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Invited Review

Preferential Solvation in Mixed Solvents X. Completely Miscible Aqueous Co-Solvent Binary Mixtures at 298.15 K

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Summary. The *Kirkwood-Buff* integrals for 18 completely miscible aqueous co-solvent binary mixtures have been recalculated from thermodynamic data, and the volume-corrected preferential solvation parameters derived from them are presented. Also presented are these latter quantities for 15 additional such mixtures, for which the volume correction has not been applied previously. The self-interaction of the water, the mutual interaction of the water and the co-solvent, and the self-interaction of the co-solvent at infinite dilution derived from these integrals and parameters are then discussed. The systems studied include aqueous hydrogen peroxide, methanol, ethanol, 1- and 2-propanol, 2-methyl-2-propanol, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, ethane-1,2-diol, glycerol, 2-methoxyethanol (at 313 and 343 K), 2-ethoxyethanol, 2-butoxyethanol, 2-aminoethanol, N-methyl- and N,N-dimethyl-2-aminoethanol, tetrahydrofuran, 1,4-dioxane, acetone, formic, acetic, and propanoic acids, piperidine, pyridine, acetonitrile, formamide, N-methyl- and N,N-dimethylformamide, N-methylacetamide, N-methylpyrrolidin-2-one (at 303 K), hexamethyl phosphoric triamide, dimethylsulfoxide, and tetramethylenesulfone (at 303 K).

Keywords. Binary aqueous solvents; Preferential solvation; *Kirkwood-Buff* integrals.

Introduction

A fairly large number of preferential solvation studies employed the *Kirkwood-Buff* integrals, G_{ij},

$$G_{ij} = \int_0^\infty (g_{ij} - 1)4\pi r^2 \mathrm{d}r \tag{1}$$

where g_{ij} is the pair correlation function, denoting the probability of finding a molecule of species i in a volume element at the distance r from the center of a molecule of species j. The product $\rho_i \cdot G_{ij}$, where ρ_i is the number density of molecules of species i in the bulk of the mixture, represents the excess, if positive, or deficiency, if negative, of molecules of species i in the space around a given

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molecule of species j. An excess means attractive interactions between molecules of i and j, *i.e.* preferential mutual solvation, whereas a deficiency means that self-interactions of i-i and j-j are preferred to mutual interactions. These integrals have been obtained for binary aqueous solvent mixtures (where in the following subscript W signifies water and subscript S the co-solvent; i and j represent any component) mainly from thermodynamic data [1–20] (where Ref. [20] constitutes Part 9 of this series), but also from structural fluctuation measurements [21, 22], and have been employed to describe preferential solvation.

From thermodynamic data the integrals are calculated using the following expressions:

$$G_{\mathrm{WS}} = RT(\kappa_{\mathrm{T}} - V_{\mathrm{W}}V_{\mathrm{S}}/VD) \tag{2}$$

$$G_{\mathrm{WW}} = RT(\kappa_{\mathrm{T}} + (x_{\mathrm{S}}/(1-x_{\mathrm{S}}))(V_{\mathrm{S}}^2/VD)) - V/(1-x_{\mathrm{S}}) \tag{3}$$

$$G_{\mathrm{SS}} = RT(\kappa_{\mathrm{T}} + ((1-x_{\mathrm{S}})/x_{\mathrm{S}})(V_{\mathrm{W}}^2/VD)) - V/x_{\mathrm{S}} \tag{4}$$

where κ_{T} is the isothermal compressibility of the mixture, x_{s} is the mole fraction of the co-solvent, V_{W} and V_{S} are the partial molar volumes of the components in the mixture, and V is the molar volume of the mixture. The function D is (assuming water to be the by far more volatile component):

$$D = RT(1 + (1-x_{\mathrm{S}})(\partial \ln f_{\mathrm{W}}/\partial(1-x_{\mathrm{S}}))_{T,P}) \tag{5}$$

where $f_{\mathrm{W}} = p_{\mathrm{W}}/(1-x_{\mathrm{S}})p_{\mathrm{W}}^{\circ}$ is the activity coefficient of water and p_{W} and p_{W}° are its fugacities above the mixture and pure water, respectively. Partial pressures can be used instead of fugacities if they are sufficiently low; otherwise, they must be corrected for the vapor virial coefficients. A corresponding expression involving $x_{\mathrm{S}}(\partial \ln f_{\mathrm{S}}/\partial x_{\mathrm{S}})_{T,P}$ can, of course, be employed too. A less desirable alternative is the use of the second derivative of the excess *Gibbs* energy of the mixture, G^{E},

$$D = RT + x_{\mathrm{S}}(1-x_{\mathrm{S}})(\partial^2 G^{\mathrm{E}}/\partial x_{\mathrm{s}}^2)_{T,P} \tag{6}$$

because of the double derivation, so that very accurate G^{E} values have to be employed. On the other hand, the partial molar volumes can be readily calculated sufficiently accurate from those of the pure components and the excess molar volume of the mixtures, V^{E} (that is invariably negative for aqueous mixtures), and its first derivative with respect to the composition. Values of the isothermal compressibility of the mixtures, κ_{T}, as a function of the composition are not generally known. Instead, since their contribution to G_{ij} is quite small, linearly interpolated values between the κ_{T} of the pure components or values of the adiabatic compressibility of the mixtures, κ_{S}, available from measurements of ultrasound speed, can be employed. The latter values might be increased by 5 to 10% to approximate the κ_{T} values: $\kappa_{\mathrm{T}} = \kappa_{\mathrm{S}} + VT/\alpha_{\mathrm{P}}^2 C_{\mathrm{P}}$, where α_{P} and C_{P} are the isobaric expansivity and molar heat capacity.

In only a fraction of these studies preferential solvation parameters, δx_{ij}, or local compositions around molecules of the components, $x_{\mathrm{ij}}^{\mathrm{L}}$, have been calculated. In some of the latter investigations, only the limiting preferential solvation parameters, $\delta x_{\mathrm{ij}}^{\circ}$, were reported. In these quantities the first subscript index pertains to a component in the environment of a molecule of the component designated by the second index for both i = j and i ≠ j. The preferential solvation takes place in a concentric region around each molecule in the mixture, designated as the correlation volume, V_{cor} (the region where $g_{\mathrm{ij}} \neq 1$, see Eq. (1)).

The preferential solvation parameters and local compositions, δx_{ij} and $x^{\mathrm{L}}_{\mathrm{ij}}$, are related to the *Kirkwood-Buff* integrals and to V_{cor} as follows:

$$\delta x_{\mathrm{WW}} = x^{\mathrm{L}}_{\mathrm{WW}} - x_{\mathrm{W}} = x_{\mathrm{W}} x_{\mathrm{S}} (G_{\mathrm{WW}} - G_{\mathrm{SW}})/(x_{\mathrm{W}}\ G_{\mathrm{WW}} + x_{\mathrm{S}}\ G_{\mathrm{WS}} + V_{\mathrm{cor,W}}) \quad (7a)$$

$$\delta x_{\mathrm{WS}} = x^{\mathrm{L}}_{\mathrm{WS}} - x_{\mathrm{W}} = x_{\mathrm{W}} x_{\mathrm{S}} (G_{\mathrm{WS}} - G_{\mathrm{SS}})/(x_{\mathrm{W}}\ G_{\mathrm{WS}} + x_{\mathrm{S}}\ G_{\mathrm{SS}} + V_{\mathrm{cor,S}}) \quad (7b)$$

It should also be remembered that $\delta x_{\mathrm{SW}} = -\delta x_{\mathrm{WW}}$ and $\delta x_{\mathrm{SS}} = -\delta x_{\mathrm{WS}}$. Positive values of δx_{WS} denote favoured mutual preferential solvation of water and the co-solvent, concomitant with disfavoured self-interaction of the co-solvent molecules; positive values of δx_{WW} denote preferential self-interaction of the water molecules and are concomitant with disfavoured mutual interaction of water with the co-solvent molecules.

The correlation volume, V_{cor}, is calculated for consecutive solvation shells, taking into account partial penetration of molecules from farther shells into nearer ones as well as the preferential solvation in these shells. Hence, the calculation must be carried out iteratively [10, 11, 15, 17, 20].

$$\begin{aligned} V_{\mathrm{cor,W}}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} &= 2522.7 \cdot (-0.085m + (0.1363/2)V_{\mathrm{W}}^{1/3} \\ &\quad + 0.1363 \cdot (m - 0.5) \cdot (x^{\mathrm{L}}_{\mathrm{WW}} V_W + (1 - x^{\mathrm{L}}_{\mathrm{WW}})V_{\mathrm{S}})^{1/3})^3 \end{aligned} \quad (8a)$$

$$\begin{aligned} V_{\mathrm{cor,S}}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} &= 2522.7 \cdot (-0.085m + (0.1363/2)V_{\mathrm{S}}^{1/3} \\ &\quad + 0.1363 \cdot (m - 0.5) \cdot (x^{\mathrm{L}}_{\mathrm{WS}} V_W + (1 - x^{\mathrm{L}}_{\mathrm{WS}})V_{\mathrm{S}})^{1/3})^3 \end{aligned} \quad (8b)$$

The numerical coefficients arise from the relationship between the molar volume and the mean molecular diameter, d, of the solvent according to *Kim* [71]:

$$d/\mathrm{nm} = -0.085 + 0.1363 \cdot (V/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})^{1/3} \quad (8c)$$

m designates the sequential number of the shell to the limits of which V_{cor} is calculated. The larger the values of V_{cor} in the denominator of Eq. (7), the smaller are the δx_{ij} values, becoming indistinguishable from zero when sufficiently many solvation shells are included (large correlation volumes). The partial molar volumes in Eq. (8) can be replaced by those of the pure components without loss of accuracy.

