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Dynamic properties of aqueous solutions of ethylene glycol oligomers as measured by the pulsed gradient spin-echo NMR technique at 25 °C

Luigi Ambrosone,[a] Gerardino D'Errico,[b] Roberto Sartorio[b] and Lucia Costantino[b]

[a] *Università del Molise DISTAAM, via Tiberio, 21A 86100 Campobasso, Italy*

[b] *Dipartimento di Chimica Università Federico II, Via Mezzocannone 4, 80134 Napoli, Italy*

Self-diffusion coefficients for binary systems containing water and an oligomer of ethylene glycol [HO—(CH_2CH_2—O)$_n$H, $n = 1$–5], have been measured at 25 °C in the whole concentration range by the pulsed gradient spin-echo NMR technique. Upon adding oligomer to pure water, both the oligomer and water self-diffusion coefficients decrease until a certain composition is reached, after which they remain approximately constant. This evidence is interpreted in terms of molecular interactions, especially hydrogen-bond formation. A relation between mutual and self-diffusion coefficients for these systems is found and commented upon.

Introduction

In recent years, Ambrosone *et al.*[1] have studied the thermodynamic and dynamic properties of non-ionic polyethoxylated surfactants with short hydrophobic tails. The aim of this work is to obtain more information on the interactions between the hydrophilic parts of these molecules.

An amphiphilic molecule possesses at the same time a polar group and a non-polar group. These molecules can, in aqueous solution, self-associate into aggregates called micelles,[2,3] where the contact between water and hydrocarbon is greatly reduced while the polar groups maintain their hydration. When considering the formation of a micellar structure in a surfactant system, the main contributions to the free energy are the elimination of unfavourable hydrocarbon–water contacts, the head-group interactions, and the inter-aggregate interactions.[4,5] In dilute micellar solutions, where inter-micellar interactions are of minor importance, the micellar form that gives the lowest free energy depends on the relative size of the alkyl chain and the head-group. Repulsion between the head-groups give stability in the order sphere > rod > disc, while elimination of hydrocarbon–water contacts gives stability in the order disc > rod > sphere.

For poly(ethylene oxide) surfactants [$C_nH_{2n+1}(OCH_2CH_2)_mOH$, C_nE_m], both the size of the alkyl chain and the head-group can be varied making this class of surfactants suitable for a systematic study. Since each ethylene oxide unit is only weakly polar, more units are required to produce a functional surfactant. The micelles formed by these surfactants are characterised by the presence of a palisade layer whose molecular organisation is similar to that of a concentrated poly(ethylene)glycol–water solution.

For this reason in this paper we analyse the spectroscopic results for the binary aqueous solutions of the first five oligomers of ethyleneglycol in the entire composition range.

In particular, both the oligomer and water self-diffusion coefficients have been determinated by the pulsed gradient spin-echo (PGSE) NMR method.

The experimental results are interpreted in terms of molecular interactions.

At the same time, we show and comment on how the self-diffusion data are related, for these systems, to the mutual diffusion data.

Experimental

Materials

The chemicals ethylene glycol [$(EG)_1$; Aldrich, purity 99%, $M_w = 62.07$], di(ethylene glycol) [$(EG)_2$; Aldrich, purity 99+%, $M_w = 106.12$], tri(ethylene glycol) [$(EG)_3$; Aldrich, purity 99%, $M_w = 150.17$], tetra(ethylene glycol) [$(EG)_4$; Aldrich, purity 99%, $M_w = 194.23$], penta(ethylene glycol) [$(EG)_5$; Aldrich, purity 99%, $M_w = 238.28$] were used without further purification. Doubly distilled degassed water was always used to prepare solutions.

