Diffusion Coefficients for the Binary System Glycerol + Water at 25 °C. A Velocity Correlation Study

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Diffusion coefficients for the binary system glycerol + water have been studied at 25 °C. Accurate mutual diffusion coefficients have been measured by the Taylor dispersion and Gouy interferometric techniques. Intradiffusion coefficients of both components have been measured by the pulsed gradient spin−echo− Fourier transform NMR technique. The collected diffusion coefficients have been combined with data of water excess chemical potential present in the literature to calculate the velocity correlation coefficients. The results have been interpreted in terms of molecular interactions.

Introduction

This research is part of a program devoted to the study of the effects of glycerol on the micellization of surfactants in aqueous solution, with the aim to discriminate between direct glycerol−surfactant interaction and indirect solvent− mediate effects. In the preliminary phase of this study, the transport properties of the binary system glycerol (2) + water (1) have been investigated, and the results are summarized in the present work. Because of some discrepancies between different data sets present in the literature, mutual diffusion coefficients, D_{12}, have been remeasured, using the Taylor dispersion technique at infinite dilution of glycerol, and the Gouy interferometric technique for the values over the whole composition range. Furthermore, intradiffusion coefficients of both components, D_1 and D_2, over the whole composition range have been measured by the pulsed gradient spin−echo−Fourier transform (PGSE− FT) NMR technique; these data are not present in the literature, to the authors' knowledge.

The data are discussed in terms of velocity correlation coefficients (VCCs) that give information on the molecular interactions in solution and show how the macroscopic transport properties are affected by the solution structure at the molecular scale.

Experimental Section

Materials. Glycerol purchased from Sigma Chemical Co. (purity > 99%) was used without further purification. For mutual diffusion coefficients, all solutions were prepared by mass using double-distilled water. For intradiffusion measurements, two sets of measurements were made, the former using double-distilled water and the latter using heavy water (Sigma Chemical Co., purity > 99.9%), see below for further discussion.

Mutual Diffusion Measurements. The mutual diffusion coefficient extrapolated to infinite glycerol dilution was determined by the Taylor dispersion method, which is widely described in the literature.[1] This method, although less precise than the interferometric methods, is fast, sufficiently accurate, and permits investigation of very dilute solutions. Samples of three aqueous solutions with decreasing glycerol mole fraction ($1 \times 10^{-6} < x_2 < 3 \times 10^{-6}$)

Table 1. Mutual Diffusion Data for the System Glycerol (2) + Water (1) at 25 °C[a]

x_2	$10^9 D_{12}/\mathrm{m^2 s^{-1}}$	B	$10^9 D_{\mathrm{T}}/\mathrm{m^2 s^{-1}}$
0.0000	*1.025*[b]	1.000	1.025
0.0213	0.865[c]	1.069	0.799
0.0773	0.604[c]	1.197	0.505
0.1636	0.395[c]	1.280	0.309
0.3134	0.214[c]	1.267	0.169
0.6377	0.0779[c]	1.252	0.0622
1.0000	*0.014*[d]	1.000	0.014

[a] x_2 is the glycerol mole fraction, D_{12} is the mutual diffusion coefficient, B is the thermodynamic factor in the mole fraction scale, and D_{T} is the thermodynamic diffusion coefficient. [b] Datum obtained by the Taylor dispersion technique. [c] Data obtained by the Gouy interferometric technique. [d] Datum extrapolated through eq 2.

were injected into a water stream flowing in a long capillary tube. The combined effect of convection and diffusion generated the nearly-Gaussian concentration profile of the pulse at the tube outlet, as monitored by a differential refractometer detector. Details of the equipment, procedure, and mathematical treatment of experimental results have been reported.[2] The limiting value was calculated by extrapolating the experimental D_{12} data to $x_2 \rightarrow 0$, obtaining $(D_{12})_{x_2 \rightarrow 0} = (1.025 \pm 0.015) \times 10^{-9}$ m²·s⁻¹.