A feature to be noted in the application of Eq. (7) is that even for ideal mixtures (where $G^{\mathrm{E}} = 0, V^{\mathrm{E}} = 0$, and $G_{\mathrm{ii}} + G_{\mathrm{jj}} = 2G_{\mathrm{ij}}$) the δx_{ij} are non-zero, as if preferential solvation existed in them. This arises from the differences of the molar volumes of the pure components, resulting in *Kirkwood-Buff* integral curves $G_{\mathrm{ii}}(x_{\mathrm{S}})$ and $G_{\mathrm{jj}}(x_{\mathrm{S}})$ that are parallel but shifted by $|V^{\circ}_{\mathrm{j}} - V^{\circ}_{\mathrm{i}}|$ from the $G_{\mathrm{ij}}(x_{\mathrm{S}})$ curve and satisfying $G_{\mathrm{ii}} + G_{\mathrm{jj}} - 2G_{\mathrm{ij}} = 0$. To overcome this, *Matteoli* [72] suggested the use of volume-corrected values, $\Delta G_{\mathrm{ij}} = G_{\mathrm{ij}} - G^{\mathrm{id}}_{\mathrm{ij}}$, where the ideal $G^{\mathrm{id}}_{\mathrm{ij}}$ are calculated from Eqs. (2)–(4) by setting $D = RT$ and $V^E = 0$. Then, volume corrected preferential solvation parameters $\delta x'_{\mathrm{ij}}$ are calculated from Eq. (7) using ΔG instead of G. Due to the differences in the volumes of the components, the actual values of the local mole fractions and the preferential solvation parameters still depend on G rather than on ΔG, but the interpretation in terms of intermolecular interactions should be done with regard to $\delta x'_{\mathrm{ij}}$. Values of the non-corrected δx_{ij} for ideal systems with various molar volumes of the co-solvent are shown in Fig. 1.

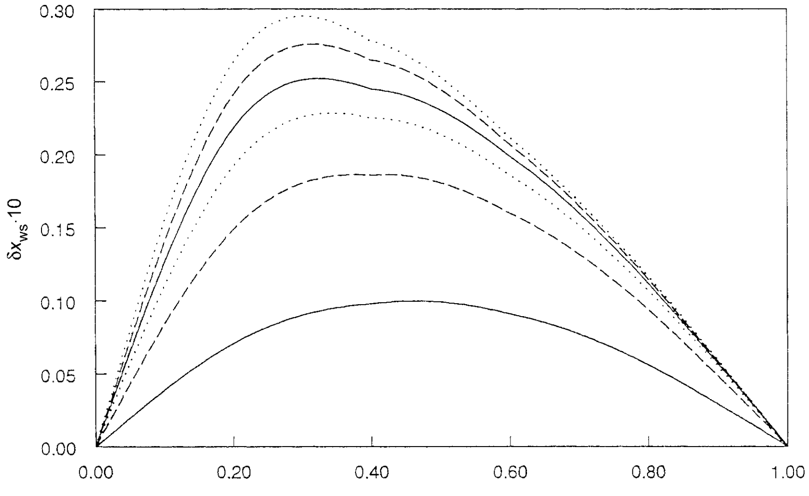

Fig. 1. Preferential solvation parameters, δx_{WS}, in ideal systems with $V_W^\circ = 18.07\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ (*i.e.* that for water) and increasing values of V_S°: 30, 50, 70, 90, 120, and $180\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ (from the bottom)

The list of completely water-miscible co-solvents of water for which the *Kirkwood-Buff* integrals of their aqueous mixtures have been reported is shown in Table 1. In the following, co-solvents are designated by the abbreviations listed in this table. Most of them have been studied at 298.15 K, but some at other temperatures (*e.g. MEA*, *DEA*, and *TEA* at 273.15 K and *TMS* at 303.15 K) or at several temperatures (*e.g.* MeOH and MeCN). A few co-solvents only partially miscible with water at 298.15 K have also been studied in this respect: 1-butanol [4], 2-butanol [4], 2-methyl-1-propanol [4], propylene carbonate [10], and triethylamine [10].

It is the purpose of this paper to present and discuss the $\delta x'_{ij}$ values of those binary aqueous solvent systems that have already been subjected to *Kirkwood-Buff* integral calculations for 298.15 K (Table 1), but for which even the non-corrected δx_{WS} preferential solvation parameters have not been reported over the entire composition range by taking into account the correlation volumes V_{cor}. These systems include aqueous mixtures of EtOH, *n*-PrOH, *t*-BuOH, *TFE*, *HF-i*-PrOH, MeOEtOH, EtOEtOH, BuOEtOH, *MEA*, Me_2NEtOH, *THF*, Dioxane, Me_2CO, *Pip*, *Py*, and *DMSO*. For the sake of completeness, N-methylethanolamine (MeNHEtOH) and N-methylpyrrolidin-2-one (N*MPy*), for which no *Kirkwood-Buff* integrals have been reported so far, are included. For those systems where δx_{ij} has been presented previously but not corrected for the volume effect, new $\delta x'_{ij}$ values have been calculated; these are also presented. As mentioned above, these parameters are a direct quantitative measure of how much (in terms of mole fractions) of the designated component i is accumulated near (if positive) or banished away from (if negative) the component j. Altogether, figures for 33 systems are shown. In a subsequent paper, other aqueous co-solvent mixtures of interest will be dealt with.

Table 1. Aqueous solvent mixtures for which *Kirkwood-Buff* integrals have been obtained at 298.15 K (except where noted otherwise in the text)

Co-solvent	Abbreviation	References	$G_{SS}^{\infty}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
Hydrogen peroxide	H_2O_2	8, 10	−53
Methanol	MeOH	2, 4, 13, 17, 18	−45
Ethanol	EtOH	1, 2, 4, 13, 18, 22	−50
1-Propanol	*n*-PrOH	4, 12, 13, 18	−46
2-Propanol	*i*-PrOH	10, 18	40 (?)
2-Methyl-2-propanol	*t*-BuOH	3, 4, 13, 18	−132
2,2,2-Trifluoroethanol	*TFE*	9	−61
1,1,1,3,3,3-Hexafluoro-2-propanol	*HF*-*i*-PrOH	9	−89
Ethane-1,2-diol	*EG*	12, 19	−98
Glycerol	*Gly*	20	−95
2-Methoxyethanol	MeOEtOH	12	−230
2-Ethoxyethanol	EtOEtOH	21	−107
2-Butoxyethanol	BuOEtOH	21	< −500 (?)
2-Aminoethanol	*MEA*	12, 14, 15	−116
Diethanolamine	*DEA*	14, 15	
Triethanolamine	*TEA*	14, 15	
N,N-Dimethyl-2-aminoethanol	Me_2NEtOH	4	−157
Tetrahydrofuran	*THF*	4, 6	−35
1,4-Dioxane	Dioxane	4	−127
Acetone	Me_2CO	4, 8	−76
Formic acid	HCOOH	10	−140
Acetic acid	MeCOOH	10	−8
Propanoic acid	EtCOOH	10	50
Ethane-1,2-diamine	*En*	12	
Piperidine	*Pip*	4	−26
Pyridine	*Py*	4	−146
Acetonitrile	MeCN	4, 7, 1	155
Formamide	*FA*	10	>600 (?)
N-Methylformamide	*NMF*	10	−129
N,N-Dimethylformamide	*DMF*	10, 14	−162
N-Methylacetamide	*NMA*	10, 19	−132
Hexamethylphosphoric triamide	*HMPT*	10	−370
Dimethylsulfoxide	*DMSO*	4, 7	−76
Tetramethylenesulfone	*TMS*	6, 10	5

Sources of Data

Aqueous EtOH

Activity coefficient expressions of both components are available from *Hansen* and *Miller* [23] for 298.15 K over the entire composition range in good agreement with earlier [24, 25] and later [26] data used by others who have calculated the *Kirkwood-Buff* integrals [1–4]. The partial molar volumes are available from the data of *Benson* and *Kiyohara* [27] and adiabatic compressibilities from *D'Arrigo* and *Paparelli* [28] and from *Omori* [29].

Aqueous n-PrOH

Activity coefficients of both components at 298.15 K are available from *Matteoli* and *Lepori* [30] in good agreement with earlier data of *Butler* [31], but leading to G^{E} values some 8% higher than those interpolated from *Westmeier*'s data [32] at 293.15 and 303.15 K that have not been used. However, the corresponding V^{E} data of *Westmeier* [32] have been employed to yield the partial molar volumes. The isothermal compressibility was calculated approximately from the compression data of *Moriyoshi* and *Uosaki* [33] as $\kappa_{\mathrm{T}} \approx \Delta V / V_{(P=0.1\,\mathrm{MPa})} \Delta P$.

Aqueous t-BuOH

The G^{E} values, interpolated for 298.15 K from *Westmeier*'s data [34] at 293.15 and 303.15 K, have not been used, since activity coefficient data for 298.15 K from *Brown* and *Ives* [35] were available that needed to be differentiated only once. However, *Westmeier*'s data [34] for V^{E}, likewise interpolated, were used to obtain the partial molar volumes. Adiabatic compressibilities were taken from *Sehgal et al.* [36].

Aqueous TFE

The G^{E} values of *Cooney* and *Morcom* [37] and the V^{E} values of *Rochester* and *Symonds* [38] at 298.15 K were used. The estimated [39] value of the isothermal compressibility of *TFE* was used to interpolate linearly the values for the aqueous mixtures.

Aqueous HF-i-PrOH

The G^{E} values of *Blandamer et al.* [9] and the the V^{E} values of *Rochester* and *Symonds* [38] for 298.15 K were used. No compressibility data were found, but in view of the similarity of the κ_{T} of *TFE* and EtOH, the value for 2-propanol was used for that of *HF-i*-PrOH with linear interpolation for the values of the aqueous mixtures.

Aqueous MeOEtOH

The activity coefficients of water at 343.15 and 363.15 K were available from *Chiavone-Filho et al.* [40] and were extrapolated to 313.15 K. Excess molar volumes, V^{E}, and adiabatic compressibility data at 283.15, 298.15, and 313.15 K were available from *Pagé et al.* [41] and were extrapolated to 343.15 K. Therefore, two sets of *Kirkwood-Buff* integrals had to be calculated (for 313.15 and 343.15 K) with the uncertainty of the temperature extrapolations kept in mind.

Aqueous EtOEtOH

Here again the activity coefficients of water at 343.15 and 363.15 *K* were available from *Chiavone-Filho et al.* [40], but in this case there were also H^{E} data at 298.15 and 303.15 K from *Tamura et al.* [42] that facilitated the extrapolation of G^{E} to

298.15 K. Data for V^E and κ_T at 298.15 K were available from the latter authors and of V^E also from *Douheret* and *Pal* [43] in reasonable agreement.

Aqueous BuOEtOH

There are older G^E data for 298.15 K and V^E data at 300.15 K from *Scatchard* and *Wilson* [44], but the G^E do not agree with the more recent data of *Koga* [45] whose activity coefficients of water have also been used here. The V^E data of *Douheret* and *Pal* [43] for 298.15 K are in agreement with those of *Scatchard* and *Wilson* [44] at 2 K higher, and both sets could be used. Adiabatic compressibilities data, κ_S, that agreed sufficiently well with the estimated [39] κ_T value of pure BuOEtOH interpolated linearly the values for the aqueous mixtures were taken from *Lara* and *Desnoyers* [46].