Self-diffusion measurements

The self-diffusion coefficients were obtained by using the FT PGSE technique.[6,7] A spectrometer operating in the ^{1}H mode at 80 MHz, and equipped with a pulsed magnetic field gradient unit, specially made by Stelar, was employed. The temperature was controlled to within ±0.1 °C with a Stelar variable temperature controller, model VTC87. The individual spin-echo peak amplitude $\boldsymbol{A}$ for a given line follows the equation:

$$\boldsymbol{A} = A_0 \exp\left[-\gamma^2 g^2 D \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \quad (1)$$

where A_0 is a constant for a given set of experimental conditions, γ is the gyromagnetic ratio of the proton, D is the self-diffusion coefficient of the species responsible for the NMR signal, g is the strength of the gradient applied, Δ and δ are time parameters in the pulse sequence. The time between the 180° and 90° pulses, Δ, was kept constant at 120–140 ms for adjusting the J modulation effects in proton-coupled systems.[6] The duration of the two gradient pulses was varied over a suitable range to observe the decay of the spin-echo signal $\boldsymbol{A}$. The decay of $\boldsymbol{A}$ as a function of δ was fitted to the above equation by a non-linear least-squares routine. The experimental errors were generally less than 5% of the determined self-diffusion coefficient. The magnitude of g, needed in our calculations, was determined from the known self-diffusion coefficient of pure water.[8]

The traditional method involves the use of solutions with a completely deuteriated component so that the other component can be studied separately. This procedure introduces

Table 1 Self-diffusion coefficients of water(1)–oligomer of ethylene glycol(2) at 25 °C

X_2	ϕ_2[a]	$D_1/10^{-5}$ cm^2 s^{-1}	$D_{OH}/10^{-5}$ cm^2 s^{-1}	$D_2/10^{-5}$ cm^2 s^{-1}
		monomer		
0.0000	0.0000	2.299	2.299	1.166[b]
0.0253	0.0982	2.263	2.232	1.030
0.0514	0.1354	1.736	1.695	0.938
0.1000	0.2511	1.487	1.415	0.772
0.2000	0.4328	0.987	0.887	0.487
0.3000	0.5704	0.751	0.633	0.359
0.3999	0.6766	0.571	0.447	0.262
0.4996	0.7579	0.422	0.315	0.207
0.7022	0.8836	0.34	0.205	0.147
0.8041	0.9303	0.30	0.152	0.116
0.9056	0.9718	0.27	0.154	0.141
1.0000	1.0000		0.106	
		dimer		
0.0000	0.0000	2.299	2.299	0.898[b]
0.0299	0.1300	1.671	1.640	0.641
0.0498	0.2047	1.526	1.476	0.524
0.1095	0.3852	0.842	0.785	0.322
0.2223	0.6031	0.474	0.406	0.169
0.3000	0.6981	0.381	0.307	0.135
0.3977	0.7834	0.299	0.219	0.0991
0.4979	0.8469	0.286	0.184	0.0807
0.6007	0.8950	0.22	0.133	0.0725
0.6904	0.9268	0.22	0.118	0.0679
0.8017	0.9579	0.21	0.0834	0.0524
0.9006	0.9815	0.16	0.0613	0.0500
1.0000	1.0000		0.0422	
		trimer		
0.0000	0.0000	2.299	2.299	0.752[b]
0.0300	0.1602	1.490	1.460	0.484
0.0497	0.2500	1.114	1.076	0.354
0.0988	0.4374	0.669	0.622	0.197
0.1998	0.6538	0.382	0.325	0.0966
0.3017	0.7703	0.268	0.207	0.0672
0.4037	0.8406	0.260	0.176	0.0511
0.4983	0.8859	0.228	0.134	0.0385
0.6028	0.9253	0.20	0.101	0.0369
0.6998	0.9516	0.19	0.0821	0.0350
0.8013	0.9696	0.20	0.0671	0.0351
0.8998	0.9849	0.19	0.496	0.0334
1.0000	1.0000		0.0341	
		tetramer		
0.0000	0.0000	2.299	2.299	0.658[b]
0.0234	0.1524	1.369	1.345	0.357
0.0510	0.3012	0.949	0.912	0.220
0.0909	0.4808	0.533	0.497	0.139
0.1667	0.6628	0.344	0.300	0.0785
0.2852	0.8035	0.196	0.152	0.0426
0.3745	0.8594	0.133	0.0979	0.0392
0.4428	0.8913	0.129	0.0861	0.0321
0.5421	0.9315	0.123	0.0732	0.0312
0.6005	0.9513	0.13	0.0695	0.0313
0.7510	0.9717	0.13	0.0552	0.0301
0.8000	0.9763	0.13	0.0488	0.0292
0.9004	0.9910	0.13	0.0383	0.0283
1.0000	1.0000		0.0283	
		pentamer		
0.0000	0.0000	2.299	2.299	0.583[b]
0.0279	0.2129	1.195	1.170	0.299
0.0493	0.3415	0.808	0.777	0.186
0.1003	0.5610	0.422	0.387	0.0786
0.1999	0.7583	0.138	0.117	0.0332
0.2992	0.8438	0.123	0.0939	0.0257
0.4033	0.8941	0.130	0.0876	0.0248
0.5048	0.9304	0.0987	0.0612	0.0245
0.7013	0.9667	0.13	0.0539	0.0211
0.8006	0.9809	0.09	0.0352	0.0210
0.8737	0.9913	0.10	0.0315	0.0209
1.0000	1.0000		0.0207	

