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Thermodynamic Properties of an Aqueous Solution of Tetraethylene Glycol Diethyl Ether

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The excess Gibbs energy of mixing, G^E; the excess enthalpy of mixing, H^E, and the excess volume of the mixing, V^E, of the tetraethylene glycol diethyl ether+water system have been measured as functions of the composition at 25°C. The G^E, which has been determined through the isopiestic measurement of the water activity, is positive over the entire range of composition and has its maximum at 40 mol% ether. As has been found for analogous systems, the *s*-curve of H^E is again found; that is, H^E is large and negative (exothermic) in the water-rich region and positive (endothermic) in the ether-rich region. The V^E is negative over the whole range of composition and has a minimum at 23 mol% ether. These results are discussed in the light of the structural modifications of water in the immediate neighborhood of the ether molecule.

That the structural modifications of water play an important role in the dissolution of hydrocarbons into water is now widely accepted. In order to investigate such a phenomenon, aqueous solutions of ethers are, in practice, probably the most convenient because the interaction between the polar group (ether oxygen) and water is not so strong, despite their elevated miscibility with water, that the effect of a polar group on the solution property can be minimized.

In a previous paper,[1] the enthalpies of the mixing of water with diethylene glycol diethyl ether and with some cyclic ethers were measured, and it was concluded that the water-water interaction persisted even in the ether-rich region (80 mol% ether, for example). In the present paper, the excess Gibbs free energy of mix-

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[1] H. Nakayama and K. Shinoda, *J. Chem. Thermodynamics*, **3**, 401 (1971).

ing, G^E; the excess enthaply of mixing, H^E; the excess entropy of mixing, S^E, and the excess volume of mixing, V^E, for the tetraethylene glycol diethyl ether+water system have been determined. The purpose of this paper is to see if the above-mentioned conclusion,[1] derived only from the concentration dependence of the partial molal excess enthalpy of water, $\bar{H}_1^E$, is consistent with the behavior of the partial molal excess entropy of water, $\bar{S}_1^E$, as well.

Tetraethylene glycol diethyl ether was chosen because the aqueous solution properties of such a compound can give fundamental information for many complicated systems, such as, for example, polyethylene glycol+water and a non-ionic surfactant with an oxyethylene chain as a hydrophilic group+water. Other advantages of this compound are its complete miscibility with water at room temperature and its low vapor pressure (less than 10^{-5} mmHg at 25°C), low enough to permit accurate determination of the water activity. No thermodynamic data for the present system have been reported.

Experimental

Materials. The tetraethylene glycol diethyl ether (3,6,9,12,15-pentaoxaheptadecane, which we will denote by TGDE hereafter) was synthesized by the condensation reaction (Williamson reaction) of *β*-ethoxy *β'*-chlorodiethyl ether ($ClCH_2CH_2OCH_2CH_2OCH_2CH_3$) (I) with the sodium salt of *β*-diethoxy ethyl alcohol ($NaOCH_2CH_2OCH_2CH_2OCH_2CH_3$) (II). Both reactants were prepared from commercially-available *β*-diethoxy ethyl alcohol (diethylene glycol monoethyl ether). The compound I was prepared according to the procedure of Hurd and others,[2] who synthesized *β*-ethoxy ethyl chloride. Some physical properties and analytical data for the compound I were as follows; bp 179.5—180.5°C/760 mmHg; n_D^{25} 1.4279.

Found: C, 47.12; H, 8.73; Cl, 23.45%. Calcd for $C_6H_{13}O_2Cl$: C, 47.22; H, 8.56; Cl, 23.23%.

The compound I was added, drop by drop, to the compound II dissolved in diethylene glycol monoethyl ether (reaction solvent), and then the mixture was heated under reflux for several hours at 110—130°C. After cooling, the organic layer was separated and distilled under reduced pressure. The crude product (120—125°C/2 mmHg) was re-distilled from sodium. The TGDE prepared in this way was further purified by fractional distillation under a vacuum. It was stored in an ampoule and then further distilled just before use. The analytical data and some physical properties of TGDE are summarized in Table 1.