Aqueous MEA

Previously, the 273.15 K data were used [14], but now the 298.15 K G^E and V^E data of *Touhara et al.* [47] could be employed. *Hawrylak et al.* [48] provided both V^E and κ_S data at 298.15 K, the former being in agreement with those of *Touhara et al.*

Aqueous MeNHEtOH

The 298.15 K G^E and V^E data of *Touhara et al.* [47] could be employed. No compressibility data were found; therefore, the means of those for *MEA* and Me_2NEtOH from *Hawrylak et al.* [48] were used.

Aqueous Me$_2$NEtOH

The same sources of data as for *MEA* were used.

Aqueous THF

The water activity coefficient data of *Treiner et al.* [49] and V^E data of *Kiyohara* and *Benson* [50] for 298.15 K were used. Values of κ_S from *Aminabhavi et al.* [51], who provided also V^E data in agreement with those of *Kiyohara* and *Benson* [50], were employed.

Aqueous Diox

Data for G^E at 298.15 K were available from *Goats* and *Sullivan* [52] and were combined with the fewer values calculated from the activities reported by *Vierk* [53] and *Bacarella et al.* [54] Also used were the V^E from *Rebollo et al.* [55] and κ_S data were taken from *Aminabhavi et al.* [51].

Aqueous Me$_2$CO

Data for G^E at 298.15 K were available from *Orye* and *Prausnitz* [56], but the data of *Villamañan* and *van Ness* [57] obtained at higher temperatures could be extrapolated to 298.15 K by means of the expressions provided by these authors. The two sets are in reasonable agreement, but the latter was used. V^E data were calculated from the densities provided for 298.15 K by *Noda et al.* [58], and compressibility data, κ_T, were taken from *Egorov et al.* [59].

Aqueous Pip

The G^E and V^E data of *Nakanishi et al.* [60] for 298.15 K were employed as well as κ_S values for 293.15 K of *Patil* [61] for the pure solvent that were used to interpolate linearly the values for the aqueous mixtures.

Aqueous Py

The water activity coefficient data of *Chan* and *van Hook* [62] and the G^E data of *Abe et al.* [63] as well as the V^E data of *Abe et al.* [63] for 298.15 K were employed, as were the κ_S data of *Sharma* and *Singh.* [64].

Aqueous NMPy

The G^E data of *Zielenkiewicz* [65] for 303.15 K had to be used, and it was assumed that the V^E data of *Davis* [66] for 298.15 K would still give valid values of the *Kirkwood-Buff* integrals. The κ_S data of *Pal et al.* [67] were employed.

Aqueous DMSO

The activity coefficient data of *Lam* and *Benoit* [68] and those of *Chan* and *van Hook* [69] in agreement with them as well as the V^E data of *de Visser et al.* [70] for 298.15 K and the κ_S data of *Aminabhavi et al.* [51] were employed.

Results

Aqueous EtOH

The *Kirkwood-Buff* integral curves $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$ resemble closely those reported by *Matteoli* and *Lepori* [4] and need not be repeated here. They do not show the rather irregular behavior reported by *Blandamer et al.* [9], however. The resulting volume-corrected preferential solvation parameters for the first solvation shell, $\delta x'_{WW}$ and $\delta x'_{WS}$, are shown in Fig. 2a. The curves show that water tends to aggregate near a water molecule, with a maximum of $\delta x'_{WW} = 0.16$ near $x_S = 0.45$, and that it tends to avoid slightly the vicinity of ethanol, with a minimum of $\delta x'_{WS} = -0.04$ near $x_S = 0.35$.

Aqueous n-PrOH

The *Kirkwood-Buff* integral curves $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$ resemble closely those reported by *Matteoli* and *Lepori* [4] and need not be repeated here. The resulting volume-corrected preferential solvation parameters for the first and second solvation shells, $\delta x'_{WW}$ and $\delta x'_{WS}$, are shown in Fig. 2b. The curves show that

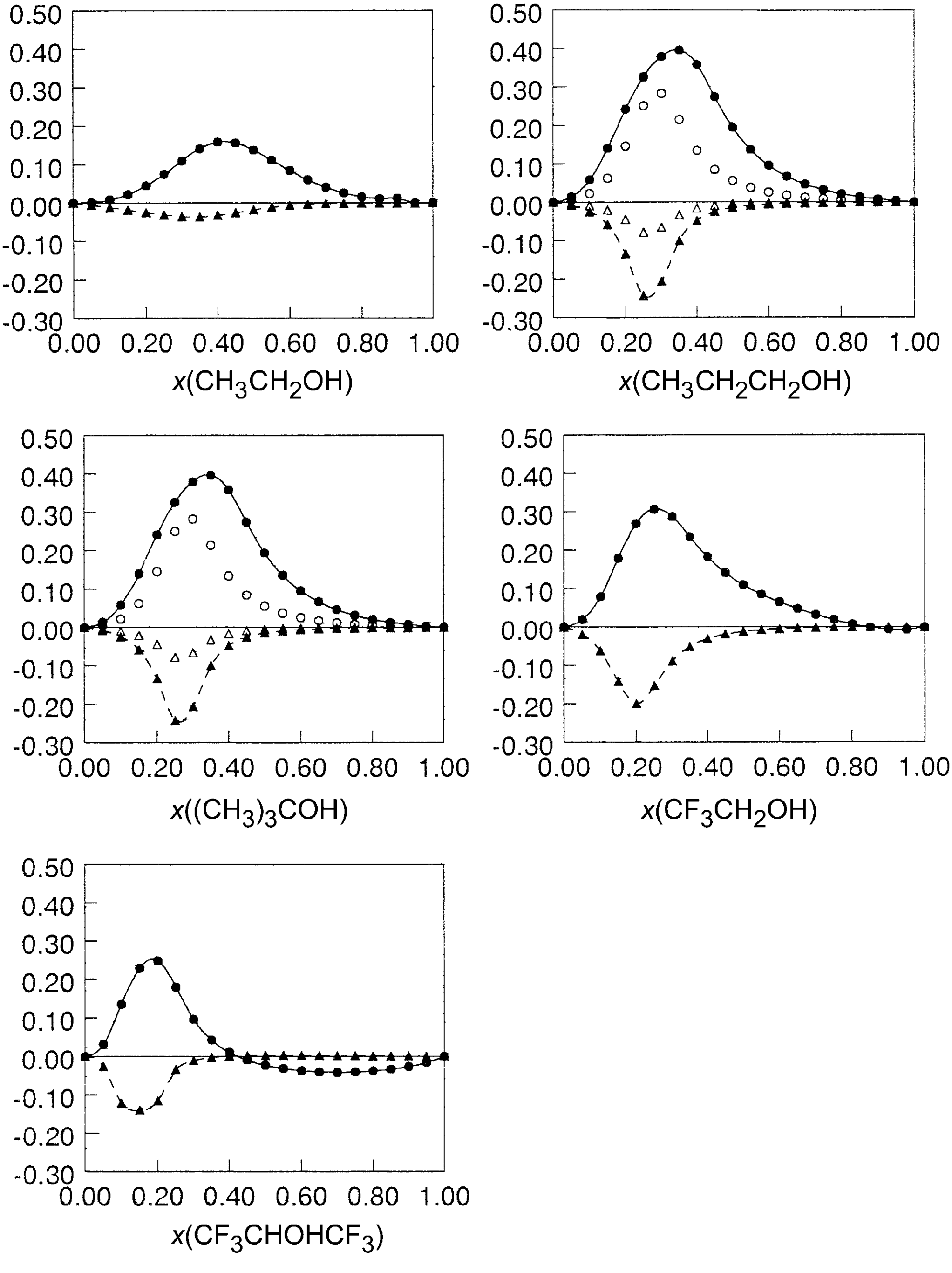

Fig. 2. Volume-corrected preferential solvation parameters $\delta x'_{\mathrm{WW}}$ (●) for water-water interactions and $\delta x'_{\mathrm{WS}}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous a) ethanol, b) 1-propanol (empty symbols for second solvation shell), c) 2-methyl-2-propanol (empty symbols for second solvation shell), d) 2,2,2-trifluoroethanol, and e) 1,1,1,3,3,3-hexafluoro-2-propanol

water tends much more than in the case of aqueous ethanol to aggregate near a water molecule, with a maximum of $\delta x'_{\mathrm{WW}} = 0.42$ in the first solvation shell and $\delta x'_{\mathrm{WW}} = 0.22$ in the second, near $x_{\mathrm{S}} = 0.30$. Even in the third solvation shell the maximal $\delta x'_{\mathrm{WW}}$ value is above 0.1 (not shown), indicating that this system is not far from microheterogeneity. The avoidance of water in the vicinity of *n*-propanol molecule is correspondingly pronounced, the minima of $\delta x'_{\mathrm{WS}}$ are -0.28 and -0.09 in the first and second solvation shells near $x_{\mathrm{S}} = 0.25$.

Aqueous t-BuOH

In this case, the *Kirkwood-Buff* integrals differ in magnitude from those reported by *Matteoli* and *Lepori* [4] and do not show the irregularities noted by those authors in very dilute (*i.e.* water-rich) mixtures. The three G_{WS}, G_{WW}, and G_{SS} curves are shown in Fig. 3a. The resulting volume-corrected preferential solvation parameters for the first and second solvation shells, $\delta x'_{\mathrm{WW}}$ and $\delta x'_{\mathrm{WS}}$, are shown in Fig. 2c. Water tends to aggregate near a water molecule as much as in the case of aqueous *n*-propanol, with a maximum of $\delta x'_{\mathrm{WW}} = 0.40$ in the first solvation shell and 0.28 in the second, near $x_{\mathrm{S}} = 0.35$ and 0.30, respectively, and in the third solvation shell (not shown) it still is 0.15. The avoidance of water of the vicinity of a *t*-butanol molecule is also pronounced, the minima of $\delta x'_{\mathrm{WS}}$ are -0.24 and -0.08 in the first and second solvation shells near $x_{\mathrm{S}} = 0.25$.

Aqueous TFE

The *Kirkwood-Buff* integral curves $G_{\mathrm{WS}}(x_{\mathrm{S}})$ and $G_{\mathrm{SS}}(x_{\mathrm{S}})$ resemble closely those reported by *Balandamer et al.* [9], but the $G_{\mathrm{WW}}(x_{\mathrm{S}})$ curve is more regular and doesn't show the second hump seen in the latter authors' results. The resulting $\delta x'_{\mathrm{WW}}$ and $\delta x'_{\mathrm{WS}}$, are shown in Fig. 2d. They lie in between those of ethanol and *n*-propanol, with a maximal $\delta x'_{\mathrm{WW}} = 0.31$ near $x_{\mathrm{S}} = 0.25$ and a minimal $\delta x'_{\mathrm{WS}} = -0.20$ near $x_{\mathrm{S}} = 0.20$.