[a] Data from ref. 38. [b] Extrapolated data.

some errors owing to the isotopic effect on the self-diffusion rate. That is, deuteriation of one component increases the viscosity of the system and decreases the diffusion rate of the other component. To eliminate this effect we performed self-diffusion measurements on the undeuteriated solution, using the double tubes Wilmad mod WGS-5BL with C_6D_6 (Aldrich, purity 99.96%, $M_w = 84.16$) for the external lock.

Results

The ^1H NMR spectra of the glycol aqueous solutions show two peaks. The first, due to the protons of CH_2CH_2O groups of the solute molecules, allows us to evaluate the solute self-diffusion coefficient, D_2. The second peak is due to the hydroxylic protons of both glycol and water. Supposing that proton exchange between solute and solvent is sufficiently rapid, the observed D_{OH} is given by:[9]

$$D_{OH} = pD_2 + (1 - p)D_1 \quad (2)$$

where p is the fraction of the glycol hydroxylic protons and D_1 is the self-diffusion coefficient of water in solution. At high oligomer concentration, the difference $D_{OH} - pD_2$ is small and very sensitive to experimental errors. The reproducibility was verified by repeating a single measurement several times. The results are collected in Table 1.

Discussion

Solute self-diffusion

When the self-diffusion coefficients, D_2, for different oligomers are plotted as a function of the mole fraction, x_2, all the oligomers show the same trend (see Fig. 1) For small solute concentrations, D_2 decreases very sharply as x_2 increases; then for x_2 larger than a certain composition, x_{2c}, D_2 tends to be insensitive to x_2. The water self-diffusion coefficient exhibits similar behaviour.

The concentration x_{2c} is different for each oligomer, corresponding roughly to one molecule of water per monomer unit. Good agreement is found between the present results and those of neutron scattering of poly(ethylene oxide) (PEO).[10] Our results can be rationalised in terms of solute chemical structure and different interactions in solution. To better understand these findings it is convenient to discuss the D_2 trend as a function of the mole fraction starting from the pure oligomers and ending at infinite dilution ($x_2 \to 0$). The pure oligomers have low mobilities themselves, caused by the presence of intermolecular hydrogen bonding. The solute aggregates set up a very extended network increasing the system rigidity. On dilution with water there is merely an interchange of hydrogen bonding between donor–acceptor molecules. Probably the most preferred interaction is the formation of hydrogen bonds between water and oligomers. For $x_2 > x_{2c}$ the water molecules are not able to significantly 'break' the oligomer network; thus the D_2 plateau is an indication of strong oligomer–oligomer associations. The presence of strong oligomer–oligomer interactions can be confirmed by comparing our results with those obtained by Kida and Uedaira[11] for methanol and acetic acid. In the methanol–water system a sharp minimum of D_2, at low concentration, is evident. However, the acetic acid–water mixture shows a broad and flat minimum at high concentration. The different behaviour is attributed to the ability of acetic acid to form trimers or higher 'associates'. The same argument can be applied to glycol oligomers. Furthermore, on the basis of these considerations we expect, in the concentrated region, small differences between the D_2 values of all oligomers. The experimental data are consistent with this expectation.