Table 1. Analytical data and some properties of TGDE

Boiling point (°C)	124—125 at 2 mmHg 159 at 11 mmHg[3] 159 at 10 mmHg[4]
Refractive index (n_D)	1.4298 at 25°C
Density (g/cm^3)	0.9712 at 25°C
Molal volume (cm^3/mol)	257.8 at 25°C
Molecular weight (experimental)[a]	250.0
Molecular weight (theoretical)	250.3
Water content (wt%)[b]	less than 0.1
Analytical data	Found: C, 57.47; H, 10.58% Calcd for $C_{12}H_{26}O_5$: C, 57.58; H, 10.47%

a) determined by the cryoscopic method in benzene solution.

b) determined by the Karl Fischer titration method.

Vapor-pressure Measurements. The vapor pressure of the water of the aqueous solution of TGDE was determined by the isopiestic method. The apparatus was generally analogous to that used by Robinson and Stokes,[5] but with considerable simplifications. Four or six cylindrical glass dishes (20 mm in diameter and 50 mm deep) were put on a copper block (100 mm in diameter and 20 mm thick) placed within a cylindrical, separable flask (1000 m*l*). Small amounts of grease were placed between the block and each dish to maintain good thermal conact. The equilibrium concentration was determined by weight. At the same time, the amount of water was checked by the Karl Fischer titration method and by refractive-index measurements. Sodium chloride solutions (in the region less than 50 mol% TGDE) and calcium chloride solutions (in the region greater than 50 mol% TGDE) were used as reference solutions. The water activities were obtained by the graphical interpolation of the activity-concentration relation given by Robinson and Stokes.[6]

Enthalpy of Mixing Measurements. The calorimeter used to measure the enthalpies of mixing was the same as that described earlier.[1] At high mole fractions of TGDE, the enthalpies of mixing were determined by measuring the heat when the pure TGDE was mixed with an aqueous solution of TGDE of a known composition. The accuracy of measurement was ±3 J·mol^{-1} at $x<0.5$ and ±5 J·mol^{-1} at $x>0.5$ (x is the mole fraction of TGDE).

Density and Phase-separation Temperature Measurements. The density of the TGDE+water mixture was measured in a 10-m*l* pyknometer which had been calibrated with distilled water. The liquid - liquid phase separation temperature was

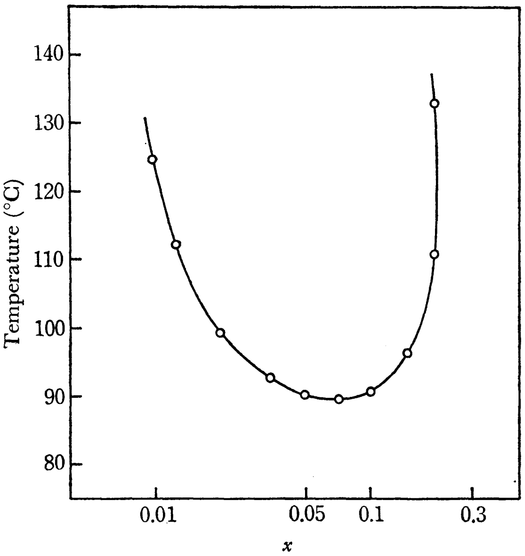

Fig. 1. The liquid-liquid phase diagram for the TGDE+water system.
x is the mole fraction of TGDE.

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[2] D. Hurd and G. W. Fowler, *J. Amer. Chem. Soc.*, **61**, 249 (1939).

[3] P. Rempp, *Bull. Soc. Chim. Fr.*, **1957**, 844.

[4] A. Kotera, K. Suzuki, K. Matsuura, T. Nakano, T. Oyama, and U. Kambayashi, This Bulletin, **35**, 797 (1962).

[5] R. A. Robinson and R. H. Stokes, *J. Phys. Chem.*, **65**, 1954 (1961).

[6] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959).

determined by heating (or cooling) solutions sealed in ampoules. The temperature shown in Fig. 1 is the average of the two temperatures; the temperature at which the phase separation occurred when the solution was heated slowly, and the one at which the solution became clear again upon slow cooling. The difference between the two temperatures was less than 1°C in all cases.