Aqueous HF-i-PrOH

In this case, the *Kirkwood-Buff* integral curves $G_{\mathrm{WW}}(x_{\mathrm{S}})$ and $G_{\mathrm{WS}}(x_{\mathrm{S}})$ resemble closely those reported by *Balandamer et al.* [9], but the $G_{\mathrm{SS}}(x_{\mathrm{S}})$ curve is considerably lower ($\sim$250 against $\sim$950 $\mathrm{cm^3\,mol^{-1}}$), although of the same general shape. The resulting $\delta x'_{\mathrm{WW}}$ and $\delta x'_{\mathrm{WS}}$, are shown in Fig. 2e and are somewhat lower (in absolute value) than those for aqueous 2,2,2-trifluoroethanol.

Aqueous MeOEtOH

The *Kirkwood-Buff* integrals $G_{\mathrm{WW}}(x_{\mathrm{S}})$, $G_{\mathrm{WS}}(x_{\mathrm{S}})$, and $G_{\mathrm{SS}}(x_{\mathrm{S}})$ for 313.15 and 343.15 K are shown in Fig. 3b. It has to be noted that the temperature has a negligible effect on $G_{\mathrm{WS}}(x_{\mathrm{S}})$ and $G_{\mathrm{SS}}(x_{\mathrm{S}})$, but does affect $G_{\mathrm{WW}}(x_{\mathrm{S}})$, the curve at 343.15 K being broader and somewhat lower than at 313.15 K. The resulting $\delta x'_{\mathrm{WS}}$ are, correspondingly, practically identical at the two temperatures (Fig. 4a), but the

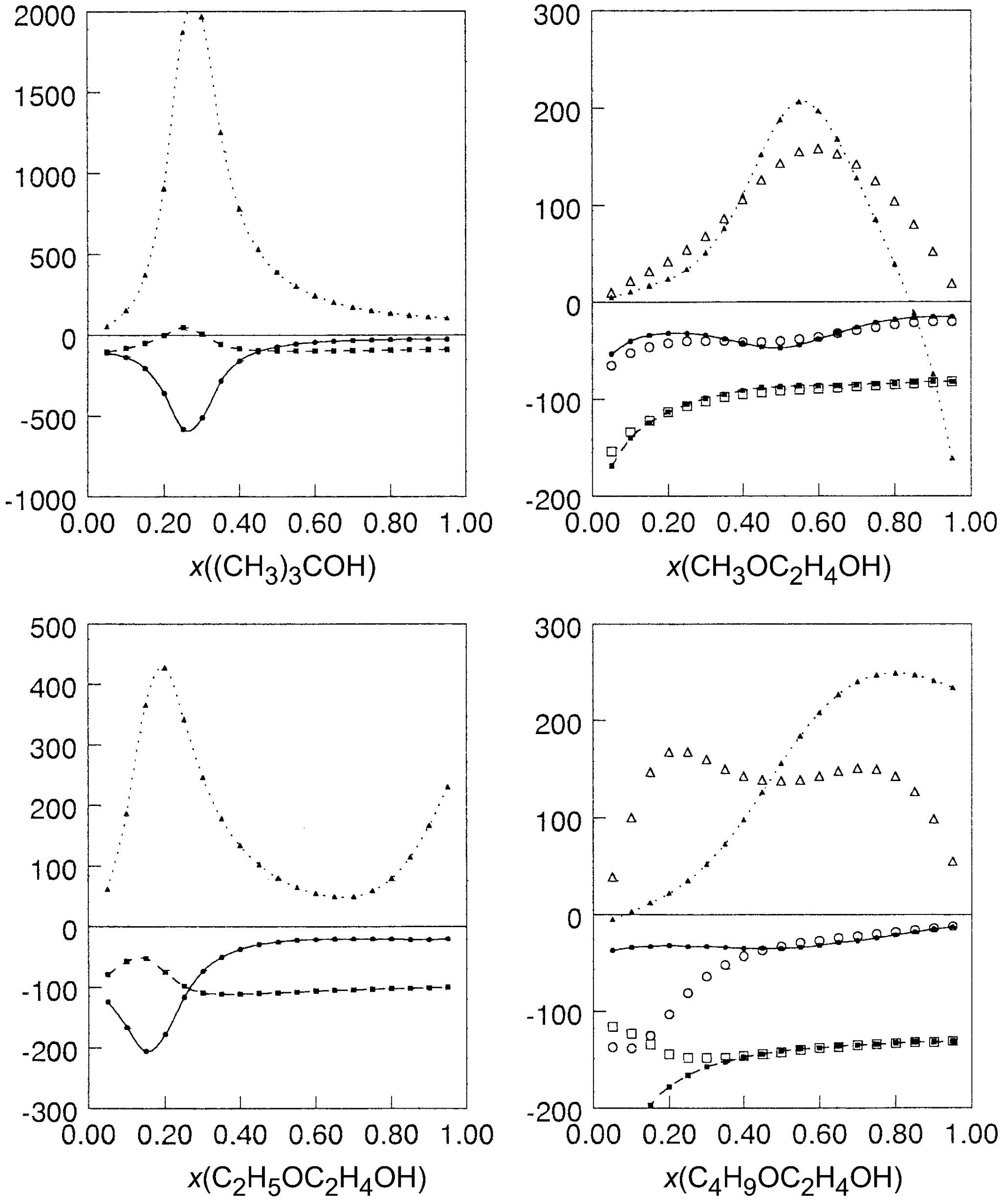

Fig. 3. *Kirkwood-Buff* integrals in cm$^3 \cdot$ mol^{-1} at 298.15 K (except frame b); G_{WW} (▲ and dotted line), G_{SS} (● and continuous line), and G_{SW} (■ and dashed line) of aqueous a) 2-methyl-2-propanol, b) 2-methoxyethanol (filled symbols at 313.15 K, empty symbols at 343.15 K), c) 2-ethoxyethanol, and d) 2-butoxyethanol (filled symbols from *Koga*'s data [45] and empty symbols from *Scatchard* and *Wilson*'s data [44]

$\delta x'_{WW}$ curves differ, that at 343.15 K being again broader and somewhat lower than that at 313.15 K. At the latter temperature, the maximal $\delta x'_{WW} = 0.10$ and the minimal $\delta x'_{WS} = -0.008$, both near $x_S = 0.50$. These values are smaller in absolute value than those for ethanol, showing the effect of the additional (etheral) oxygen atom on the interactions.

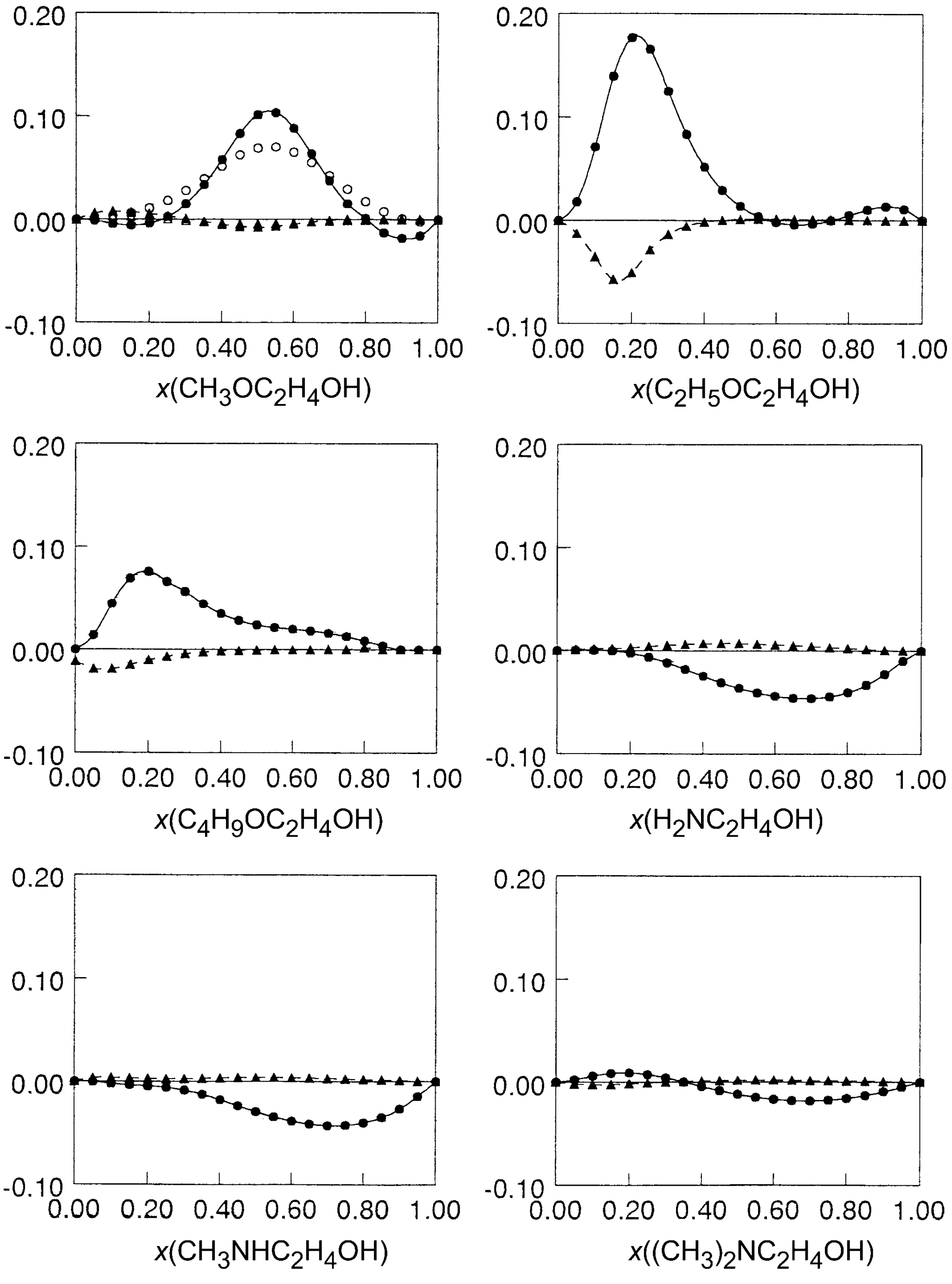

Fig. 4. Volume-corrected preferential solvation parameters $\delta x'_{WW}$ (●) for water-water interactions and $\delta x'_{WS}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous a) 2-methoxyethanol (filled symbols at 313.15 K, empty symbols at 343.15 K), b) 2-ethoxyethanol, c) 2-butoxyethanol (from *Koga*'s data [45]), d) 2-aminoethanol, e) 2-N-methylaminoethanol, and f) 2-N,N-dimethylaminoethanol

Aqueous EtOEtOH

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$, are shown in Fig. 3c. The upturn of the $G_{WW}(x_S)$ curve at $x_S > 0.7$ is probably an artifact due to inaccuracy of the G^E extrapolation to 298.15 K. Otherwise, the curves show the expected behavior, exhibiting more extreme values than the corresponding curves for 2-methoxyethanol in the more water-rich mixtures, the ethyl group being more hydrophobic than the methyl group. The *Kirkwood-Buff* integral curves obtained by *Kato* from *Rayleigh-Brillouin* scattering [21] are quite different, however, and are deemed not to be correct. The calculated $\delta x'_{WW}$ and $\delta x'_{WS}$ are shown in Fig. 4b. Their extrema are larger than those of 2-methoxyethanol and in more water-rich mixtures: the maximal $\delta x'_{WW} = 0.18$ near $x_S = 0.20$ and the minimal $\delta x'_{WS} = -0.06$ near $x_S = 0.15$.