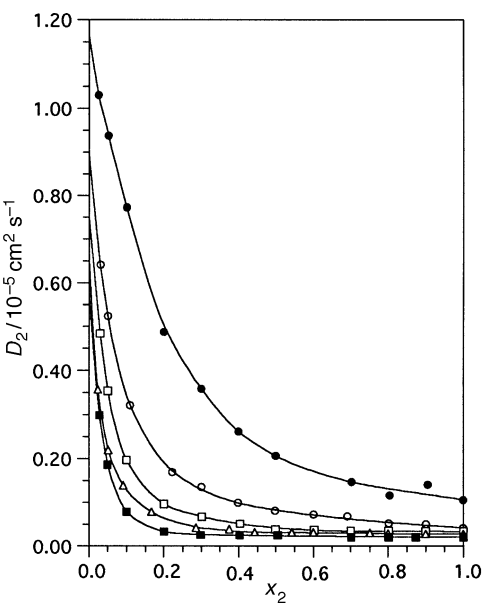

Fig. 1 Solute self-diffusion coefficients in water(1)–glycol oligomer(2) mixtures at 25 °C. Monomer (●); dimer (○); trimer (□); tetramer (△); pentamer (■).

As a unique exception the monomer does not display either a minimum or a plateau. The first evidence indicates two hydroxy groups to be sufficient to give strong solute–solute interactions; the second one shows that the absence of the ether oxygen prevents the formation of an extended network.

In dilute solution ($x_2 < x_{2c}$) the mobility of oligomer increases as water is added, indicating that the network is broken by the added water molecules. The rapid increase in this region may be attributed to strong solute–water hydrogen bonds. In these interactions, besides solute hydroxy groups, the ether oxygens are also involved. In fact, increasing the degree of oligomerisation, the hydroxy group content of each molecule decreases, but the $D_2(x_2)$ slope increases.

To study the solvent–solute interactions it is necessary to analyse the D_2 values at infinite dilution. As is evident from Fig. 1 the sharp slope makes the D_2 extrapolation to $x_2 = 0$ difficult. Fortunately when D_2 is plotted *versus* the volume fraction, ϕ_2, the extrapolation is easier. The results are reported in Table 1; they are in good agreement with those obtained by extrapolation from mutual diffusion data (*vide infra*).

For polymers, generally, the diffusion constants at infinite dilution are interpreted on the basis of Flory's[12] theory. According to this theory, the diffusion coefficient at infinite dilution, D_2^{∞}, is proportional to $M_w^{-(0.5+\beta)}$, where M_w is the molecular weight and β is a constant which varies from 0 to 0.1 when going from a θ solvent to a good solvent. When this relation is applied to our oligomers, $\beta = 0.01 \pm 0.01$ is found (see Fig. 2), indicating the absence in these systems of intramolecular interactions . The D_2^{∞} for samples containing high molecular weight PEO[13] show $\beta = 0.1$. We can then infer that for our substances the oligomer–solvent contacts are advantageous. These conclusions are in good agreement with those previously obtained by volumetric data.[14]

Mutual diffusion and self-diffusion

For multi-component systems the knowledge of mutual diffusion coefficients and their dependence on the concentration is of technical and scientific importance. These coefficients represent the rate at which concentration gradients approach their equilibrium values. It can be demonstrated that a single mutual coefficient, D^V, is sufficient, in a binary system, to describe this rate in the volume fixed reference frame.[15] The mutual diffusion process is a net transport of matter due to

