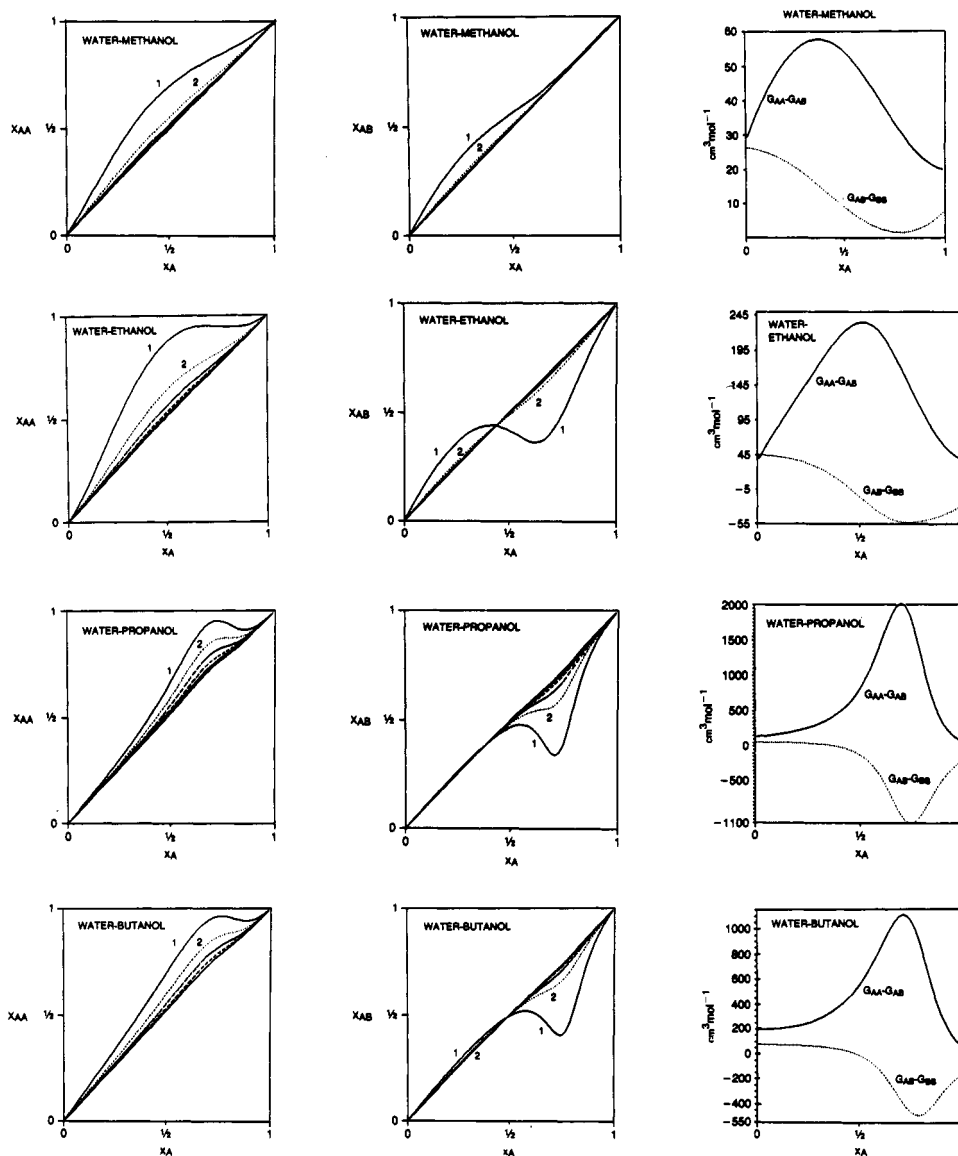


Fig. 4. Preferential solvation in four systems of water (component A) and an organic liquid (component B). [All at 25°C and atmospheric pressure]. For each system (as indicated in the figures) we present the local mole fraction of A around B, the linear coefficients in the preferential solvation of both A and B. The various curves of $x_{A,A}$ and $x_{A,B}$ correspond to different values of n , defined in equation [3.12]. The larger the value of n the closer the corresponding curve to the diagonal line.

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad [3.11]$$

where σ_{AA} and σ_{BB} are the effective molecular diameters of A and B, respectively. With the above definition of σ_{AB} we define a series of correlation distances.

$$R_C = \sigma_{AB}(n + 1)/2 \quad [3.12]$$

Thus, $n = 1$ corresponds roughly to the first coordination sphere. We used values $n = 2, 3, 4, 5$ to compute $x_{A,A}(R_C)$. These were plotted in Figure 4 as a function of the bulk mole fraction of water, x_A in the various mixtures.

In all cases we found that for $n = 6$ the relative deviation $(x_{A,A}(R_C) - x_A)/x_A$ becomes less than 0.01, which we consider to be an effective limit of the correlation distance. In other words, for $R_C > 6\sigma_{AB}$ the local composition approaches the bulk composition.

For each of the systems reported in Figure 4 we have also calculated the linear coefficient of the PS of both A and B.

The case of water-methanol is outstanding in the sense that the PS of both water (component A) and of methanol (component B) are positive in the entire range of compositions. This means that at any composition, water molecules are preferred by both water and by methanol as solvaton. The absolute magnitude is clearly larger for the PS of water around water as compared with water around methanol.

