ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 7, pp. 1218–1226. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.M. Zaichikov, M.A. Krest'yaninov, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 7, pp. 1134–1143.

Thermodynamic Characteristics and Intermolecular Interactions in Aqueous Solutions of Oxyethylated Glycols

A. M. Zaichikov[a] **and M. A. Krest'yaninov**[b]

[a] *Ivanovo State University of Chemical Technology,*
pr. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: thermo@isuct.ru

[b] *Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

Received October 9, 2006

Abstract—The thermodynamic characteristics of aqueous solutions of mono-, di-, tri-, and tetraethylene glycols were calculated in the entire range of compositions of the mixtures for various temperatures. The specific and nonspecific terms of the total energy of intermolecular interaction were determined within the framework of a model approach using the internal pressure as a measure of nonspecific interactions in a liquid. The concentration ranges with different types of intercomponent association and of structural organization of solutions depend on the temperature and number of ether groups in the glycol molecules.

DOI: 10.1134/S1070363207070134

Kartsev et al. [1] considered application of the internal pressure and its temperature coefficient to studying transformations of the three-dimensional H-bond network in binary aqueous solutions of glycols. For the water–ethylene glycol system, these parameters were estimated only for water-rich solutions, and for aqueous solutions of oxyethylated derivatives $HOCH_2(CH_2OCH_2)_nCH_2OH$ they were not examined at all. Proceeding with thermodynamic studies of aqueous solutions of various nonelectrolytes, we calculated in this work the internal pressure and its temperature coefficient for the entire range of aqueous solutions of mono-, di-, tri-, and tetraethylene glycols. One of the main goals of this study was to determine how the number of ether groups ($–CH_2OCH_2–$) in glycol molecules affects the structural organization and intercomponent association in water–glycol systems.

For a wide range of pure liquids and aqueous solutions, Kartsev et al. [1, 2] showed that the internal pressure p_{int} and its temperature coefficient are very sensitive to structural changes. The quantity p_{int} characterizes the variation of the internal energy U of a liquid in the course of small isothermal expansion [2, 3] and can be calculated from Eq. (1):

$$p_{\text{int}} = -(\partial U/\partial V)_T = p - T\alpha/\beta_T, \quad (1)$$

where V is the molar volume; α and β_T, coefficients of isobaric (volumetric) expansion and isothermal compression, respectively. The term p (atmospheric pressure) in (1) can be neglected, because its contribution to p_{int} is less than 0.1% [2].

The results of the calculation of the internal pressure of aqueous glycol solutions by Eq. (1) at various temperatures are given in Tables 1 and 2. The thermal expansion coefficients were calculated from Eq. (2) after approximation of the molar volumes [4–6] by quadratic polynomials with respect to temperature:

$$\alpha = 1/V(\partial V/\partial T)_P. \quad (2)$$

The isothermal compressibility coefficients were calculated from Eq. (3):

$$\beta_T = 1/u^2\rho + \alpha^2 VT/C_{\text{p}}, \quad (3)$$

where u is the ultrasound speed; ρ, density; and C_{p}, heat capacity of the solutions. In the calculations we used data on $u(T)$ and $\rho(T)$ of aqueous solutions of monoethylene glycol [4, 5, 7] and oxyethylated glycols [5, 6, 8, 9]. Data on the heat capacity of aqueous glycol solutions were taken from [10, 11]. Our calculations showed that the coefficient of isothermal compressibility of aqueous ethylene glycol solutions well agrees with the values calculated from their compressibility at 298.15 K [12].

The data obtained allowed us to estimate the temperature coefficient of the internal pressure ($\Delta p_{\text{int}}/\Delta T$) at different ΔT for systems presented in the tables. Figure 1 shows that, for aqueous solutions of mono-, di-, and triethylene glycol, $\Delta p_{\text{int}}/\Delta T < 0$ in the entire range of compositions of the binary mixtures. Since negative values of $\Delta p_{\text{int}}/\Delta T$ are characteristic of systems with hydrogen bond networks [1, 2], we can conclude that the solutions under consideration are also three-dimensionally associated. In solutions of tetraethylene glycol, an inversion of the temperature coefficient of the internal pressure is observed in the middle interval of concentrations. The calculations show that all the glycols except tetraethylene glycol are solvents with negative temperature coefficients (Fig. 1). Water, whose negative coefficient of internal pressure is the largest in the absolute value [2], also belongs to this group. Since the temperature coefficient for tetraethylene glycol is positive (Fig. 1), it can be classed with liquids that do not have a network structure [2].