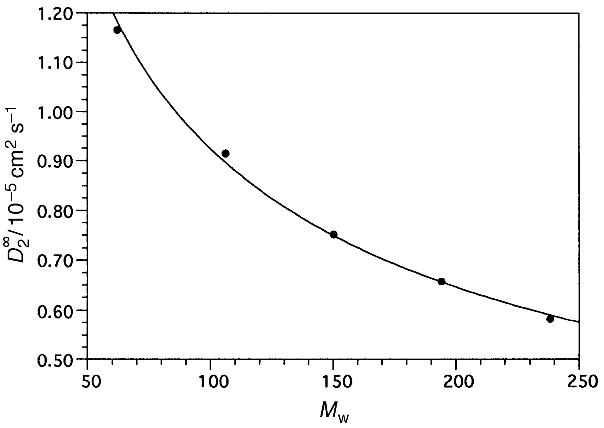

Fig. 2 D_2^∞ *versus* the molecular weight for the glycol oligomer

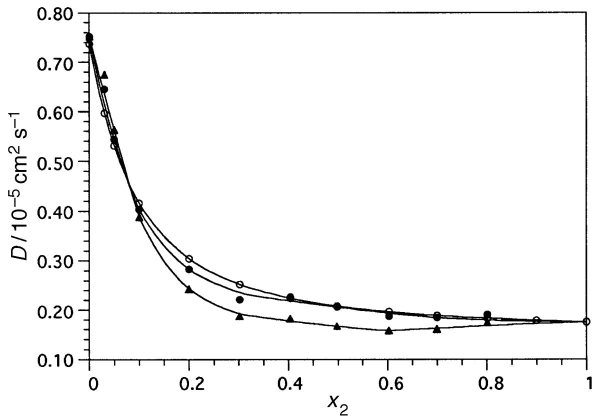

Fig. 3 Experimental mutual diffusion coefficients (○), and calculated mutual diffusion coefficient, according to the Darken equation (▲) and to our model (●) for the water(1)–tri(ethylene glycol)(2) system

the concentration gradient (or chemical potential gradient). On the contrary the self-diffusion describes the random Brownian motion of the molecules in a homogeneous system. The self-diffusion coefficient, D_2, is then a measure of the mobility of component i in the mixture and can be expressed in terms of the velocity correlation function of the molecules:

$$D_\alpha = \frac{1}{3}\int_0^\infty \langle \boldsymbol{u}_\alpha(t)\boldsymbol{u}_\alpha(0)\rangle_\infty \tag{3}$$

where $\boldsymbol{u}_\alpha(t)$ is the velocity of particle α at time t and $\langle\ldots\rangle_\infty$ denotes an ensemble average taken in the thermodynamic limit. The three coefficients D^V, D_1, D_2 of a binary solution are different except at infinite dilution of component i where self- and mutual diffusion are indistinguishable:

$$\lim_{x_i\to 0} D^V = D_i^\infty \tag{4}$$

Several liquid models indicate how D^V migth be expected to vary with concentration.[16–20] The most used one is the Darken relation:[16]

$$D^V = (x_2 D_1 + x_1 D_2)\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T,P} \tag{5}$$

where a_i is the activity of species i on the mole fraction scale. Although in some cases the Darken equation does provide a reasonable prediction for D^V, there are many cases where large deviations have been noted. The conditions for fulfilment of eqn. (5) can be expressed in terms of the frictional coefficient[21] ζ_{ij}:

$$\zeta_{11}\zeta_{12} = \zeta_{12}^2 \tag{6}$$

or the velocity time–correlation function (tcf)[22] f_{ij}:

$$f_{11} + f_{22} = 2f_{12} \tag{7}$$

but these conditions are not necessarily fulfilled even for a thermodynamically ideal solution. In general, the Darken equation is a good approximation for systems that show no tendency towards chemical interactions such as solvation and complex formation.[23]

Concerning our systems, D^V is known for the monomer,[24] dimer,[24] trimer[24,25] and tetramer.[25] Using the experimental data present in the literature,[26–28] we calculated $(\partial \ln a_1/\partial \ln x_1)_{T,P}$; these values, then were used to compute the mutual coefficient using eqn. (5). As expected, the calculated values fit the experimental data in the dilute region, where the thermodynamic factor is approximately unity. Unexpectedly, we found that, regardless of the thermodynamic factor, the relation:

$$D^V = \phi_2 D_1 + \phi_1 D_2 \tag{8}$$

reproduces the experimental data in the entire composition range with an average error of 3%. In Fig. 3 the results for the water–trimer mixtures are reported.