Aqueous BuOEtOH

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$ obtained from both the *Koga* [45] activity coefficient and the *Scatchard* and *Wilson* [44] G^E data are shown in Fig. 3d. Although the $G_{WS}(x_S)$ and $G_{SS}(x_S)$ curves for $x_S \geq 0.4$ from both sources agree with each other, they disagree for more water-rich mixtures, and the two $G_{WW}(x_S)$ curves are completely different. The expected gradual change from methoxy- through ethoxy- to butoxyethanol is not observed for either set of curves for butoxyethanol, although that based on the *Scatchard* and *Wilson* data [44] conform to the qualitative trend (but the extremal values are much lower than expected for the more hydrophobic butyl group), whereas those based on the *Koga* data [45] do not. The *Kirkwood-Buff* integrals reported by *Kato* from *Rayleigh-Brillouin* scattering [21] at 294 K reach only to $x_S = 0.2$ and show very large extrema (*e.g.* $G_{SS}(x_S = 0.05) \approx 13000\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$), completely at odds with those of other homogeneous aqueous mixtures. They would signify phase separation at 294 K that actually takes place only at the considerably higher temperature of about 323 K. The derived $\delta x'_{WW}$ and $\delta x'_{WS}$ values based on the *Scatchard* and *Wilson* data [44] are shown in Fig. 4c. Those based on the *Koga* data [45] (not shown) exhibit negative $\delta x'_{WW}$ and positive $\delta x'_{WS}$ values in water-rich mixtures that are completely counter-intuitive and contrary to the behaviour of other systems. The $\delta x'_{WW}$ and $\delta x'_{WS}$ values are lower than expected but of correct sign and shape and have the maximal $\delta x'_{WW} = 0.075$ near $x_S = 0.20$ and the minimal $\delta x'_{WS} = -0.019$ near $x_S = 0.15$, *i.e.* at more water-rich compositions that for the methoxy- and ethoxy-ethanols as expected.

Aqueous MEA

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$ at 298.15 K (not shown) resemble those obtained by the present author [14] at 273.15 K (shown there) but are shifted slightly towards more positive values, and also those reported by *Matteoli* and *Lepori* for 298.15 K [4] except $G_{WW}(x_S)$, these authors' curve turning upward whereas the present one turns downward at $x_S > 0.5$. The calculated $\delta x'_{WW}$ and $\delta x'_{WS}$, are shown in Fig. 4d, agreeing well with those reported for 273.15 K

[14] and are seen to be quite small (the minimal $\delta x'_{\mathrm{WW}} = -0.046$ and the maximal $\delta x'_{\mathrm{WS}} = 0.007$). The main feature for the system involving the very hydrophilic 2-aminoethanol is that $\delta x'_{\mathrm{WW}}$ is negative and $\delta x'_{\mathrm{WS}}$ is positive, signifying strong attraction between water and the co-solvent.

Aqueous MeNHEtOH

The *Kirkwood-Buff* integrals $G_{\mathrm{WW}}(x_{\mathrm{S}})$, $G_{\mathrm{WS}}(x_{\mathrm{S}})$, and $G_{\mathrm{SS}}(x_{\mathrm{S}})$ (Fig. 6a) resemble closely those for 2-aminoethanol, but the distances between the curves are somewhat larger, reflecting the larger molar volume of the methyl derivative. The resulting $\delta x'_{\mathrm{WW}}$ and $\delta x'_{\mathrm{WS}}$ (Fig. 4e) are also very similar to those for 2-aminoethanol, but the extrema are even smaller (the minimal $\delta x'_{\mathrm{WW}} = -0.043$ and the maximal $\delta x'_{\mathrm{WS}} = 0.004$), signifying the expected somewhat lower hydrophilicity of the methyl derivative.

Aqueous Me$_2$NEtOH

The *Kirkwood-Buff* integrals $G_{\mathrm{WW}}(x_{\mathrm{S}})$, $G_{\mathrm{WS}}(x_{\mathrm{S}})$, and $G_{\mathrm{SS}}(x_{\mathrm{S}})$ (not shown) are similar to those of the un- and singly-substituted aminoethanols with another widening of the spacing between the curves. The agreement with the curves reported by *Matteoli* and *Lepori* [4] is similar to that noted above for 2-aminoethanol. The resulting $\delta x'_{\mathrm{WW}}$ and $\delta x'_{\mathrm{WS}}$, shown in Fig. 4f, follow the trend set by the un- and singly-substituted aminoethanols, with $\delta x'_{\mathrm{WW}}$ now showing slightly positive values at water-rich compositions, demonstrating that the self association of water in this region overcomes the mutual association due to the two methyl groups.

Aqueous THF

The *Kirkwood-Buff* integrals $G_{\mathrm{WS}}(x_{\mathrm{S}})$, and $G_{\mathrm{SS}}(x_{\mathrm{S}})$, resemble closely those reported by *Matteoli* and *Lepori* [4], but $G_{\mathrm{WW}}(x_{\mathrm{S}})$ of these authors shows a single maximum of $\sim 3500\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at $x_{\mathrm{S}} \approx 0.5$, whereas the present calculation gives a double-humped curve with maxima of 850 and $450\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at $x_{\mathrm{S}} = 0.25$ and 0.75, respectively. Still, even with these lower G_{WW} values, considerable water-water association takes place, the maximal $\delta x'_{\mathrm{WW}}$ being 0.33 near $x_{\mathrm{S}} = 0.30$ as shown in Fig. 5a for the first solvation shell. This self association persists to farther shells, as shown in Fig. 5a also for the second one, and even in the fifth shell it is not completely negligible (maximal $\delta x'_{\mathrm{WW}} = 0.028$). The mutual association of water with tetrahydrofuran is correspondingly depressed, with the minimal $\delta x'_{\mathrm{WS}} = -0.20$ at $x_{\mathrm{S}} = 0.25$, and this persists again to farther solvation shells.

Aqueous Diox

All *Kirkwood-Buff* integrals resemble closely those reported by *Matteoli* and *Lepori* [4] and need not be shown here. The $\delta x'_{\mathrm{WW}}$ values show even larger self-association of water than in aqueous tetrahydrofuran, the maximal $\delta x'_{\mathrm{WW}} = 0.57$ at $x_{\mathrm{S}} = 0.65$,

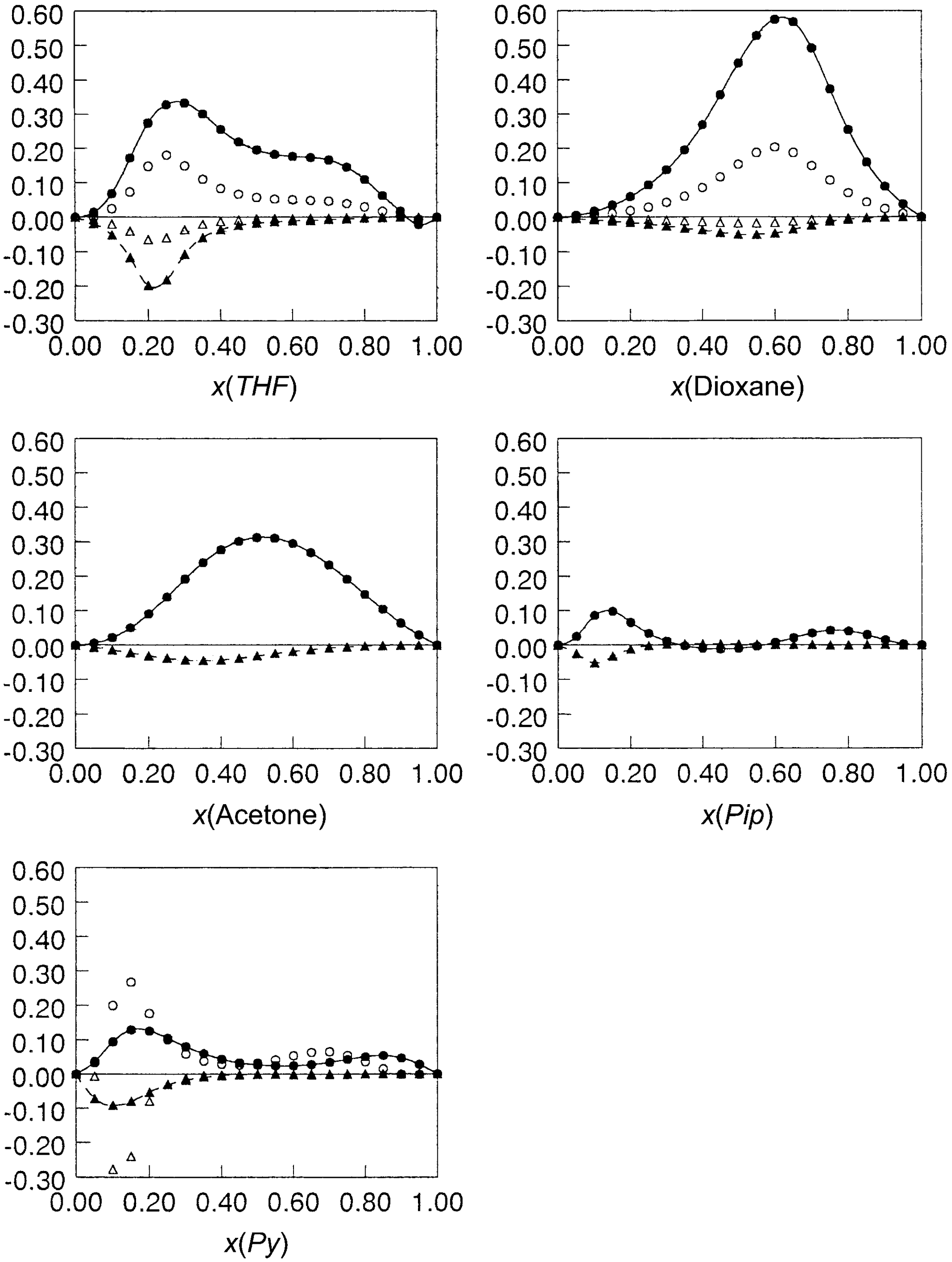

Fig. 5. Volume-corrected preferential solvation parameters $\delta x'_{\mathrm{WW}}$ (●) for water-water interactions and $\delta x'_{\mathrm{WS}}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous a) tetrahydrofuran (empty symbols for second solvation shell), b) 1,4-dioxane (empty symbols for second solvation shell), c) acetone, d) piperidine, and e) pyridine (filled symbols from *Chan*'s data [62] and empty symbols from *Abe*'s data [63]