Figure 1 shows that in all the systems the function $(\Delta p_{int}/\Delta T) = f(X)$ (X is the mole fraction of glycol) has a bend in a certain concentration range, similarly to the previously studied aqueous solutions of propanediols [1]. To reveal the character of changes in the functions $(\Delta p_{int}/\Delta T) = f(X)$, these functions can be represented in the coordinates $(\Delta p_{int}/\Delta T)/X = f(X)$, to make the bend sharper [13]. Calculations show that, in the water–ethylene glycol system, the bend is observed in the range $0.09 < X < 35$. As shown by Kartsev et al. [1], the concentration region in which the functions $(\Delta p_{int}/\Delta T) = f(X)$ have a bend is the range of intense transformations of three-dimensionally associated solutions. The composition corresponding to the onset of the bend is limiting for the existence of the intact H-bond network of water, and the composition at which the bend ends corresponds to the most stable water–nonelectrolyte associate. These problems will be discussed in part below, and primarily it seems interesting to consider the use of internal pressure for analyzing intermolecular interactions in the systems under consideration.

Knowledge of p_{int} allows, using Dack's method [3, 14] and taking the internal pressure as a measure of nonspecific interactions, evaluation of the contribution of these interactions to the total intermolecular interaction in the systems [Eq. (4)]:

$$U_{nsp} = p_{int}V \approx -TV\alpha/\beta_T. \qquad (4)$$

The validity of concept [14] is confirmed by the fact that, in nonpolar liquids in which only van der Waals interactions occur, the internal pressure is identical to cohesion (D), and in nonelectrolytes associated through hydrogen bonds the absolute values of cohesion are considerably higher. It was shown in [14, 15] that, as p_{int} reflects mainly the nonspecific van der Waals interactions and D, the whole spectrum of interactions, the difference $D - p_{int}$ corresponds to the contribution of specific interactions to the intermolecular interaction (per init volume of the liquid). There-

Table 1. Internal pressure ($-p_{int} \times 10^{-6}$, Pa) of aqueous solutions of ethylene glycol at various temperatures (X is mole fraction of ethylene glycol)

X	278.15 K	298.15 K	338.15 K
0	90.5	169.4	418.2
0.0200	94.5	192.7	439.7
0.0400	98.3	224.6	460.3
0.0606	140.0	257.9	481.6
0.0900	199.5	304.3	503.6
0.1216	258.1	349.0	521.3
0.1826	349.0	418.1	549.1
0.2437	411.1	464.8	564.1
0.3050	451.7	494.1	580.4
0.3678	484.3	509.4	587.6
0.4293	500.9	517.9	590.3
0.4916	509.8	521.6	589.5
0.5543	513.1	522.0	585.5
0.6178	509.7	522.4	578.7
0.6809	510.2	520.3	569.7
0.7436	509.7	518.1	559.7
0.8044	508.2	516.0	550.3
0.8738	505.0	513.3	542.4
0.9371	502.1	510.4	541.4
1.0000	501.5	507.9	546.6

