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THERMODYNAMIC BEHAVIOUR OF SOME GLYCOL–WATER MIXTURES. EXCESS AND PARTIAL VOLUMES

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ABSTRACT

Densities of water–glycol (mono-, di-, tri- and tetraethyleneglycol) mixtures have been measured over the entire composition range at 298.15 K. Mixtures involving monoethyleneglycol (MEG) have also been studied at different temperatures from 308.15 to 288.15 K. Deviations, V^E, from ideal volumes of mixing have been calculated: negative values are observed for all systems. They increase with the number of ether functions present in the organic molecule; a slight dependence of V^E towards temperature has been shown in the water–MEG mixtures. Partial molal volumes have also been calculated for both components of each system; they exhibit an extremum in the water-rich region.

INTRODUCTION

We are engaged in a systematic investigation of the physical and thermodynamic properties of aqueous organic solvents. Initially, excess volumes and the dielectric behaviour of water–acetonitrile mixtures have been studied[1, 2] in order to establish a correlation with acid–base properties, estimated through solvation parameters, $({}^{\prime}D_g^0)_H$, related to free enthalpy of transfer, whose changes in terms of mole fraction of organic solvent show no extremum[3]. No enhancement of water-structure has been demonstrated to take place, even in the water-rich region. The behaviour of water—monoethyleneglycol (MEG) systems is somewhat similar to that of water–acetonitrile systems if we consider the above mentioned acid–base properties[4]. It seems then worthwhile to compare both systems from a structural point of view, by examining deviations from different ideal physical properties. It is the purpose of the present work to study the volumetric behaviour of water–MEG systems over the whole composition range to detect possible structural changes.

The influence of several variables also needs to be examined, in so far as they may give rise to an enhancement of the tridimensional water-lattice. First, variation of

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temperature can stabilize a structure as shown elsewhere[5]. Secondly, successive introductions of oxyethylene groups inside the organic molecule have been made, which may lead to a counteraction between the disassociative power of the hydroxyl groups of the glycol and the hydrophobic character of the hydrocarbon chain. Consequently, we have studied the volumetric behaviour of water–MEG systems at different temperatures and water–polyethyleneglycol (di- to tetraethyleneglycols) solvents. Volumes of mixing have been calculated from density measurements and partial molal volumes of the components of the binary systems estimated.

EXPERIMENTAL

Solvents

Ethyleneglycol and its derivatives were prepared as follows from commercial Fluka products. The best grade available was first dried over dehydrating agents and then fractionally distilled. The glycols were distilled under reduced pressure and the middle fraction was dried over anhydrous Na_2SO_4 for a long time before being redistilled. Finally, they were stored under previously purified dry nitrogen. The final products had a specific conductance less than $5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$.

Water was purified from an ion-exchanger before being stored like the organic solvents. Its specific conductance was always less than $1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

All solvent mixtures were made up by weight from thoroughly degassed samples of water and glycols under nitrogen, pressure and vacuum corrected, using Mettler B 5 and B 6 balances. This precaution is necessary, particularly at low temperatures, to avoid air bubbles appearing after making up mixtures, as nitrogen is generally less soluble in the mixtures than in the two separate solvents.

Method

Measurements were carried out in a water-bath, temperature of which was kept constant at 308.15 ± 0.02 K and 298.15 ± 0.02 K, using a high-precision Colora thermostat. At lower temperature, i.e. 288.15 K, a TUK-30 D Lauda Kryostat was used; then, the temperature was kept constant to within 0.1 K. In every case, it was checked by means of a calibrated platinum resistance thermometer and a Leeds and Northrup Mueller bridge. Density of binary mixtures and of pure glycols were measured in a Y-shaped pycnometer, where solvent was introduced with a 5 cm^3 syringe. The accuracy is about $2 \times 10^{-4}\ g\ cm^{-3}$ in density and about 0.01 $cm^3\ mol^{-1}$ in volume. The reliability of this method has been proved by a comparison of the density of the ethyleneglycol with literature data[6], which shows satisfactory agreement.

Calculations

Except for least square fittings, calculations were performed with an electronic calculator Wang 370. Least square fitting calculations were carried out using a DIGITAL PDP-10 computer. For convenience, water will be identified as component

TABLE 1

DENSITIES, $d_{277.15}^{T}$ OF WATER–MONO ETHYLENE GLYCOL SYSTEMS AT VARIOUS TEMPERATURES, T, FOR DIFFERENT MOLE FRACTIONS, x_2, OF MONOETHYLENE GLYCOL

x_2	$d_{277.15}^{308.15}$	$d_{277.15}^{298.15}$	$d_{277.15}^{288.15}$
0	0.99406	0.99707	0.99913
0.0312	1.0068	1.0097	1.0125
0.0676	1.0197	1.0228	1.0260
0.1106	1.0324	1.0369	1.0404
0.1621	1.0446	1.0492	1.0545
0.2248	1.0571	1.0620	1.0676
0.3031	1.0683	1.0746	1.0800
0.4035	1.0788	1.0848	1.0914
0.5367	1.0878	1.0943	1.1011
0.7222	1.0965	1.1030	1.1097
0.9983	1.1035	1.1100	1.1172