Furthermore, we found that for all of the oligomers, within the experimental error, a linear relation between D_1 and D_2 holds (see Fig. 4):

$$D_1 = qD_2 \tag{9}$$

It is interesting to consider the microscopic implications of the experimental evidence. To extract molecular information from the diffusion coefficients it is necessary to determine the contributions to these quantities due to the reference frame choice and the contribution due to interactions among molecules. With this purpose Rainieri and Timmerman[29] introduced the concept of microscopic reference velocity in tcf. Subsequently Rainieri and Friedman,[30] starting with Green–Kubo formulae for the phenomenological coefficient of irreversible thermodynamics, derived an expression for tcf, valid for every internal reference frame R. They obtained:

$$a_{[R],\alpha} D_\alpha + x_\alpha \sum_{\beta=1}^{n} a_{[R],\beta} D^d_{[R],\alpha\beta} = 0 \tag{10}$$

where $a_{[R],\alpha}$ is the weight factor (evaluated at equilibrium state) that defines the references velocities[31] and $D^d_{[R],\alpha\beta}$ is the distinct diffusion coefficient or cross correlation relative to internal reference frame R. $D^d_{[R],\alpha\beta}$ gives a measure of the correlation in terms of the joint correlation function for one particle of species α and a distinct particle β (the same as or different from species α). When eqn. (10) is written for a binary system relatively to a volume-fixed reference frame, where

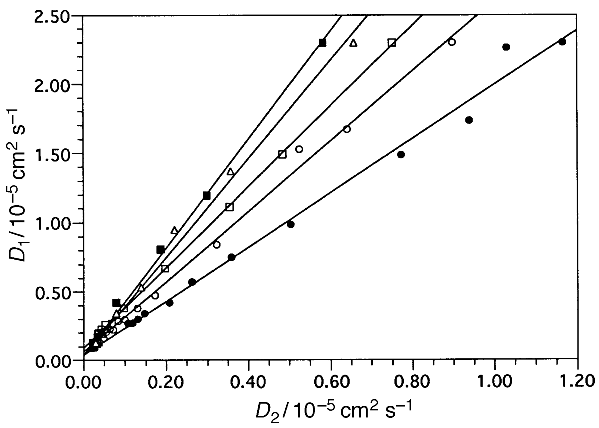

Fig. 4 Water self-diffusion coefficient *versus* oligomer self-diffusion in water(1)–glycol oligomer(2) mixtures at 25 °C. Monomer (●); dimer (○); trimer (□); tetramer (△); pentamer (■).

$a_{[R],\alpha} = \phi_a$, one finds:

$$\phi_\alpha D_\alpha + x_\alpha \sum_{\beta=1}^{2} \phi_\beta D^{d}_{[V],\alpha\beta} = 0 \tag{11}$$

We define, now, the new distinct coefficients:

$$\Gamma_{[V]\alpha,\beta} = \frac{v}{v_\alpha} D^{d}_{[V]\alpha\beta} \tag{12}$$

where v and v_a are the molar volume of solution and partial molar volume of component α. With the aid of eqn. (12), eqn. (11) can be solved easily with respect to D_α. When this result is substituted into eqn. (8), one obtains

$$-D^{V} = \Gamma_{21}\phi_1^2 + (\Gamma_{11} + \Gamma_{22})\phi_1\phi_2 + \Gamma_{12}\phi_2^2 \tag{13}$$

This relationship represents a combination of experimental [eqn. (8)] and theoretical [eqn. (11)] results; therefore a generic property of [eqn. (13)] is valid for eqn. (8) also. In particular we note that eqn. (13) is a quadratic negative semi-definite form. The general condition for this quadratic form to be always negative[32] is

$$\Gamma_{12} < 0, \qquad \Gamma_{21} < 0 \tag{14}$$

$$(\Gamma_{11} + \Gamma_{22})^2 - 4\Gamma_{12}\Gamma_{21} \leqslant 0 \tag{15}$$

Eqn. (14) is true for every system. This is a consequence of the fact that $D^{d}_{[V]12}$ is negative throughout the whole composition range no matter how strongly attractive the interactions between species 1 and 2 could be. However, Γ_{11} and Γ_{22} may be positive or negative depending on the nature of the interactions in solution. In other words only eqn. (15) is relevant for systems that verify eqn. (8). Nevertheless the experimental eqn. (9) imposes another constraint on the system.