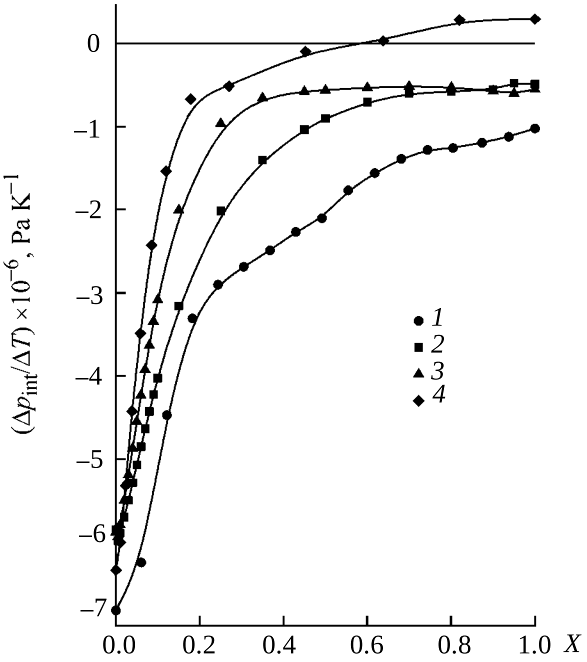


Fig. 1. Temperature coefficient of the internal pressure of aqueous solutions of (*1*) ethylene glycol, (*2*) diethylene glycol, (*3*) triethylene glycol, and (*4*) tetraethylene glycol as a function of composition (here and hereinafter, X is the mole fraction of glycol).

Table 2. Internal pressure ($-p_{\text{int}} \times 10^{-6}$, Pa) of aqueous solutions of oxyethylated glycols at various temperatures (X is the mole fraction of glycol)

Diethylene glycol			Triethylene glycol			Tetraethylene glycol		
X	298.15 K	348.15 K	X	298.15 K	348.15 K	X	298.15 K	348.15 K
0.0	169.4	467.7	0.0	169.4	467.7	0.0	169.4	239.7
0.005	183.2	482.1	0.005	198.0	494.8	0.01056	229.3	289.3
0.007	188.4	485.6	0.007	203.9	497.4	0.02286	295.8	349.0
0.01	196.3	490.7	0.01	215.5	504.9	0.03814	373.6	417.8
0.02	222.2	507.0	0.02	253.4	528.3	0.05819	452.9	487.8
0.03	247.5	522.1	0.03	289.8	549.1	0.08510	524.5	548.8
0.04	271.9	536.0	0.04	324.3	567.7	0.11966	571.5	586.9
0.05	295.4	548.7	0.05	356.8	584.1	0.17848	593.1	599.8
0.06	317.7	560.3	0.06	387.0	598.5	0.26975	575.8	580.9
0.07	340.0	571.7	0.07	414.9	611.0	0.45223	548.5	549.5
0.08	358.9	580.2	0.08	440.5	621.9	0.63798	530.4	530.2
0.09	376.6	587.7	0.09	463.8	631.1	0.81965	522.3	519.6
0.1	393.2	594.4	0.1	484.9	638.9	1.0	516.5	513.6
0.15	458.6	616.4	0.15	562.6	662.8			
0.25	520.7	621.5	0.25	603.6	651.9			
0.35	533.1	603.2	0.35	591.8	624.6			
0.45	529.9	581.8	0.45	572.8	601.8			
0.5	527.3	572.5	0.5	564.7	592.8			
0.6	521.8	557.1	0.6	550.5	577.2			
0.7	513.5	543.6	0.7	536.4	562.3			
0.8	499.6	528.7	0.8	522.2	548.6			
0.9	485.9	513.7	0.9	511.9	540.7			
0.95	485.2	509.1	0.95	509.9	540.0			
1.0	479.4	504.0	1.0	508.2	535.9			

Table 3. Excess enthalpies (J mol^{-1}) in the water–tetraethylene glycol system at 298.15 K (X is the mole fraction of tetraethylene glycol)

X	$-H^E$	X	$-H^E$	X	$-H^E$
0.0100	289.9	0.4058	2215	0.8863	555.8
0.0501	1240	0.4980	2006	0.9540	240.4
0.1151	1897	0.6021	1687	0.9810	100.2
0.2008	2265	0.7019	1366		
0.3013	2335	0.8042	927.6		

fore, the specific term can be calculated from Eq. (5) [3]:

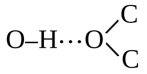
$$U_{\text{sp}} = U_{\text{t}} - U_{\text{nsp}} = DV - p_{\text{int}}V = -\Delta H_v + RT + TV\alpha/\beta_T, \qquad (5)$$

where U_{t} is the total energy of intermolecular interaction; ΔH_v, enthalpy of vaporization of solutions; and R, universal gas constant. Within the framework of this approach, the specific and nonspecific terms of the intermolecular interactions in aqueous solutions of glycols at 298.15 K are plotted in Fig. 2. The enthalpies of vaporization of the solutions were calculated from Eq. (6):

$$\Delta H_v = [(1 - X)\Delta H_{v1} + X\Delta H_{v2}] - H^E, \qquad (6)$$

where ΔH_{v1} and ΔH_{v2} are the enthalpies of vaporization of water [16] and glycols [17–19]. The enthalpies of mixing of mono-, di-, and triethylene glycols with water (H^E) were taken from [20, 21], and the enthalpies of mixing of tetraethylene glycol with water were measured in this study (Table 3).

Figure 2 shows that, with increasing number of ether groups, the terms $|U_{\text{nsp}}|$ for the examined glycols increase in the absolute value. An increase in the nonspecific term in going from ethylene glycol to tetraethylene glycol was revealed previously [22] and is most probably due to the fact that the dipole moments of the glycol molecules linearly increase in the same direction [23]. With $|U_{\text{sp}}|$, the trend is opposite. On introduction of even one ether group into the ethylene glycol molecule, the specific term of the total intermolecular interaction ceases to be prevalent. The same conclusion follows from the IR data for glycols [24], according to which the strength of the intermolecular hydrogen bond appreciably decreases in going from ethylene glycol to tetraethylene glycol. This is caused by the fact that the stronger H bonds between oxygen atoms of hydroxy groups, forming three-dimensional networks in mono- and diethylene glycols [25], are replaced by weaker bonds



$$\text{O–H}\cdots\text{O}\begin{matrix}\diagup \text{C}\\ \diagdown \text{C}\end{matrix}$$

in tri- and tetraethylene glycols. Along with increased length of the molecular backbone in oxyethylated glycols, which significantly hinders the association because of the steric effect, the weaker proton-donor power of oxyethylated glycols compared to ethylene glycol is also responsible for the lower contribution of the specific term in oxyethylated glycols [26].

As the mole fraction of mono- and diethylene glycols in solutions is increased to 0.3–0.4, the absolute value of the specific term in mixtures decreases by 3–6 kJ mol^{-1} (Fig. 2). On adding water to these glycols, the specific term varies similarly, but the deviation of U_{sp} from the additivity in glycol-rich solutions is less pronounced. This behavior of the functions $U_{\text{sp}}(X)$ is most probably due to the fact that additions of components of binary systems to each other break the network formations both in water and in glycols. An increase in the mole fraction of triethylene glycol to 0.35 is accompanied by a decrease in the specific term $|U_{\text{sp}}|$ by ~15 kJ mol^{-1} (Fig. 2). Despite essentially different behavior of the function $U_{\text{sp}}(X)$ in this system, mixtures of mono-, di-, and triethylene glycol with water, on the whole, preserve a common network of hydrogen bonds, as indicated by negative values of their temperature coefficients. A still greater decrease in $|U_{\text{sp}}|$ is observed in the water–tetraethylene glycol system; it is comparable with that observed on adding aprotic *N*-methylpyrrolidone to water [27]. Such similarity in the behavior of the functions $U_{\text{sp}}(X)$ in these systems is due to the fact that, on the one hand, both solvents do not have networks of H bonds and, on the other hand, both are strong electron donors and therefore form strong heteroassociates with water. An increase in the number of ether groups and concentration of glycols is accompanied by a regular (linear at $X > 0.4$) increase in the nonspecific term $|U_{\text{nsp}}|$ in the mixtures. In pure tetraethylene glycol, the relative contribution of this term to the total intermolecular interaction reaches 90%. The calculations show that, in mixtures of water with glycols, the temperature factor exerts the strongest effect on nonspecific interactions, which become appreciably weaker with increasing temperature.