Results and Discussion

The liquid - liquid phase diagram for the TGDE+water system is shown in Fig. 1, in which the logarithms of x is plotted on the abscissa. This system has a lower critical solution temperature, one which is equal to 89.5°C. The critical concentration is about $x=0.072$. At 120°C, for example, a solution of $x \approx 0.01$ is in equilibrium with a solution of $x \approx 0.2$. The fact that the ether-rich phase still has a considerable amount of water indicates that the water molecules surrounding the ether molecule are appreciably stabilized. Four mixtures of mole fractions of 0.22, 0.33, 0.61, and 0.71 have been heated to 150°C. No separation of a second liquid phase is observed.

Table 2. Enthalpy of mixing H^E of tetraethylene glycol diethyl ether (TGDE) + water at 25°C. x is the mole fraction of TGDE

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
0.0106	−531.4	0.4383	−682.4
0.0346	−1323	0.4829	−577.0
0.0662	−1708	0.5168	−463.2
0.0973	−1813	0.5954	−242.7
0.1456	−1772	0.6881	−53.1
0.1962	−1662	0.7880	+48.5
0.2964	−1236	0.8865	+67.8
0.3708	−941.4		

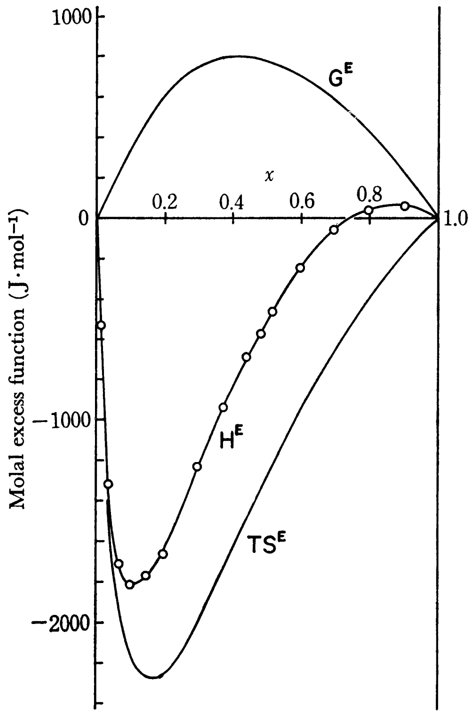

Fig. 2. The molal excess functions of the TGDE+water system at 25°C.

The enthalpies of the mixing, H^E, of the TGDE+water system at 25°C are presented in Table 2 and are shown in Fig. 2. The same general behavior as has been observed for the ethylene glycol dimethyl ether+water[7] and diethylene glycol diethyl ether+water[1] systems is also found for the present system; that is, the H^E is large and negative (exothermic) in the water-rich region and positive (endothermic) in the ether-rich region. However, the exothermicity is, as a whole, more remarkable in this system than in either of the systems cited above.

As has been mentioned earlier,[1] the exothermic heat of mixing in the water-rich region is probably attributable to the structural modifications of water around the ether molecule. The large exothermic heat of mixing observed in the present system, compared with that of diethylene glycol diethyl ether and of ethylene glycol dimethyl ether, is consistent with the prediction that the effect due to the structural modifications of water is more remarkable in an aqueous solution of large hydrocarbon molecules than in one of small ones, when compared at the same mole fraction.

Table 3. Isopiestic data at 25°C for the system TGDE + water

x	m_{NaCl}	m_{CaCl_2}	a_1	γ_1
0.0153	0.4823	—	0.9842	1.000
0.0313	1.049	—	0.9652	0.996
0.0473	1.598	—	0.9463	0.993
0.0727	2.241	—	0.9235	0.996
0.1048	2.742	—	0.903	1.009
0.1528	3.207	—	0.885	1.045
0.1878	3.451	—	0.875	1.078
0.2433	3.788	—	0.861	1.137
0.3021	4.108	—	0.847	1.214
0.3481	4.387	—	0.834	1.279
0.4015	4.849	—	0.813	1.360
0.4580	5.345	—	0.791	1.459
0.4675	—	2.896	0.763	1.434
0.5184	—	3.122	0.733	1.521
0.6306	—	3.822	0.647	1.753
0.6982	—	4.403	0.571	1.891
0.7511	—	4.990	0.500	2.008
0.8412	—	6.418	0.355	2.233

The isopiestic data for the TGDE+water system at 25°C are summarized in Table 3. The second and third columns give the isotonic concentration (in molality) of the reference solutions, which are in equilibrium with the aqueous solution of TGDE with the mole fraction x. The fourth column gives the activity of water, a_1, while the last column gives the activity coefficient of water, γ_1, which is defined by the relation: $\gamma_1 = a_1/(1-x)$. The water activity shows a positive deviation from ideality over most of the composition range, though a negative deviation is observed in the water-rich region ($x<0.1$).