In the case of ethanol we observe a still positive PS of water around water (this is actually the same behavior for all the systems studied in this report). However, the PS of water around ethanol changes sign as the composition becomes more and more rich in water.

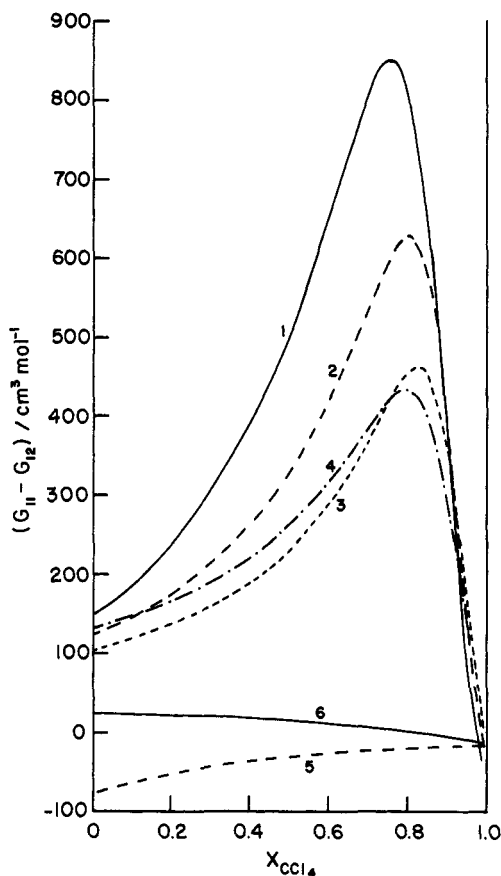


Fig. 5. Values of $G_{11} - G_{12}$ for CCl_4 (component 1) and an organic liquid (compound 2). The curves correspond to: 1 - methanol; 2 - ethanol; 3 - n-propanol; 4 - n-butanol; 5 - THF; 6 - p-dioxane. All curves are for 25 °C and atmospheric pressure.

This is not unexpected. Since $\delta_{A,B}^0 = -\delta_{B,B}^0$ it follows that the PS of ethanol with respect to ethanol becomes positive, in the water-rich region. This trend becomes even more pronounced for the cases of propanol and n-butanol.

In Figures 5 and 6 we report similar data of $G_{11} - G_{12}$ (1 being CCl_4 and 2 the second organic liquid as indicated in the captions) and of $G_{12} - G_{22}$. In all of the CCl_4 -alcohol curves we observe a maximum of the PS of CCl_4 around CCl_4 in the region of $0.7 < X_{\text{CCl}_4} < 0.9$ and a minimum of the PS of CCl_4 around the alcohol. It should be noted that the values of $G_{12} - G_{22}$ are almost an order of magnitude larger than the corresponding values of $G_{11} - G_{12}$. In contrast, the values of both $G_{12} - G_{22}$ and $G_{11} - G_{12}$ are nearly zero for the CCl_4 -THF and CCl_4 -dioxane system. A small value of both $G_{12} - G_{22}$ and $G_{11} - G_{12}$ in the entire range of concentration is indicative of a symmetrical ideal behavior of the mixture, i.e. from

$$G_{11} - G_{12} \approx G_{12} - G_{22} \sim 0$$

it follows

$$G_{11} + G_{22} - 2G_{12} \sim 0$$

i.e., the systems CCl_4 -THF and CCl_4 -dioxane behave very nearly as symmetrical ideal solutions.

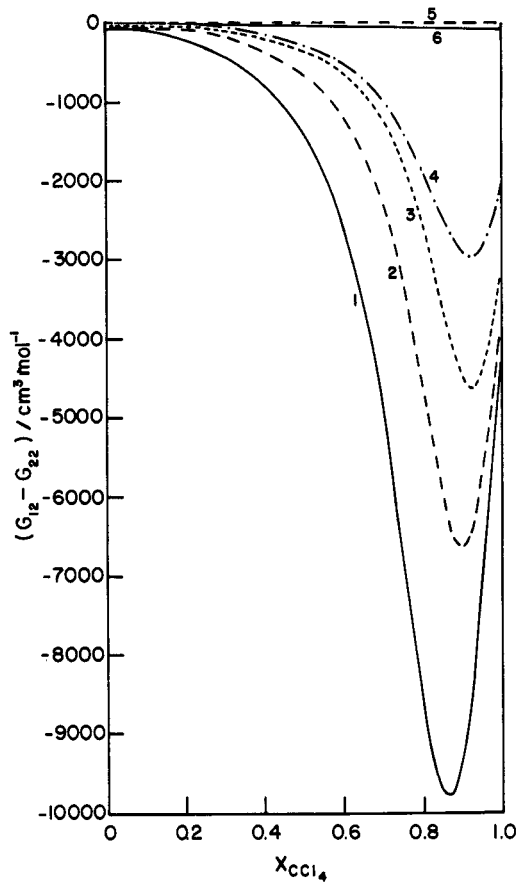


Fig. 6. Values of $G_{12} - G_{22}$ for the same systems as in Figure 5.

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