When the experimental relation, eqn. (9), is introduced into eqn. (11) and eqn. (12) used, one has

$$q = \frac{\Gamma_{11}}{\Gamma_{21}} = \frac{\Gamma_{12}}{\Gamma_{22}} \tag{16}$$

or equivalently

$$\Gamma_{11}\Gamma_{22} = \Gamma_{12}\Gamma_{21} \tag{17}$$

Taking in account eqn. (12), eqn. (17) gives

$$D^{d}_{[V]11} D^{d}_{[V]22} = (D^{d}_{[V]12})^2 \tag{18}$$

which is formally similar to eqn. (6).

Substitution of eqn. (17) into eqn. (15) yields

$$\Gamma_{11} = \Gamma_{22} \tag{19}$$

or

$$D^{d}_{[V]11} = \frac{v_1}{v_2} D^{d}_{[V]22} \tag{20}$$

From this relationship it follows that the 1–1 and 2–2 cross correlations, per volume unit, are equal. This is evidence that solvent–solvent and solute–solute interactions are similar in entity and nature. Finally we observe that when eqn. (18)–(20) are combined a similar relationship between $D^{d}_{[V]11}$ and $D^{d}_{[V]12}$ or $D^{d}_{[V]22}$ and $D^{d}_{[V]12}$ may be found, indicating that all of the interactions in oligomer solutions are similar in nature. This is probably the reason for the peculiar behaviour observed in these systems.

Furthermore this behaviour might be fundamental to explain the formation and the structure of poly(ethylene oxide) alcohols micelles.

Water self-diffusion

The observed water self-diffusion coefficient is, for all of the systems analysed, lower than that of pure water (see Fig. 5). This difference is due to two effects: obstruction and hydration. The translational motion of the water molecules is obstructed by the presence of solute aggregates. When a water molecule is close to obstructing volumes, the change in its position during the diffusing time will be lower than in the absence of obstructing volumes, and this implies a decrease of the observed self-diffusion coefficient. Since the obstructing volume increases with the degree of oligomerisation in the water-rich region, where the obstruction effect is predominant, a decrease in water self-diffusion coefficient with n is expected. A corresponding increase in concentration dependence of this coefficient is also predominant. This is consistent with the experimental results. Regarding the hydration effect, since the solute volume increase linearly with the degree of oligomerisation, the solute–water interactions, for the different oligomers, may be compared if the obstruction term is eliminated. To do this the solute shape must be known. In the literature, expressions for the obstruction effect for systems with spherical and spheroidal obstructing particles have been given.[33] Results for different particle shapes indicate a small difference in obstruction for spherical and prolate shapes. Therefore, we will assume a spherical shape for solutions of the oligomers:

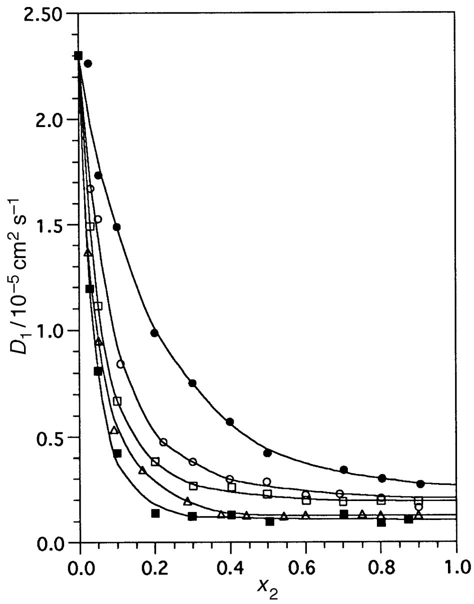

Fig. 5 Water self-diffusion coefficients in water(1)–glycol oligomer(2) mixtures at 25 °C. Monomer (●); dimer (○); trimer (□); tetramer (△); pentamer (■).

$$D_1^0 = (1 + \phi_2/2)D_1 \tag{21}$$

where D_1 is the observed self-diffusion coefficient, ϕ_2 the volume fraction (excluded volume) and D_1^0 the self-diffusion coefficient in the absence of obstruction. The results of eqn. (21) are plotted in Fig. 6 as a function of mole fraction of the solute, x_{mon} (referring to the mole fraction of 'monomeric' units).