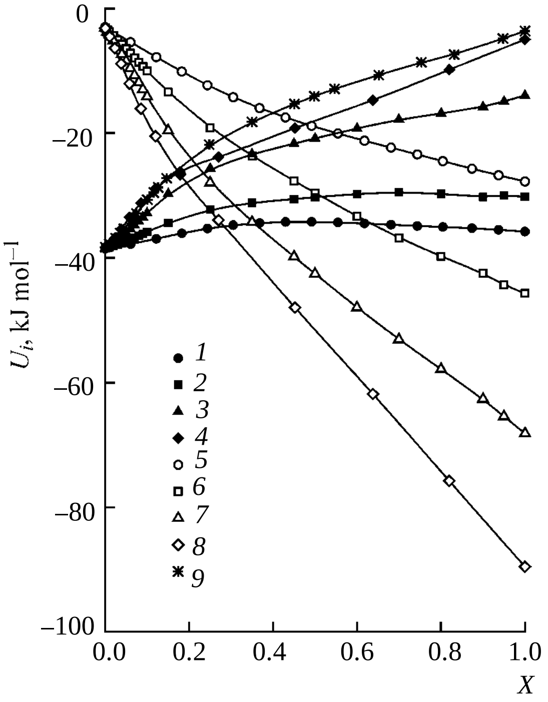


Fig. 2. Contributions (*1–4*) U_{sp} and (*5–8*) U_{nsp} to the total energy of intermolecular interactions in aqueous solutions of (*1, 5*) ethylene glycol, (*2, 6*) diethylene glycol, (*3, 7*) triethylene glycol, and (*4, 8*) tetraethylene glycol at 298.15 K; (*9*) U_{sp} in the water–*N*-methylpyrrolidone system at 298.15 K.

Koga [28] showed that the second derivatives of a number of thermodynamic functions can be used for analyzing changes in the structural state of aqueous nonelectrolyte solutions. It is known that the partial molar enthalpy of ith component of a binary system (H_i^E) is identical to the enthalpy of its solution in a mixture of the corresponding composition and can be estimated calorimetrically. It is, however, impossible to determine experimentally the derivative of this quantity, which involves determination of the partial derivative of the partial molar excess enthalpy of component *i* with respect to composition:

$$H_{i-i}^E = (1 - X_i)(\partial H_i^E/\partial X_i). \qquad (7)$$

The physical sense of this quantity is the effect of an addition of ith component on H_i^E. Negative values of H_{i-i}^E indicate that addition of a component makes its existence in solution more preferable, or attractive (in enthalpy terms). The positive values indicate that

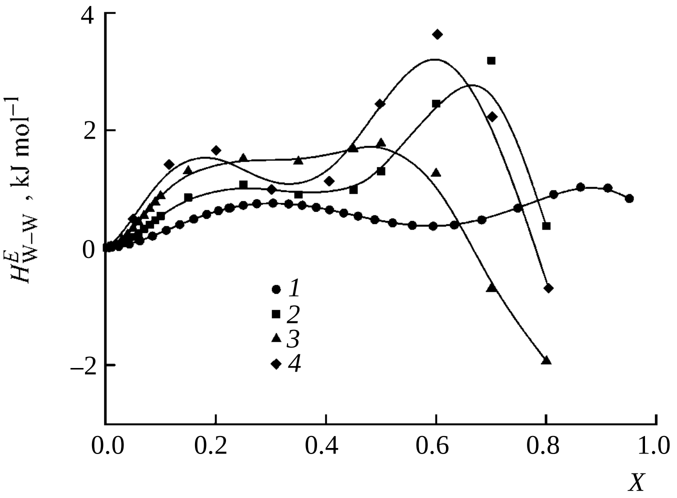


Fig. 3. Concentration dependence of the enthalpy function of interaction H^E_{W-W} in aqueous solutions of (*1*) ethylene glycol, (*2*) diethylene glycol, (*3*) triethylene glycol, and (*4*) tetraethylene glycol and 298.15 K.

the interaction of the component molecules is replulsive.