Mutual diffusion coefficients were measured, at various glycerol concentrations, with a Gouy diffusiometer[3,4] using a two-lens apparatus in which parallel light passing through a single-channel cell generates the fringe pattern on its focus. The initial boundary was formed with the siphoning technique. Details of the equipment and procedure have been reported.[5] The mutual diffusion coefficients, D_{12}, were calculated using a series of programs well described in the literature.[6,7] The experimental data are collected in Table 1. The experimental uncertainty is within (0.1 to 0.2) %.

Intradiffusion Measurements. Intradiffusion coefficients of both water, D_1, and glycerol, D_2, were measured using the PGSE−FT NMR method.[8,9] Experiments were carried out on a Varian FT 80 NMR spectrometer operating in the ¹H mode, equipped with a pulsed magnetic field gradient unit, specially made by Stelar (Mede, Italy). Details of the equipment, procedure, and mathematical treatment of experimental results have been reported.[5]

The PGSE NMR method requires the presence of a deuterated substance as reference in the measurement

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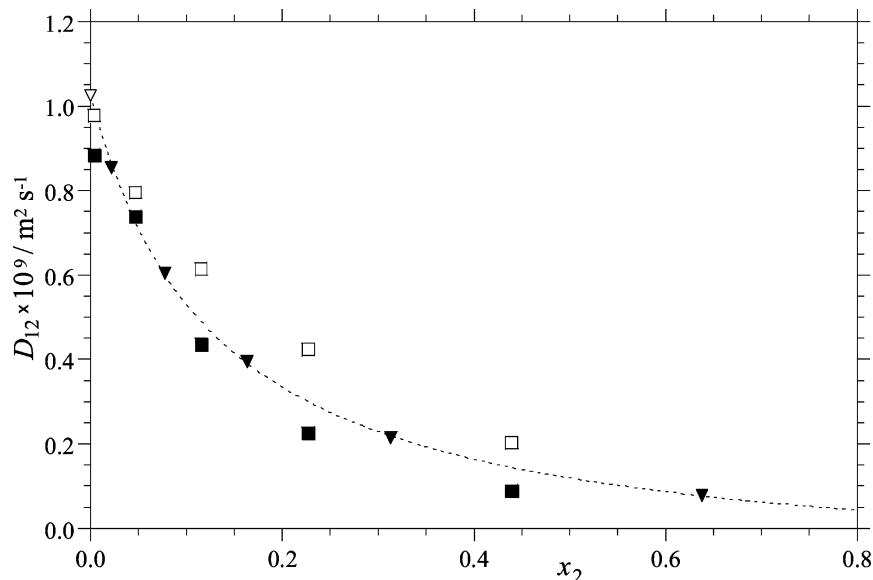
Figure 1. Mutual diffusion coefficients of glycerol + water solutions at 25 °C: $\triangledown$, $(D_{12})_{x_2 \to 0}$ measured by the Taylor dispersion technique, this work; $\blacktriangledown$, D_{12} measured by the Gouy interferometric technique, this work; $\blacksquare$, Nishijima and Oster, 1960; $\square$, Ternström et al., 1996; dotted line, interpolation of the data of this work (eq 2).

Table 2. Intradiffusion Data for the System Glycerol (2) + Water (1) at 25 °C[a]

x_2	$10^9 D_2/\text{m}^2\text{s}^{-1}$	$10^9 D_{OH}/\text{m}^2\text{s}^{-1}$	$10^9 D_1/\text{m}^2\text{s}^{-1}$
Measured in D_2O			
0.0000			1.872^b
0.0051	0.74	1.68	1.69
0.0060	0.71	1.66	1.67
0.0089	0.68	1.56	1.58
0.0113	0.64	1.53	1.54
0.0128	0.63	1.47	1.49
0.0190	0.58	1.35	1.37
0.0339	0.49	1.05	1.09
0.0432	0.43	0.97	1.01
0.0701	0.35	0.71	0.76
0.0979	0.26	0.58	0.64
0.1503	0.17	0.38	0.43
0.2840	0.092	0.179	0.23
0.3768	0.065	0.110	0.150
Measured in H_2O			
0.1269	0.25	0.59	0.67
0.2160	0.148	0.31	0.38
0.3541	0.093	0.157	0.21
0.4288	0.075	0.115	0.159
0.5403	0.048	0.070	0.112
0.7150	0.022	0.036	0.054
0.8028	0.0155	0.0188	0.039
0.9100	0.0113	0.0130	0.024
1.0000	0.0025		0.014^c