TABLE 2

DENSITIES, $d_{277.15}^{298.15}$, OF WATER–POLYETHYLENE GLYCOL SYSTEMS FOR VARIOUS GLYCOLS, FOR DIFFERENT MOLE FRACTIONS, x_2, OF GLYCOL

$(x_2)_{DEG}$	$d_{277.15}^{298.15}$	$(x_2)_{TEG}$	$d_{277.15}^{298.15}$	$(x_2)_{TTEG}$	$d_{277.15}^{298.15}$
0	0.99707	0	0.99707	0	0.99707
0.0185	1.0111	0.0132	1.0119	0.0102	1.0125
0.0407	1.0254	0.0291	1.0274	0.0227	1.0278
0.0678	1.0406	0.0489	1.0434	0.0382	1.0444
0.1017	1.0554	0.0740	1.0594	0.0582	1.0609
0.1451	1.0701	0.1071	1.0742	0.0849	1.0769
0.2029	1.0828	0.1524	1.0890	0.1221	1.0913
0.2836	1.0941	0.2185	1.0994	0.1779	1.1036
0.4042	1.1031	0.3238	1.1098	0.2706	1.1124
0.6038	1.1096	0.5180	1.1161	0.4550	1.1178
0.7623	1.1118	0.6931	1.1182	0.6380	1.1200
0.9982	1.1134	0.8211	1.1194	0.7834	1.1204
		0.9958	1.1204	1.0000	1.1209

1 and glycol as component 2. Compositions are stated as mole fractions (x_2) of organic solvent rather than temperature-dependent volume fractions (ϕ_2).

RESULTS

Partial molar volumes

Densities, d, of binary mixtures of water with monoethyleneglycol at 308.15, 298.15 and 288.15 K are reported in Table 1. In Table 2 the densities at 298.15 K of

TABLE 3

VALUES OF THE LEAST SQUARE PARAMETERS IN EQN. (2)

	H_2O-MEG (308.15 K)			H_2O-MEG (298.15 K)			H_2O-MEG (288.15 K)		
	V_1	V_2		V_1	V_2		V_1	V_2	
		(1)[a]	(2)[b]		(1)	(2)		(1)	(2)
A_0	18.120	54.558	54.436	18.063	54.594	54.309	18.023	54.341	53.928
A_1	0.226	−1.655	3.507	0.549	−14.823	−3.292	0.723	−22.898	−6.351
A_2	−5.337	105.45	18.787	−6.761	243.56	64.605	−7.881	343.56	89.910
A_3	8.747	−891.46	−90.324	9.018	−1 664.18	−225.63	9.336	−2 310.2	−305.60
A_4	−5.278	4 677.8	156.04	−1.152	7 015.6	358.12	2.835	9 508.8	480.87
A_5	0.031	−14 728.0	−123.59	−5.323	−17 421.0	−272.95	−10.941	−22 722.0	−364.69
A_6	0.780	20 282.0	37.386	2.794	19 177.0	80.756	5.038	23 741.0	107.49
σ	0.001	0.001	0.005	0.002	0.001	0.010	0.003	0.001	0.014

	H_2O-DEG (298.15 K)			H_2O-TEG (298.15 K)			H_2O-TTEG (298.15 K)		
	V_1	V_2		V_1	V_2		V_1	V_2	
		(1)	(2)		(1)	(2)		(1)	(2)
A_0	18.056	92.554	90.792	18.065	129.85	125.78	18.074	167.93	161.52
A_1	1.599	−74.392	8.975	1.612	−175.63	58.112	1.538	−324.48	99.92
A_2	−26.352	1 644.4	74.597	−43.237	5 508.0	−171.43	−57.07	11 237.0	−378.46
A_3	74.382	−16 010.0	−370.77	155.63	−73 621.0	252.47	221.2	−163 193.0	780.09
A_4	−101.94	89 167.0	671.47	−255.29	530 453.0	−175.57	−380.5	1 237 296.0	−897.74
A_5	69.754	−269 185.0	−549.81	200.41	−1 961 902.0	37.314	308.7	−4 714 953.0	540.53
A_6	−18.989	338 432.0	170.07	−60.760	2 896 395.0	7.391	−95.83	7 085 634.0	−132.52
σ	0.003	0.003	0.038	0.008	0.023	0.033	0.015	0.060	0.026

[a] (1): $0 < x_2 < 0.20$.