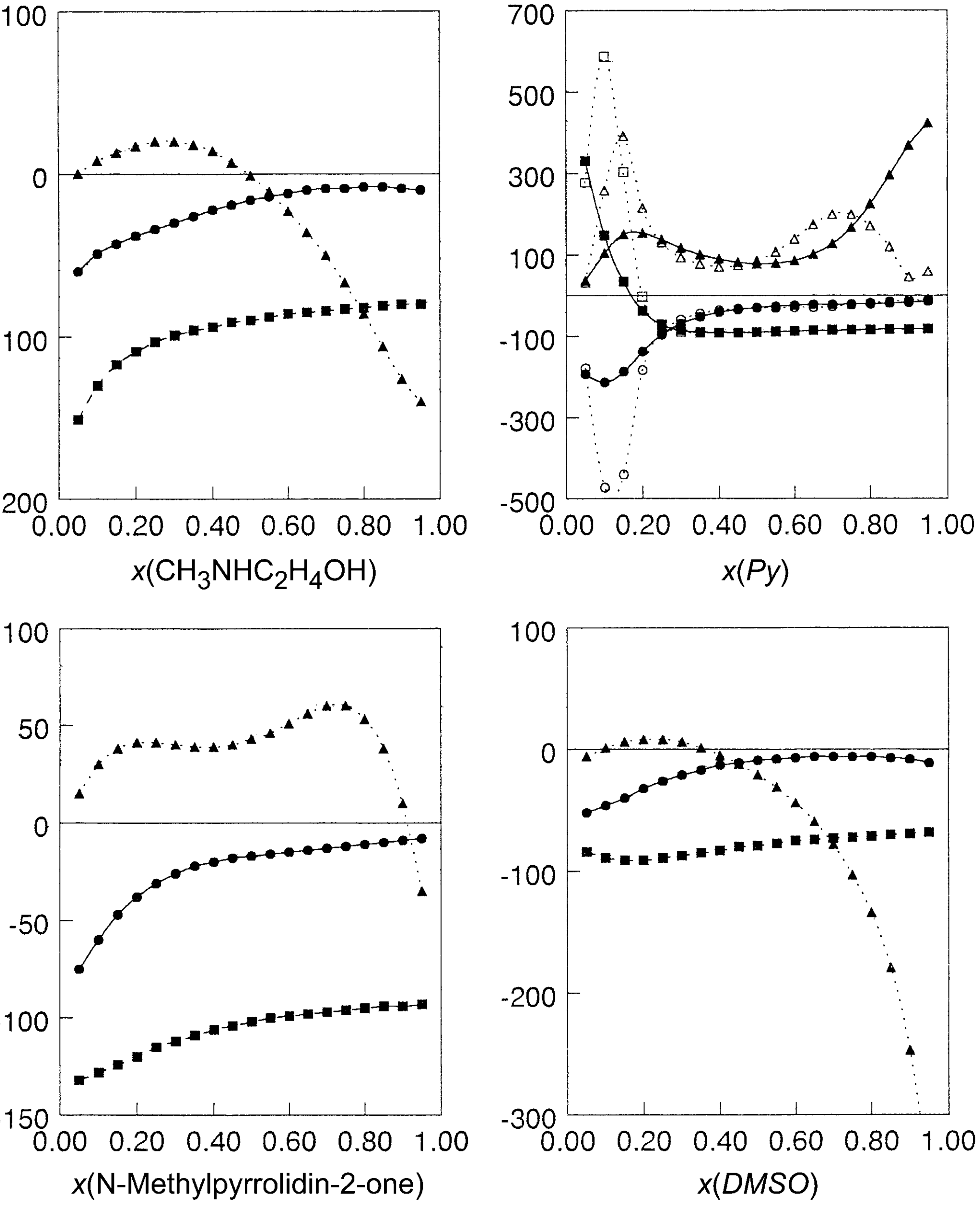

Fig. 6. *Kirkwood-Buff* integrals in $cm^3 \cdot mol^{-1}$ at 298.15 K (except frame b); G_{WW} (▲ and dotted line), G_{SS} (● and continuous line), and G_{SW} (■ and dashed line) of aqueous a) 2-N-methylaminoethanol, b) pyridine (filled symbols from *Chan*'s data [62] and empty symbols from *Abe*'s data [63], c) N-methylpyrrolidin-2-one, and d) dimethylsulfoxide

and again persists to farther solvation shells (see Fig. 5b). However, the depression of the mutual interaction of water and dioxane is not as far reaching as in the case of aqueous tetrahydrofuran, the minimal $\delta x'_{WS} = -0.052$ at $x_S = 0.55$, and hardly persists ($\delta x'_{WS} > -0.007$) in the third solvation shell due to the existence of two oxygen atoms in the dioxane molecule.

Aqueous Me_2CO

All *Kirkwood-Buff* integrals resemble closely those reported by *Matteoli* and *Lepori* [4] and need not be shown here. The $\delta x'_{WW}$ values shown in Fig. 5c are less pronounced than in the ethers, with water-water interactions reaching the maximal $\delta x'_{WW} = 0.31$ near $x_S = 0.5$ and the mutual water-acetone interactions reaching the minimal $\delta x'_{WS} = -0.045$ at $x_S = 0.35$.

Aqueous Pip

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$ and $G_{WS}(x_S)$ resemble closely those reported by *Matteoli* and *Lepori* [4], but $G_{SS}(x_S)$ is considerably lower (maximally 12 rather than 300 $cm^3\,mol^{-1}$), although of the same shape. The present $G_{WW}(x_S)$ curve extends towards higher x_S than the *Matteoli* and *Lepori* curve and confirms the upturn reported there, leading to a second hump. The calculated positive $\delta x'_{WW}$ and negative $\delta x'_{WS}$ are quite small, however, their absolute values being smaller than 0.1 (see Fig. 5d).

Aqueous Py

The two existing sets of data (*Abe et al* [61] for G^E, *Chan* and *van Hook* [61] for the activity coefficients) are inconsistent as far as the derived *Kirkwood-Buff* integrals are concerned; both sets are shown in Fig. 6b. Those obtained from the former data agree with the curves reported by *Matteoli* and *Lepori* [4], whereas those obtained from latter data do not. The derived $\delta x'_{WW}$ and $\delta x'_{WS}$ values differ too, of course, but only for $x_S < 0.4$, and both sets are shown in Fig. 5e. Those obtained from the *Abe et al.* [61] data are about twice as large (in absolute values) than those calculated from the *Chan* and *van Hook* [60] data, and it is difficult to decide which set resembles closer the actual situation. Both sets lead to small ($\delta x' < 0.07$) self- and mutual preferences at $x_S > 0.4$ (Fig. 5e).

Aqueous NMPy

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$, $G_{WS}(x_S)$, and $G_{SS}(x_S)$ have not been reported previously, and the values obtained for 303.15 K are shown in Fig. 6c. The latter two curves resemble closely the expected ones for ideal mixing (Fig. 1), but $G_{WW}(x_S)$ deviates at $x_S > 0.3$. The calculated $\delta x'_{WW}$ and $\delta x'_{WS}$ values are very small, as shown in Fig. 7a, and at $x_S > 0.2$ are negative for $\delta x'_{WW}$ and positive for $\delta x'_{WS}$, signifying slight preference of mutual over self-association in the solvation shells as in the cases of the ethanolamines.

Aqueous DMSO

The *Kirkwood-Buff* integrals $G_{WW}(x_S)$ and $G_{SS}(x_S)$ differ somewhat from those reported by *Matteoli* and *Lepori* [4], and only $G_{WS}(x_S)$ agrees with it; all three curves are shown in Fig. 6d. They are altogether fairly small and lead accordingly to rather small negative $\delta x'_{WW}$ and positive $\delta x'_{WS}$ values (Fig. 7b). As expected, the self interaction of water in the solvation shells is depressed, the minimal $\delta x'_{WW} =$

-0.058 at $x_S = 0.75$, whereas the mutual interaction, with a maximal $\delta x'_{WS} = 0.006$ near $x_S = 0.45$, is small.

Review of Previously Reported Systems

Although the preferential solvation parameters of many additional aqueous co-solvent mixtures have been previously reported, these had not been corrected for the volume effects, so that nearly ideal systems still apparently showed preferential solvation. The preferential solvation in such mixtures is indeed real, due to the discrepancy in molar volumes, but does not reflect the expected similarity of the self- and mutual interactions, leading to no preferential solvation interactions. That is, such systems have very small values of $|\delta x'_{WW}|$ and $|\delta x'_{SW}|$, considered to be insignificant when ≤ 0.01. It is therefore instructive to include here also additional systems to those recorded in Table 1 for the sake of comparison with the information presented above. The thermodynamic data that had been employed previously [10, 11, 14, 17, 20] were used also for the present calculations. The first solvation shell volume-corrected preferential solvation parameters at 298.15 K are shown in Figs. 7–9.

Aqueous H_2O_2

This system is close to ideal (see Fig. 7c). For the disfavoured water self-interactions, the minimal $\delta x'_{WW} = -0.013$ at $x_S = 0.70$, whereas the favoured mutual interaction has a maximal $\delta x'_{WS} = 0.009$ near $x_S = 0.35$, both extrema being quite small, preferential solvation is hardly significant.