^{a} x_2 is the glycerol mole fraction, D_2 is the glycerol intradiffusion coefficient, D_{OH} is the intradiffusion coefficient experimentally measured by following the OH ^{1}H NMR peak, and D_1 is the water intradiffusion coefficient. ^{b} Datum from ref 14. ^{c} Datum extrapolated through eq 4.

region. In the present work, two different methods have been alternatively used. In the first method, the measurements were carried out on solutions prepared with undeuterated water, using the coaxial tubes (Wilmad model WGS-5BL) with C_6D_6 as an external reference and lock. However, in dilute solutions, the water signal can hinder the glycerol signal. In the second method, D_2O is used as solvent. This procedure, enhancing the intensity of the glycerol signal, allows the analysis of very dilute solutions.

In the same measurement, it is possible to determine both glycerol and water intradiffusion coefficients, D_2 and D_1, respectively. D_2 is determined by following the CH_2 NMR signal ($\delta = 3.7$), while D_1 is determined by following

the NMR signal of OH protons ($\delta = 4.7$); actually, both water and glycerol contribute to the latter signal. Since the proton exchange between glycerol OHs and water is much faster than the single spin$-$echo sequence, by following the hydroxyl signals a D_{OH} values is determined, which is a mean value that can be split between glycerol and water contributions according to the expression

$$D_{OH} = \frac{2x_1}{3x_2 + 2x_1} D_1 + \frac{3x_2}{3x_2 + 2x_1} D_2 \quad (1)$$

where x_1 and x_2 are the mole fractions of water and glycerol, respectively, and the coefficients 2 and 3 take into account the different number of OH groups in the water and glycerol molecules. Values of D_1 can be calculated from eq 1. The measured D_2 and D_{OH} and the computed D_1 values are collected in Table 2. The experimental uncertainty is within $(3-4)$ %.

Experimental Results

Mutual diffusion coefficients, D_{12}, measured in this study for the glycerol + water system are shown in Figure 1, compared with other measurements' sets found in the literature. The values obtained by the Gouy interferometric technique are substantially higher than those obtained by Nishijima and Oster,[10] using the interferometric micro-diffusion method, and lower than those obtained by Ternström et al.,[11] using the holographic interferometry. No evident reason for these discrepancies can be found; it should be pointed out that the Gouy interferometry is generally more accurate than other experimental techniques employed in the past. D_{12} data obtained by the Gouy interferometry in this study are well fitted by the relation

$$D_{12} \times 10^9/\text{m}^2 \cdot \text{s}^{-1} =$$
$$\frac{(1.024 \pm 0.010) - (0.91 \pm 0.05)x_2}{1 + (7.5 \pm 0.3)x_2} \pm 0.004 \quad (2)$$