[b] (2): $0.05 < x_2 < 1$.

binary mixtures of water with diethyleneglycol (DEG), triethyleneglycol (TEG) and tetraethyleneglycol (TTEG) are summarized.

Partial molal volumes $\bar{V}_{H_2O}$ and $\bar{V}_{glycol}$ were computed from the relationship

$$\bar{V}_i = \left(\frac{1}{d} + (1 - w_i) \frac{\partial \left(\frac{1}{d} \right)}{\partial w_i} \right) PM_i \tag{1}$$

where w_i is the weight fraction of component i and PM_i is the molecular weight. d has been developed in a polynomial form $\sum_j a_j x_2^j$. Therefore, for $\bar{V}_i$ we get

$$\bar{V}_i = \left(\frac{1}{d} + (1 - w_i) \frac{\partial}{\partial w_i} (\sum_j a_j x_2^j) \right) PM_i = \sum_j A_j x_2^j \tag{2}$$

where A_j coefficients are chosen by the method of least squares. It was found that seven coefficients are required to give accurate results for $\bar{V}_1(x)$. Due to the strong asymmetry of the curves $\bar{V}_2(x)$, a very bad agreement was obtained even if a higher degree development was made. In order to get a reasonably good description of this variable, two overlapping areas were delimited over the whole composition range and separate equations were proposed for each of them, including seven coefficients as for $\bar{V}_1(x)$. All these coefficients are reported in Table 3.

Excess volumes of mixing

Excess volumes of mixing V^E have been calculated using the following equation

$$V^E = \sum_i x_i (\bar{V}_i - V_i^0) \tag{3}$$

where V_i^0 holds for the molar volume of component i. They have also been fitted by least square treatment, using the subsequent equation

$$V^E = x_2 (1 - x_2) \sum_{j=0}^{4} A'_j (1 - 2x)^j \tag{4}$$

Generally, it was found that five parameters in eqn. (4) were sufficient to

TABLE 4

VALUES OF THE LEAST SQUARE PARAMETERS IN EQN. (4)

Mixture (T)	A_0'	A_1'	A_2'	A_3'	A_4'	*(cm³ mol⁻¹)*
H_2O–MEG (308.15 K)	−1.2373	−0.5366	−0.2850	−0.1289	−0.4400	0.001
H_2O–MEG (298.15 K)	−1.3202	−0.5586	−0.4059	−0.2586	+1.1109	0.001
H_2O–MEG (288.15 K)	−1.4146	−0.7024	−0.5766	−0.3517	+1.6530	0.002
H_2O–DEG (298.15 K)	−2.4611	−1.3995	−1.5305	−0.6484	+2.2407	0.006
H_2O–TEG (298.15 K)	−2.7256	−2.0677	−2.0609	−1.0380	+1.2657	0.011
H_2O–TTEG (298.15 K)	−3.2913	−2.5857	−2.6602	−2.0724	+1.2921	0.015

reproduce the experimental values. The standard deviation, σ, was consistent with the estimated precision of the equipment. The A_j' coefficients are summarized in Table 4.

DISCUSSION

Excess volumes of mixing

Negative values are observed for the excess volumes of mixing in the whole range of composition. They can be well explained by the occupation of the cavities of the water network by the other component.

For water–MEG mixtures, the position of the minimum of $V^E(x_2)$ lies at $x_2 \simeq 0.4$. A slight dependence on temperature exists, V^E becoming more negative as the temperature decreases, which can be interpreted on the basis of higher structuring of the mixed solvent.

A much more important effect is observed when passing from mono- to tetraethyleneglycol, which gives rise to more and more negative values of V^E; at the same time, the abscissae of the minima are shifted towards lower values of x_2, respectively 0.34, 0.30 and 0.28 for water–DEG, –TEG and –TTEG mixtures.

It can be seen that a certain lack of symmetry characterizes these curves, which is natural. While the excess function of any thermodynamic quantity for liquid mixtures is expected to have a symmetrical shape when the components are "normal" liquids consisting of spherical molecules without specific interaction, this symmetry mostly fails in the case of mixtures involving associated liquids. As a matter of fact, when an organic liquid is added to water, at least two types of interactions may be considered as well as the possible filling of cavities. The first is hydrogen-bond formation between water and the polar group (*s*) of the molecules considered, while the second lies in the structural modification of the water around these molecules, the latter effect, "iceberg" formation, being important for the investigation of interactions with the hydrocarbon chain. The asymmetry of $V^E(x_2)$ is then due to these two kinds of interactions.