Aqueous MeOH

This solvent system has been dealt with in detail over a wide temperature range [17]. For 298.15 K, the resulting volume-corrected preferential solvation parameters are shown in Fig. 7d. For the water self-interactions, the maximal $\delta x'_{WW} = 0.037$ at $x_S = 0.65$, whereas for the mutual interaction the minimal $\delta x'_{WS} = -0.017$ near $x_S = 0.10$. The maximal $\delta x'_{WW}$ value can be compared with those shown above for aqueous ethanol and *n*-propanol: 0.16 and 0.42, showing the expected gradual change.

Aqueous i-PrOH

The results for this system are shown in Fig. 9a, where for the water self-interactions the maximal $\delta x'_{WW} = 0.165$ at $x_S = 0.50$, whereas for the mutual interaction the minimal $\delta x'_{WS} = -0.031$ near $x_S = 0.30$. The preferential solvation is considerably smaller than for *n*-propanol and *t*-butanol (maximal $\delta x'_{WW} = 0.40$) and is comparable with that of ethanol.

Aqueous EG

This system is, as expected, much more nearly ideal than the monoalcohols and is depicted in Fig. 7e. As for aqueous hydrogen peroxide, for the disfavoured water self-interactions the minimal $\delta x'_{WW} = -0.012$ at $x_S = 0.50$, whereas the favoured

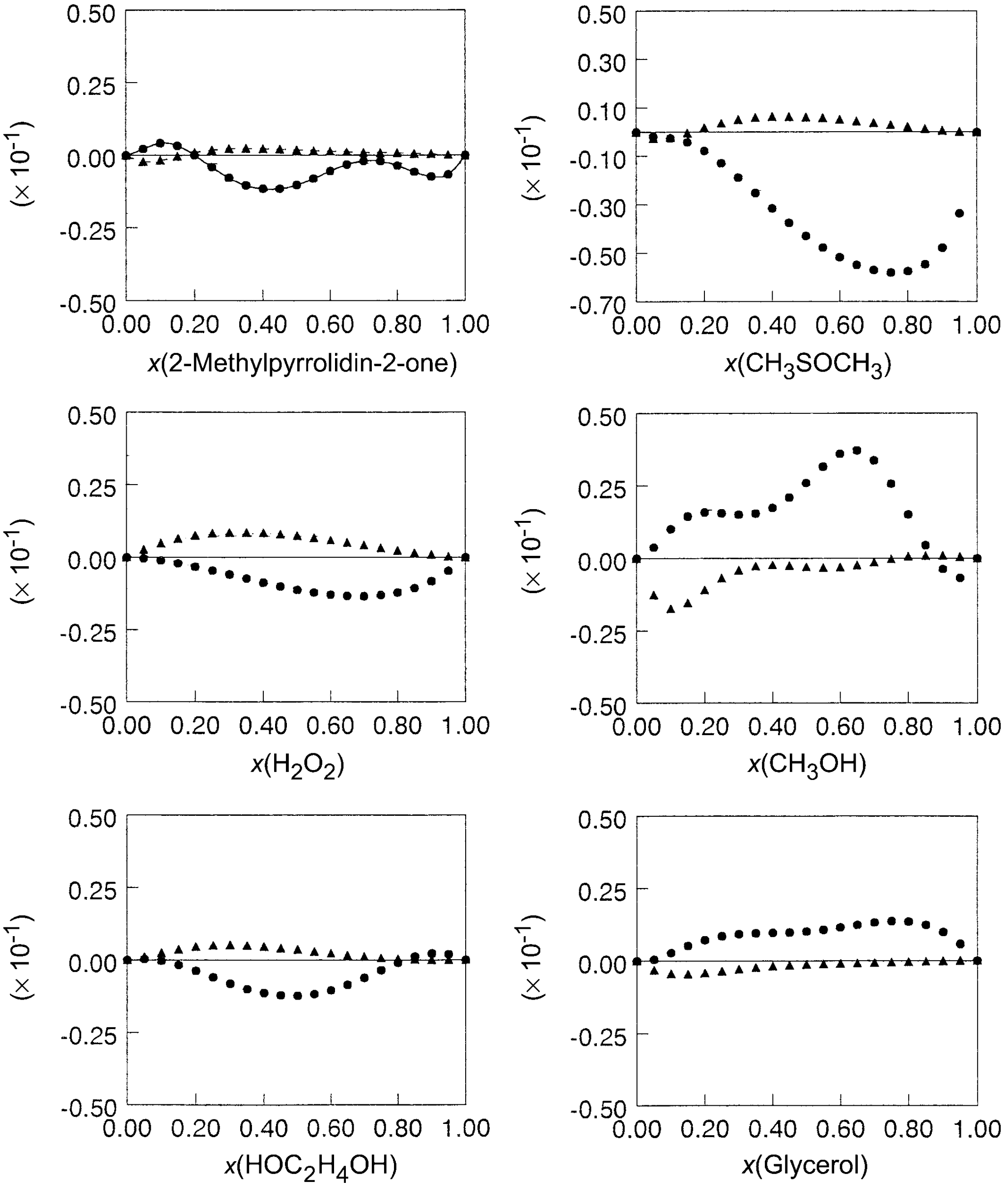

Fig. 7. Volume-corrected preferential solvation parameters $\delta x'_{\mathrm{WW}}$ (●) for water-water interactions and $\delta x'_{\mathrm{WS}}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous a) N-methylpyrrolidin-2-one (at 303.15 K), b) dimethylsulfoxide, c) hydrogen peroxide, d) methanol, e) ethylene glycol, and f) glycerol; note the ordinate scale (the numbers are multiples of 10^{-1})

mutual interaction has a maximal $\delta x'_{\mathrm{WS}} = 0.005$ near $x_{\mathrm{S}} = 0.35$, both extrema being quite small and preferential solvation being hardly significant.

Aqueous Gly

This binary solvent system has been dealt with in detail previously [20], and the volume-corrected preferential solvation parameters are shown in Fig. 7f. As for

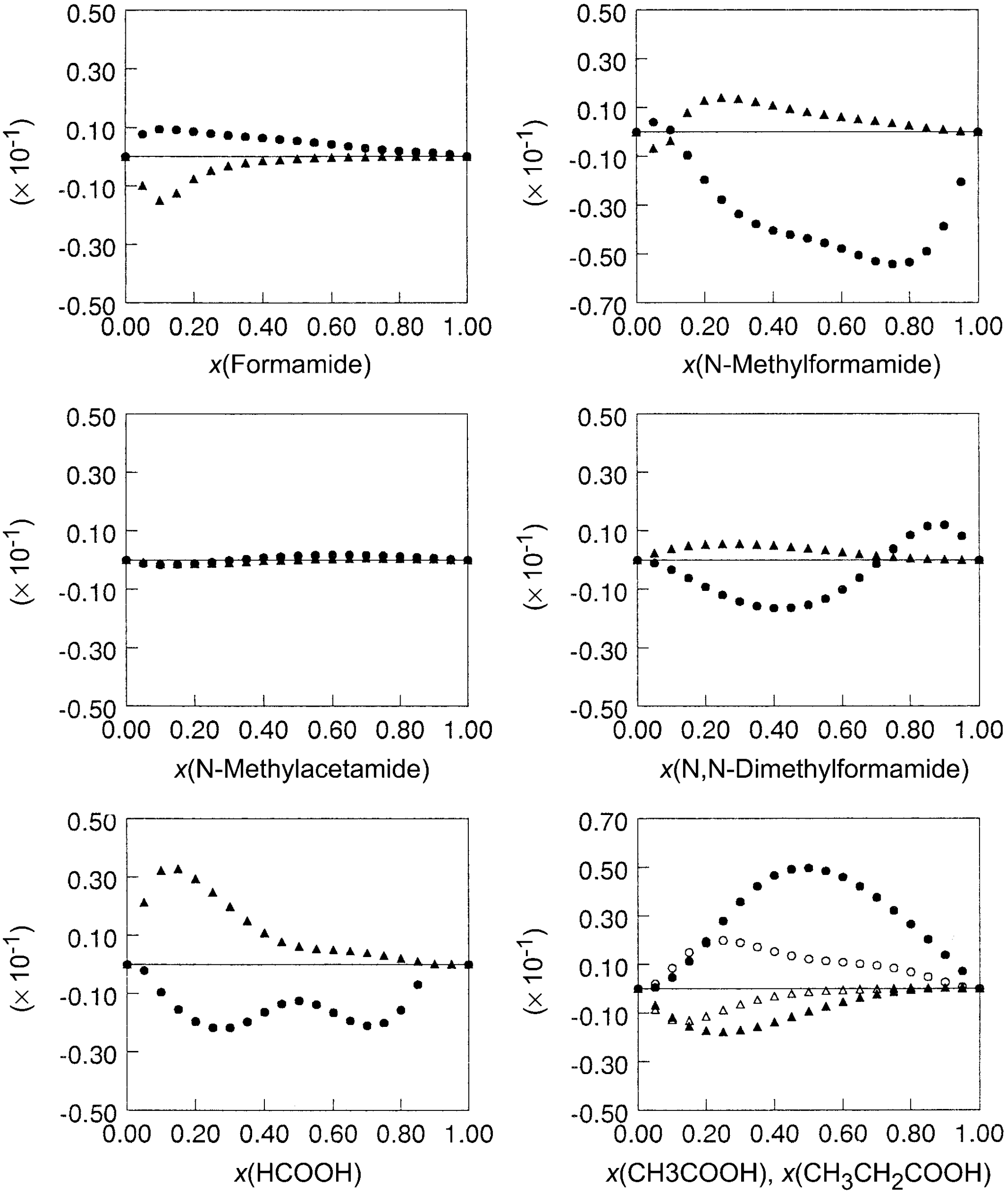

Fig. 8. Volume-corrected preferential solvation parameters $\delta x'_{\mathrm{WW}}$ (●) for water-water interactions and $\delta x'_{\mathrm{WS}}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous a) formamide, b) N-methylformamide, c) N-methylacetamide, d) N,N-dimethylformamide, e) formic acid, and f) acetic acid (filled symbols) and propanoic acid (empty symbols); note the ordinate scale (the numbers are multiples of 10^{-1})

aqueous ethylene glycol, the system is close to ideal, but the self interactions of water are now favoured over the mutual interactions. The maximal $\delta x'_{\mathrm{WW}} = 0.014$ at $x_{\mathrm{S}} = 0.75$, whereas the disfavoured mutual interaction has a minimal $\delta x'_{\mathrm{WS}} = -0.005$ near $x_{\mathrm{S}} = 0.15$, both extrema being again rather small.