The limiting value for $x_2 \to 0$, $(D_{12})_{x_2 \to 0} = (1.024 \pm 0.010) \times 10^{-9}$ m$^2 \cdot$s^{-1}, is in very good agreement with the datum obtained by the Taylor dispersion technique, $(D_{12})_{x_2 \to 0} =$
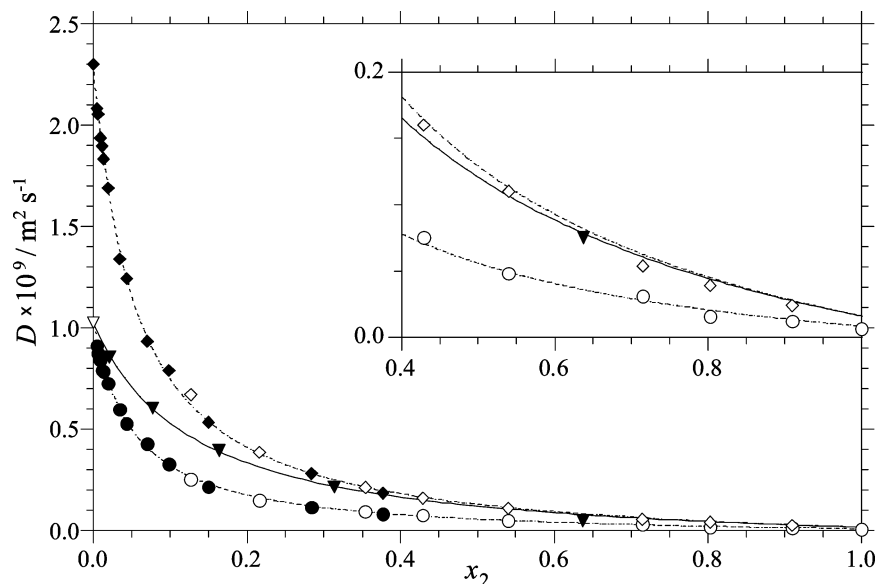
Figure 2. Comparison of mutual diffusion and intradiffusion coefficients of glycerol (2) + water (1) solutions at 25 °C: $\diamond$, D_1 in light water; $\blacklozenge$, D_1 in heavy water multiplied by the factor 1.23; $\circ$, D_2 in light water; $\bullet$, D_2 in heavy water multiplied by the factor 1.23; $\triangledown$, $D_{12}{}^\infty$ measured by the Taylor dispersion technique; $\blacktriangledown$, D_{12} measured by the Gouy interferometric technique; solid line, interpolation of the D_{12} data (eq 2); dotted line, interpolation of the D_1 and D_2 data (eqs 4−5). The inset shows a vertical expansion of the data in the more concentrated concentration range.

$(1.025 \pm 0.015) \times 10^9$ m$^2\cdot$s^{-1}. This agreement lends weight to the correctness of the present results.

Intradiffusion coefficients are affected by the solvent isotope substitution, and consequently, a correction is needed to obtain the values in light water from the corresponding values obtained in D$_2$O. Goldammer and Hertz[12] proposed to multiply the experimental coefficients measured in D$_2$O by the factor 1.23, which is the ratio of normal and deuterated water self-diffusion coefficients, as well as the reciprocal of the ratio of their viscosities. In principle, this correction neglects the possible differences in the interactions of these two solvents with the solute. In fact, D$_2$O is slightly more structured than H$_2$O,[13] so that the hydrophobic effect and the formation of hydrogen bonds could be favored. As a consequence, the ratio of solute intradiffusion coefficients in D$_2$O and H$_2$O can also depend on the solute nature and concentration. Intradiffusion coefficients of both water, D_1, and glycerol, D_2, are shown in Figure 2. The data obtained in heavy water, multiplied by the factor 1.23, are in very good agreement with the data obtained in light water, confirming the validity of the correction proposed by Goldammer and Hertz. Inspection of Figure 2 clearly shows that, as predicted by theoretical considerations,[4] D_2 tends to D_{12} in the limit of $x_2 \rightarrow 0$ and D_1 tends to D_{12} for $x_2 \rightarrow 1$, i.e.

$$(D_2)_{x_2\rightarrow 0} = (D_{12})_{x_2\rightarrow 0} \quad \text{and} \quad (D_1)_{x_2\rightarrow 1} = (D_{12})_{x_2\rightarrow 1} \quad (3)$$

D_1 data obtained both in heavy water, multiplied by 1.23, and in light water and are well fit by a single equation

$$D_1 \times 10^9/\text{m}^2\cdot\text{s}^{-1} = \frac{2.299 - (1.99 \pm 0.15)x_2}{1 + (18.2 \pm 0.3)x_2} \pm 0.02 \quad (4)$$

where $D_1{}^* = 2.299 \times 10^{-9}$ m$^2\cdot$s^{-1} is the water self-diffusion at 25 °C.[14] Analogously, D_2 data are well fit by a single equation

$$D_2 \times 10^9/\text{m}^2\cdot\text{s}^{-1} = \frac{1.025 - (0.81 \pm 0.09)x_2}{1 + (20.9 \pm 0.6)x_2} \pm 0.01 \quad (5)$$

where it has been imposed that, in the limit of $x_2 \rightarrow 0$, $D_2 = D_{12} = 1.025 \times 10^9$ m$^2\cdot$s^{-1}, as determined by the Taylor dispersion technique.