One has to consider not only the interactions between water and the hydroxy group of the glycol but also the nature and magnitude of possible interaction between the ether oxygen atoms of DEG, TEG and TTEG and water. An insufficient explanation would lie in the fact that a similar volumetric behaviour is observed for all the systems considered, meaning that interaction between water and the ether function is low, compared to that with the hydroxy group. However, various phenomena, such as phase separation temperature dependence of the enthalpy of mixing and clathrate hydrate formation indicate that the hydrogen bond between an ether oxygen or ketone and water is a weak one[7]. Moreover, Nakayama[7] has found that the partial molal excess enthalpies of all the components of the water–DEG system are negative over the entire range of composition; they can well be distinguished from those of water–ether mixtures. One can then ascertain that the strong interaction between the OH group and the water overshadows the effect of the comparatively weak interaction between the ether oxygen atom and water. Owing to that, the influence of hydrocarbon chain compared to ether functions seems prominent, giving rise to more and more important negative values.

Partial molal volumes

If we consider precedent variations $V^E(x_2)$, it is possible to detect a slight inflection point before the minimum. The presence of such a point is undoubtedly connected with the occurrence of an extremum in the partial molal volumes vs. x_2 relationship of the components, the consequence of a rigorous thermodynamic interrelation between V^E and the corresponding partial molal volumes.

As a matter of fact, the partial molal volume, $\bar{V}_2$, of glycol decreases while its mole fraction increases, reaches a minimum value and then increases gradually to the molar volume, V_2^0. In the whole range of composition, $\bar{V}_2$ is always smaller than $\bar{V}_2^0$. On another hand, partial molal volume of water, $\bar{V}_1$, increases very slightly when x_2 increases, reaches an indistinct maximum and then decreases progressively.

At 298.15 K, the positions of the extremums lie respectively at $x_2 = 0.050$, 0.040, 0.028 and 0.025 for water–MEG, –DEG, –TEG and –TTEG systems. The influence of temperature on the first system is not negligible, since the extremums move from $x_2 = 0.012$ at 308.15 K to 0.060 at 288.15 K. The ordinates of the extremum of the relative partial molal volumes ($\bar{V}_1 - \bar{V}_1^0$) are of very low magnitude for the different systems studied (< 0.022 cm^3); they become more and more important concerning ($\bar{V}_2 - \bar{V}_2^0$), when one passes from MEG to TTEG ($-$ 1.62 to $-$ 8.68 cm^3).

Our results concerning water–MEG systems are in close agreement with data published by Nakanishi[8] at the temperature of 293.15 K. More recent results given by Ray and Néméthy[9] exhibit a quasi-constancy of $\bar{V}_i$ for $x_2 = 0.64$ to 0.74, instead of the slight decrease shown by Nakanishi[8] and us.

One can see elsewhere that the position of extremums $\bar{V}^E(x_2)$ and $\bar{V}_i(x_2)$ is quite different. Cavity occupation of the water-lattice by organic molecules simply results in smooth ($\bar{V}_i - V_1^0$) curves; moreover, one should clarify the nature of the extremums of these latter curves. It seems likely that they are related to the magnitude of the "iceberg" effect in connection with the importance of the hydrocarbon chain. One might conclude that their position corresponds to the upper limit of the region, where stabilization of the water structure can take place.

The behaviour of these dihydric compounds is rather similar to that of their monohydric homologues[8]. The explanation is certainly provided by observing that the magnitude of ($\bar{V}_2 - V_2^0$) increases with the number of carbon atoms introduced by successive oxyethylenegroups, evidence again being given that the ether functions do not play a predominant role, in spite of the number of hydrogen bonding sites. The effect of the hydrocarbon chain counterbalances that of the hydroxy groups of glycols, affecting advantageously a long range order in water although weaker than for monohydric compounds. An opposite effect would be obtained, if hydroxy groups were predominant, as in glycerol for instance[8].

We agree with the conclusions of Nakanishi and coworkers[10] relative to another class of dihydric compounds: one can reasonably assume that a "substitutional" mixing occurs for water–MEG systems, according to the terminology of Franks[11], as for water–methanol systems, which transforms gradually to an "interstitial" contribution due to a possible cavity occupation by the hydrocarbon chain, the polar character of the second OH group getting progressively less important. Enhancement of the water structure becomes more and more important from water–MEG to –TTEG systems.

Finally, if we try to relate acid–base properties of water–acetonitrile and water–MEG solvents, which were found to be comparable[3, 4], one can observe that in both cases, no strong enhancement of the water-lattice has been detected, contrary to monohydric compounds, whose acid–base behaviour was quite different[3]. Nevertheless, no rigorous quantitative correlation can be drawn from these results, due to the fact that acid–base properties were related to free enthalpy changes, which are likely to undergo a compensative effect from both of its components, enthalpy and entropy.

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