The activity coefficient of TGDE γ_2 is calculated by using the Gibbs-Duhem equation. From these results,

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[7] E. Tommila and V. Turkki, *Suom. Kemistilehti*, **40B**, 207 (1967).

the molal excess Gibbs energy of mixing, G^E, is obtained; it is plotted in Fig. 2. The G^E is defined by the following equation:

$$G^E = \boldsymbol{R}T\{(1-x)\ln\gamma_1 + x\ln\gamma_2\}.$$

Figure 2 also includes the excess entropy of mixing multiplied by the absolute temperature, T, TS^E, which is merely the difference between H^E and G^E. The concentration dependence of these excess functions is similar to that of the 1,4-dioxane+water system.[8] As may be seen from Fig. 2, the concentration dependence of H^E (and of TS^E) is peculiar in contrast to that of G^E, which is positive over the entire range of composition and is approximately symmetrical with a relatively small maximum (805 J·mol^{-1}) at $x \approx 0.4$. Thus, we can expect that information about the dissolution state of each component may be drawn from the analysis of H^E and (or) TS^E rather from than that of G^E.

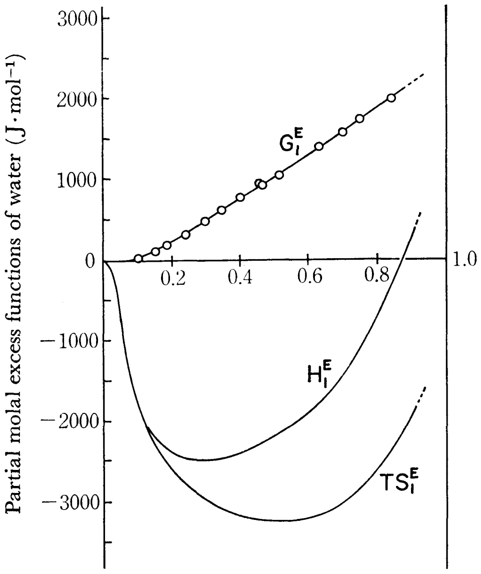

Fig. 3. The partial molal excess functions of water in the TGDE+water system at 25°C.

In Fig. 3, the partial molal excess functions of water in the TGDE+water system at 25°C are plotted against x. The G_1^E is calculated from the vapor-pressure data (Table 3) using the relation: $G_1^E = \boldsymbol{R}T\ln\gamma_1$. The H_1^E is obtained by the graphical differentiation of the H^E *vs.* x curve (Fig. 2). The TS_1^E quantity is simply the difference between H_1^E and G_1^E.

In the previous paper,[1] as a reasonable explanation of the concentration dependence of H_1^E for the aqueous solution of diethylene glycol diethyl ether and of some cyclic ethers, it has been suggested that the hydrogen-bond formation between water molecules is dominant even in the ether-rich region, and that, with an increasing water concentration, the solvating layer of the ether molecule is gradually constructed through this water-water interaction. A similar explanation will hold for the present system, since the H_1^E *vs.* x curve is essentially similar to that of the previous systems. However, it is not only of interest, but also of importance, to see if the concentration dependence of the S_1^E is also consistent with this view. In conclusion, we can say that, judging from the following discussion, the behavior of S_1^E can also be interpreted in the same way.