Discussion

The actual driving forces for mutual diffusion are the chemical potential gradients, which are related through the Gibbs−Dühem equation. However, to handle diffusive processes, it is much easier, in practice, to use Fick's law that relates solute fluxes to concentration gradients, i.e., to directly measurable quantities. As a result of this choice, the mutual diffusion coefficient is given by the product of an equilibrium thermodynamic factor, B, that accounts for the change of chemical potential with concentration, and a mobility factor, M, that depends on size of the diffusing molecules, mechanism of interchange of molecules during the diffusion process, viscosity, etc. In a binary system

$$D_{12} = M_1 B_1 = M_2 B_2 \quad (6)$$

B can be expressed as a function of mole fraction, according to the Laity notation[15]

$$B_2 = 1 + \frac{\text{d} \ln f_2}{\text{d} \ln x_2} = 1 + \frac{\text{d} \ln f_1}{\text{d} \ln x_1} = B_1 = B \quad (7)$$

where x_i and f_i are the mole fraction and the rational activity coefficient of component i, respectively. In this way, a unique mobility term is defined for both the components, $M_2 = M_1 = D_T$, called the thermodynamic diffusion coefficient. Equation 7 can be rearranged as

$$B = 1 + \frac{x_i}{RT} \frac{\text{d}\mu_i^E}{\text{d}x_i} \quad (8)$$

where

$$\mu_i^E = RT \ln f_i \quad (9)$$
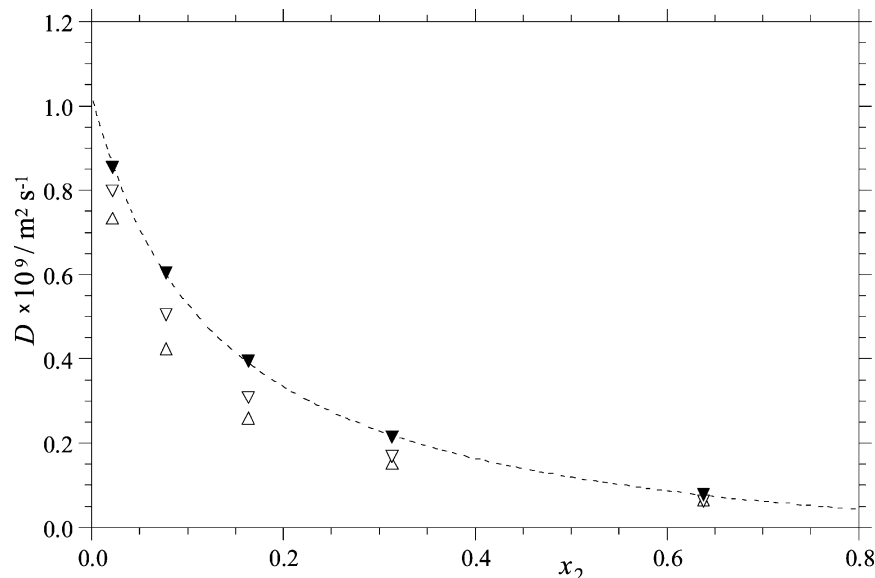
is the excess chemical potential.

Figure 3. Comparison of mutual diffusion and thermodynamic diffusion coefficients of glycerol + water solutions at 25 °C: ▼, D_{12} measured by the Gouy interferometric technique; ▽, D_T computed from the D_{12} and B values; △, D_T computed through eq 12; dotted line, interpolation of the D_{12} data (eq 2).

Concerning the glycerol + water mixtures, Marcus[16] found the excess chemical potential of water, determined by To et al.,[17] to be well fit by the following relation

$$\mu_1^E/J\cdot mol^{-1} = -4437x_2^2 + 9677x_2^3 - 9187x_2^4 + 2002x_2^5 \quad (10)$$

where x_2 is the mole fraction of glycerol. The thermodynamic factor can be straightforwardly computed from eqs 8 to 10, obtaining

$$B = 1 + 3.580x_2 - 15.29x_2^2 + 26.53x_2^3 - 18.86x_2^4 + 4.038x_2^5 \quad (11)$$

The uncertainty on B cannot be evaluated in the absence of quoted uncertainties on eq 10.