Concerning the solvent–solute interactions, in the literature it has been noted, on the same mass basis, that longer chains release more heat than shorter ones in mixing with water for concentrated solutions.[34] Hence, one may assume some kind of synergism among the various ethoxy groups present in the same chain by hydration.[34] Kjellander and Florin[35] suggested cooperation of the water molecules hydrating neighbouring sites. This effect has to be expected in the dilute region. However, Biros *et al.*,[34] analysing the molar enthalpy of mixing, found that the synergism in question is due to cooperation of the binding sites themselves. In this case the cooperation is shown in the concentrated region.

Our results seem to confirm the latter theory. In fact the D_1 curves are different from each other even in the limiting value at $x_{mon} = 1$ (see Fig. 6). This reflects a difference in the translational water mobility occurring already for the first shell water molecule interacting with the chain. Furthermore, in the

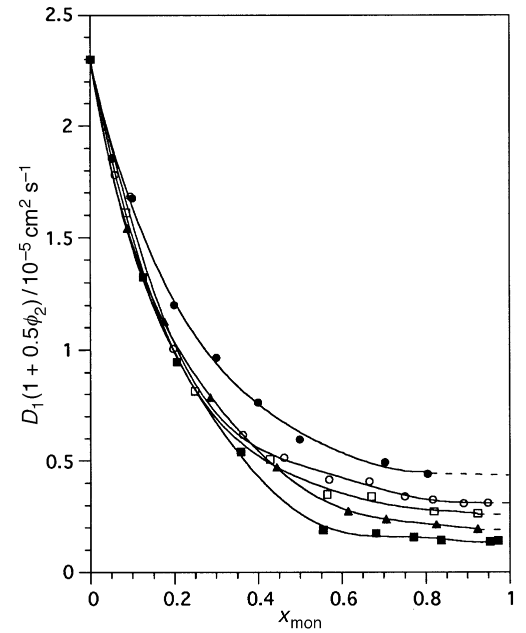

Fig. 6 Self-diffusion coefficients of water(1), corrected by the obstruction factor, in water(1)–oligomer of ethylene glycol(2) mixtures at 25 °C. Monomer (●); dimer (○); trimer (□); tetramer (△); pentamer (■).

dilute region these curves are coincident. The monomer is an exception, because it does not contain an ether oxygen.

The self-diffusion coefficient of water in the solution can also decrease by the formation of a water–solute complex. If the lifetime of this complex is sufficiently longer than the time of molecular reorientation, the water self-diffusion coefficient ought to be similar to that of the solute. However, for the systems under consideration (as shown in Fig. 7), the solvent self-diffusion coefficient, although it decreases sharply by one order of magnitude, is larger than the solute diffusion coefficient, even at high solute concentration where all the water molecules are in contact with the glycol oligomers. This is evidence that complexes with long lifetimes are absent.

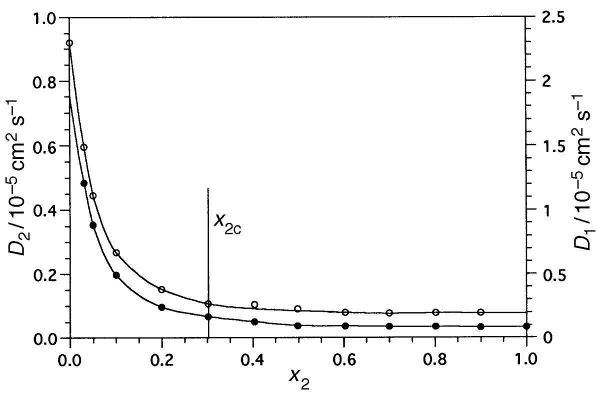

Fig. 7 Self-diffusion coefficients in water(1)–tri(ethylene glycol)(2) mixtures at 25 °C. D_1 (○); D_2 (●).

Indeed for aqueous solutions of poly(ethylene oxide) at high molecular weight a complex with three water molecules per monomer unit has been suggested.[36,37] In this case the solvent molecules are probably strongly trapped in the polymer coils.

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