In the initial stage, for instance $x>0.8$, added water molecules will form hydrogen bonds with the ether oxygen atoms. The value of S_1^E in this region will reflect the state of the water molecule, which is subject to the restraint of the ether. If such a hydrogen-bond formation continues until all of the oxygen atoms form at least one hydrogen bond with water, the value of S_1^E at a high mole fraction of ether would continue up to, say, $x=0.3$ or less. However, as may be seen from Fig. 3, the S_1^E decreases remarkably with an increase in the water concentration. This behavior is consistent with the above idea that an alternative, more ordered arrangement of the water molecule arises even at high mole fractions of the ether.

Now, some care must be taken in choosing an ideal entropy for the definition of an excess entropy of mixing. Since the TGDE molecule is a chain molecule whose chain length is comparable to that of heptadecane, it is reasonable to use, instead of $-\boldsymbol{R}\ln(1-x)$ as before, the following expression for a partial molal excess entropy of water in an ideal solution, S_1^{ideal}:

$$S_1^{\text{ideal}} = -\boldsymbol{R}\{\ln(1-\phi)+\phi(1-1/M)\}$$

where ϕ is the volume fraction of the TGDE and, where M is the ratio of the molal volume of the ether to that of water, which is equal to 14.3 at 25°C. However, the concentration dependence of this newly-defined S_1^E is essentially similar to that of the previous S_1^E, though the numerical value becomes much more negative. As a result of this, the above-mentioned interpretation of the S_1^E curve need not be changed.

The excess volume of mixing, V^E, is shown in Fig. 4, together with the partial molal excess volumes of the mixing of both components, V_1^E and V_2^E. The V_1^E and V_2^E are obtained by the graphical differentiation

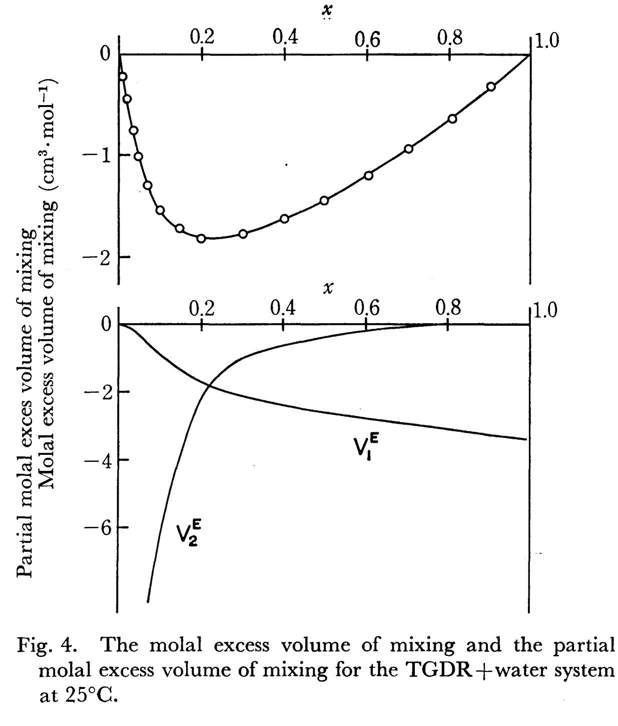

Fig. 4. The molal excess volume of mixing and the partial molal excess volume of mixing for the TGDR+water system at 25°C.

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[8] J. R. Goates and R. J. Sullivan, *J. Phys. Chem.*, **62**, 188 (1958).

of the V^E *vs.* x curve. The V^E is negative over the entire range of composition and has its minimum $(-1.82\ \mathrm{cm^3 \cdot mol^{-1}})$ at $x=0.23$. The V_2^E decreases appreciably with an increase in the water mole fraction and reaches about $-23\ \mathrm{cm^3 \cdot mol^{-1}}$ at an infinite dilution. The V_1^E is about $-3.4\ \mathrm{cm^3 \cdot mol^{-1}}$ at $x \rightarrow 1$, which means a 19% depression in the molal volume of normal water. This appreciable contraction may be ascribed to the breakdown of the bulky structure characteristic of liquid water when it is dissolved in a large amount of ether. In the intermediate region, $(0.2<x<0.8$, for instance) V_1^E is $-2 \sim -3\ \mathrm{cm^3 \cdot mol^{-1}}$. This indicates that the water layer surrounding the ether is more dense than normal water. This observation is presumably related to the dense structure of water that would exist in the "iceberg" structure.