From the knowledge of D_{12} and B, the thermodynamic diffusion coefficient, D_T, can be computed, see Table 1. D_{12} and D_T trends, compared in Figure 3, are very similar; particularly, both of them decrease with x_2. The corresponding change in the B values is much lower, see Table 1. This gives evidence that the mobility contribution prevails on ruling the behavior of diffusion coefficients. A very similar behavior was found for the aqueous mixtures of ethylene glycol oligomers.[18] An opposite effect can be found in some systems, such as surfactant solutions, where both D_{12} and B decrease with solute concentration while mobilities increase.[19,20]

For binary systems that do not present large deviation from ideality, D_T can be directly related to the intradiffusion coefficients of both components through the relation[4]

$$D_T = x_1D_2 + x_2D_1 \quad (12)$$

Inspection of Figure 3 shows that, for the system glycerol + water, the D_T values computed through eq 12 are in fair agreement with those computed from the experimental D_{12} and B values. However, especially for $x_2 < 0.3$, a sensible difference can be detected, indicating significant deviations from ideality. In this connection, it is worth noting that Stokes and Robinson[21] used the equilibrium osmotic coefficient data to infer the association between water and glycerol molecules.

In the present work, to achieve a deeper insight into the system characteristics, the VCCs[22,23] have been computed. VCCs are more sensitive to specific interactions than the experimental diffusion coefficients and allow an analysis from the microscopic point of view.[24,25]

The time integrals over velocity correlation functions give access to a more direct kinetic interpretation of observed physical quantities. The intradiffusion coefficient D_i of component i can be defined as[26]

$$D_i = \frac{1}{3} \int_0^\infty \langle v_s^i(0)v_s^i(t) \rangle \, dt \quad (13)$$

where v_s^i is the velocity of a single particle numbered s of component i at times 0 and t, respectively. The pointed brackets indicate the ensemble average.

The velocity correlation coefficients reflect the correlation in the motion of two different particles s and r

$$f_{ij} = \frac{N}{3} x_j \int_0^\infty \langle v_s^i(0)v_r^j(t) \rangle \, dt \quad (14)$$

where N is the total number of particles in the system. Equation 14 characterizes the motion correlation between different particles, which can be of the same ($i = j$) or of different ($i \neq j$) components.

The VCCs can be expressed as a function of the experimental quantities D_1, D_2, and D_{12}[21]

$$f_{ij} = -D_{12} \frac{M_1M_2}{(x_1M_1 + x_2M_2)^2B} x_j \qquad i \neq j \quad (15)$$

$$f_{ii} = D_{12} \frac{M_j^2 x_j}{(x_1M_1 + x_2M_2)^2B} - D_i \quad (16)$$

where M_i is the molecular weight of component i and B is the thermodynamic factor in the mole fraction scale, as defined by eq 7. An indication of strong molecules self-aggregation is given by the condition
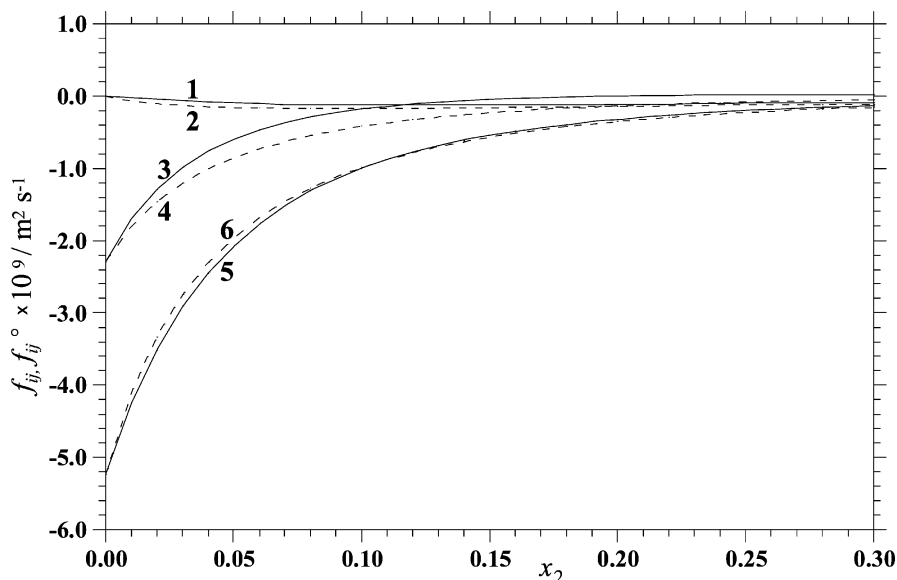
$$f_{ii} > 0 \qquad i = 1,2 \quad (17)$$