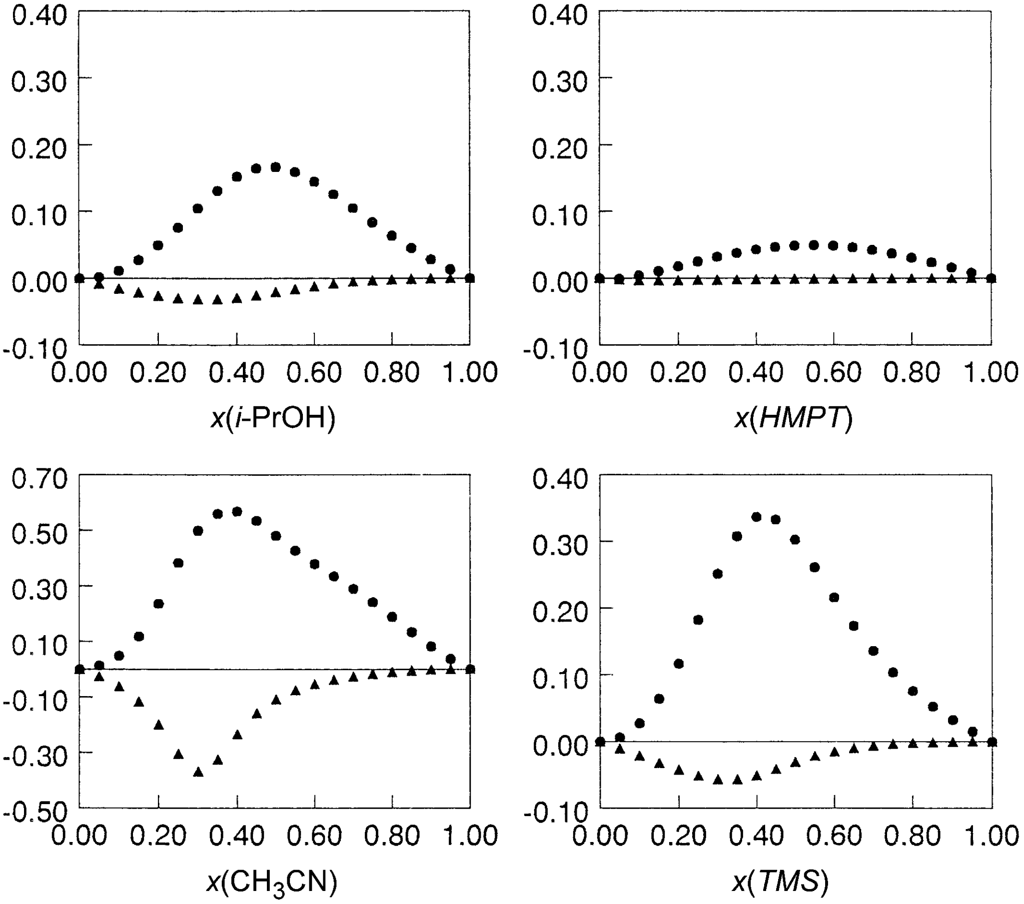

Fig. 9. Volume-corrected preferential solvation parameters $\delta x'_{\mathrm{WW}}$ (●) for water-water interactions and $\delta x'_{\mathrm{WS}}$ (▲) for water – co-solvent interactions in the first solvation shell at 298.15 K of aqueous: a) 2-propanol, b) hexamethyl phosphoric triamide, c) acetonitrile, and d) tetramethylenesulfone (at 303.15 K)

Aqueous HCOOH

The volume-corrected preferential solvation parameters are shown in Fig. 8e. For this very hydrophilic co-solvent, the water self-interactions are disfavoured, with a minimal $\delta x'_{\mathrm{WW}} = -0.022$ at $x_{\mathrm{S}} = 0.30$, whereas the favoured mutual interaction has a maximal $\delta x'_{\mathrm{WS}} = 0.033$ near $x_{\mathrm{S}} = 0.15$. These values for the extrema are rather small, showing that the system is not far from ideality.

Aqueous MeCOOH

The volume-corrected preferential solvation parameters are shown in Fig. 8f (filled symbols). This system shows an intermediate magnitude of non-ideality, the water-water interactions being favoured, with maximal $\delta x'_{\mathrm{WW}} = 0.050$ at $x_{\mathrm{S}} = 0.50$, whereas the disfavoured mutual water-acid interaction has a minimal $\delta x'_{\mathrm{WS}} = -0.018$ at $x_{\mathrm{S}} = 0.25$.

Aqueous EtCOOH

The volume-corrected preferential solvation parameters are shown in Fig. 8f, too (empty symbols). Surprisingly, this system exhibits lower non-ideality than the aqueous acetic acid system, the water-water interactions being favoured, but with maximal $\delta x'_{\mathrm{WW}} = 0.020$ only at $x_{\mathrm{S}} = 0.25$, whereas the disfavoured mutual water-acid interaction has a minimal $\delta x'_{\mathrm{WS}} = -0.013$ at $x_{\mathrm{S}} = 0.15$. No good explanation for this behaviour is apparent.

Aqueous FA

The volume-corrected preferential solvation parameters are shown in Fig. 8a, indicating that this system is nearly ideal. The extrema are very small, and preferential solvation is hardly significant. The water self-interactions are favoured, but with maximal $\delta x'_{\mathrm{WW}} = 0.009$ only at $x_{\mathrm{S}} = 0.15$, and the mutual interactions have a minimal $\delta x'_{\mathrm{WS}} = -0.013$ at $x_{\mathrm{S}} = 0.15$.

Aqueous NMF

The volume-corrected preferential solvation parameters are shown in Fig. 8b, the water self interactions being disfavoured in this case, with minimal $\delta x'_{\mathrm{WW}} = -0.054$ at $x_{\mathrm{S}} = 0.75$ and the favoured mutual interactions have a maximal $\delta x'_{\mathrm{WS}} = 0.014$ at $x_{\mathrm{S}} = 0.25$. The better compatibility of this co-solvent than of formamide with water is unexpected, although the extreme values are fairly small in either case.

Aqueous NMA

The volume-corrected preferential solvation parameters are shown in Fig. 8c. The behavior of this system is practically indistinguishable from ideal behavior: the absolute extreme values of the volume-corrected preferential solvation parameters are below 0.002, so that no preferential solvation takes place.

Aqueous DMF

The volume-corrected preferential solvation parameters are shown in Fig. 8d. The water self-interactions are disfavoured at low co-solvent concentrations, with minimal $\delta x'_{\mathrm{WW}} = -0.016$ at $x_{\mathrm{S}} = 0.40$ but somewhat favoured at high co-solvent concentrations, reaching $\delta x'_{\mathrm{WW}} = 0.012$ at $x_{\mathrm{S}} = 0.90$. The favoured mutual interactions have a small maximal $\delta x'_{\mathrm{WS}} = 0.006$ at $x_{\mathrm{S}} = 0.30$. Little preferential solvation is noted for this system.

The behavior of these four aqueous amide systems can be compared with that of aqueous N-methylpyrrolidin-2-one (Fig. 7a) and with that of the following system (Fig. 9b) which are also fairly close to being ideal.

Aqueous HMPT

The volume-corrected preferential solvation parameters are shown in Fig. 9b. The extrema are not large the water self-interactions being favoured but with maximal

$\delta x'_{\mathrm{WW}} = 0.050$ at $x_{\mathrm{S}} = 0.55$; the mutual interactions have a minimal $\delta x'_{\mathrm{WS}} = -0.003$ at $x_{\mathrm{S}} = 0.20$. Although the phosphoryl group and the three amidic oxygen atoms are exposed to water, the six methyl groups exert effectively their hydrophobic nature.

Aqueous acetonitrile

This solvent system has been dealt with in detail over a wide temperature range [11]. For 298.15 K, the resulting volume-corrected preferential solvation parameters are shown in Fig. 9c. This system exhibits large deviations from ideal mixing (immiscibility is noted below 272.0 K), and preferential solvation that extends over many solvation shells (microheterogeneity) still occurs at 298.15 K [11]. For the water self-interactions, the maximal $\delta x'_{\mathrm{WW}}$ is 0.56 at $x_{\mathrm{S}} = 0.35$, whereas for the mutual interaction the minimal $\delta x'_{\mathrm{WS}} = -0.37$ near $x_{\mathrm{S}} = 0.30$. Of the systems considered here, only the aqueous *n*-propanol, *t*-butanol, and tetramethylenesulfone mixtures approach aqueous acetonitrile in exhibiting that large preferential solvation. The temperatures at which the latter two systems are presented here are, however, only slightly higher than the melting points of the neat co-solvents, a fact that ought to affect the behavior of these two systems.

Aqueous TMS

The volume-corrected preferential solvation parameters (for 303.15 K) are shown in Fig. 9d. The water self-interactions are strongly favoured, with maximal $\delta x'_{\mathrm{WW}} = 0.34$ at $x_{\mathrm{S}} = 0.40$, and the disfavoured mutual interactions have a minimal $\delta x'_{\mathrm{WS}} = -0.06$ at $x_{\mathrm{S}} = 0.30$. The pronounced preferential solvation extends over several solvation shells (not shown) and is similar in magnitude to that noted in aqueous acetone or tetrahydrofuran.

Limiting Self Interaction of the Co-Solvent

A further interesting piece of information that can be derived from the *Kirkwood-Buff* integrals is the limiting (*i.e.* infinite dilution) self-interaction of the co-solvent in aqueous solution, $G^{\infty}_{\mathrm{SS}} = \lim(x_{\mathrm{S}} \to 0)G_{\mathrm{SS}}$. The values that have been obtained in the present work and previously [10] are shown in Table 1. It has been previously suggested that large negative values of this quantity result for hydrophilic co-solvents that are good electron-pair donors. Conversely, hydrophobic co-solvents that are poor electron-pair donors should have positive values, *i.e.* should self-aggregate. These expectations are borne out qualitatively by the data in Table 1, although the multivariate expression previously reported [10] agrees with the extended data only in view of the large errors assigned to the coefficients. It must also be recognized that the molar volumes of the co-solvents should play a role in the magnitude of G^{∞}_{SS}, since in an ideal system $G^{\infty,\mathrm{id}}_{\mathrm{SS}} = RT\kappa_T - V^{\circ}_{S}$. Thus, for *HMPT* $G^{\circ}_{\mathrm{SS}} = -370\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ is understandable in view of its large electron-pair donicity and molar volume, as is $G^{\infty}_{\mathrm{SS}} = 155\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ for MeCN in view of its small molar volume and poor donicity. Some of the $G^{\infty}_{\mathrm{SS}}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ entries in Table 1, however, are probably erroneous (*i*-PrOH (+40), 2-BuOEtOH (< −500), and *FA* (>600)), and can be ascribed to inaccuracies in the double derivative of G^E at the limiting concentrations.

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