Figure 4. Velocity cross-correlation factors for the system glycerol (2) + water (1) at 25 °C: **1**, f_{22}; **2**, $f_{22}°$; **3**, f_{11}; **4**, $f_{11}°$; **5**, f_{21}; **6**, $f_{21}°$.

However, f_{11} and f_{22} have a tendency to be negative quantities even in the case of weak molecules self-association.[27] Consequently, a more sensitive criterion has to be introduced. According to Hertz's approach,[27] formulas for standard velocity cross correlation coefficients $f_{ij}°$ can be derived by using the law of effective linear momentum conservation and applying the ideal mixing rule

$$f_{ij}° = -\frac{M_i x_j}{(x_1 M_1 + x_2 M_2)} D_i (1 + x_i P_{ij}) \qquad i \neq j \quad (18)$$

$$f_{ii}° = -\frac{M_i x_i}{(x_1 M_1 + x_2 M_2)} D_i (1 - x_j P_{ij}) \qquad (19)$$

where

$$P_{ij} = \frac{M_j D_j}{M_i D_i} - 1 \qquad (20)$$

The quantities $f_{ij}°$ and $f_{ii}°$ are representative of a fictitious ideal reference system formed by noninteracting components; in their computation, the mutual diffusion coefficient, accounting for the global motion of the species in the system, is not involved. The relationship between the f_{ii} and $f_{ii}°$ coefficients plays the role of indicator for the molecular association effects. As discussed in detail elsewhere,[23,24] molecular association leads to more correlated motions than those expected for an "ideal" system. The general association criterion is

$$f_{ii} > f_{ii}° \quad i = 1,2 \qquad (21)$$

The VCCs and the corresponding standard correlation coefficients for the glycerol (2) + water (1) mixtures are reported in Figure 4. The uncertainties on the intradiffusion coefficients, (3−4) %, causes an average uncertainty on the VCCs values of 0.01×10^9 m^2·s^{-1}. In the absence of the quoted B uncertainty, its propagation on the f_{ii} and f_{12} uncertainties cannot be evaluated. However, it should be noted that, to invalidate the discussion reported in the following, a B uncertainty of at least 50% would be needed, which seems far above what is reasonable from inspection of literature data.[16,17]

Inspection of Figure 4 shows that the f_{ii} values are always negative, tending to become null with increasing glycerol mole fraction. Overall, the trends of all the f_{ii} coefficients are not far from those of the corresponding $f_{ii}°$, which implies a behavior of the system close to ideality. However, a deeper inspection of Figure 4 shows that f_{11} is slightly larger than $f_{11}°$. This difference, which exceeds the uncertainties on the f_{11} and $f_{11}°$ values, indicates a weak enhancement of the water self-association. Interpretation of this evidence, and its connection with molecular interactions in solution, is not straightforward. It could be in principle ascribed to a weak hydrophobic effect of the CH and CH$_2$ groups of glycerol. However, the hydrophobic effect usually leads to an enhancement of the solute−solute interactions ($f_{22} > f_{22}°$), which is not true in the present case. In the past, calorimetric data on the glycerol + water system have been interpreted in terms of a "hydrophilic structure making" effect of glycerol.[28] The VCCs analysis seems to support this interpretation, and consequently, the structuring effect of glycerol on water molecules could be interpreted in terms of an enhancement of the interaction among the water molecules which hydrate the OH groups of the solute.

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