Figure 3 shows the enthalpy functions of interaction of water (H^E_{W-W}) in the mixtures under consideration. The calculation was based on the results of this study (Table 3) and published data [20, 21]. Because the experimental data for solutions rich in oxyethylated glycols were insufficient, the functions H^E_{W-W} for these mixtures were calculated only for $X \le 0.8$. Figure 3 shows that, with an increase in the number of ether groups in glycol molecules, the functions $H^E_{W-W}(X)$ gradully increase in the greater part of the concentration range. However, in glycol-rich solutions (Fig. 3), negative values of H^E_{W-W} appear, suggesting preferential interaction of water molecules with each other.

Among approaches used for studying various terms of intermolecular interaction in structuring processes in solutions, Kirkwood–Buff theory (8) [29–31] is actively used:

$$G_{ij} = \int_0^\infty (g_{ij} - 1)4\pi r^2 dr, \tag{8}$$

where g_{ij} is the radial distribution function of *i*th molecule around the central *j*th molecule. In water–glycol systems, these quantities were calculated similarly to [27, 31], using data from [4, 32–36]. The calculated functions $G_{ij}(X)$ in aqueous solutions of the glycols studied are plotted in Fig. 4; they agree well with the corresponding values obtained for water–ethylene glycol mixtures [30]. The data obtained show pairwise similarity of G_{ij} in mixtures of water with mono- and diethylene glycol (Figs. 4a, 4b), and of water with tri- and tetraethylene glycol (Figs. 4c, 4d).

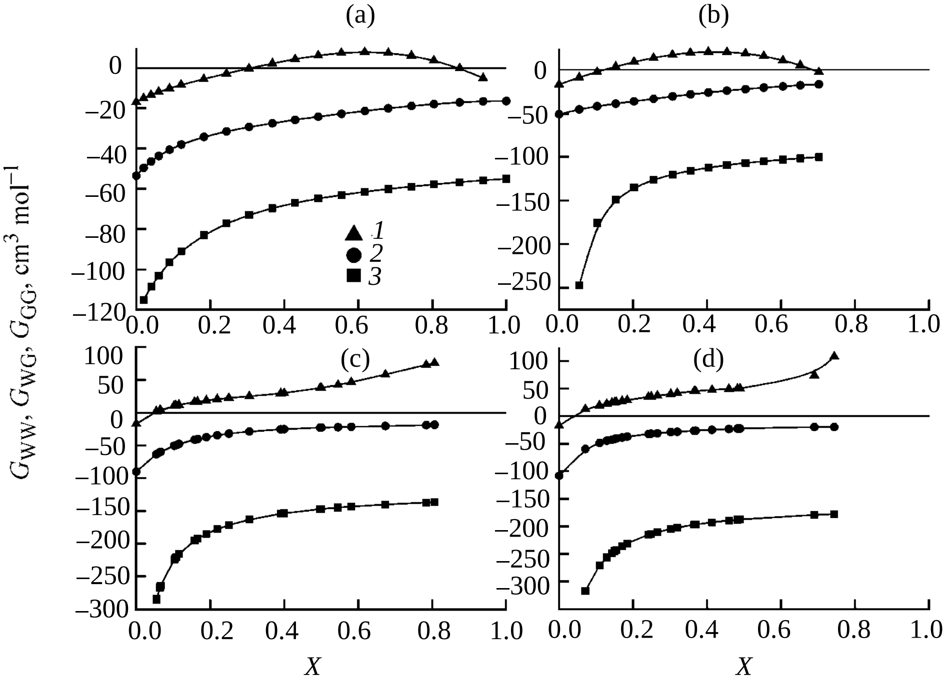


Fig. 4. Composition dependences of the Kirkwood–Buff integrals (*1*) G_{WW}, (*2*) G_{WG}, and (*3*) G_{GG} in aqueous solutions of (a) ethylene glycol, (b) diethylene glycol, (c) triethylene glycol, and (d) tetraethylene glycol at 298.15 K.

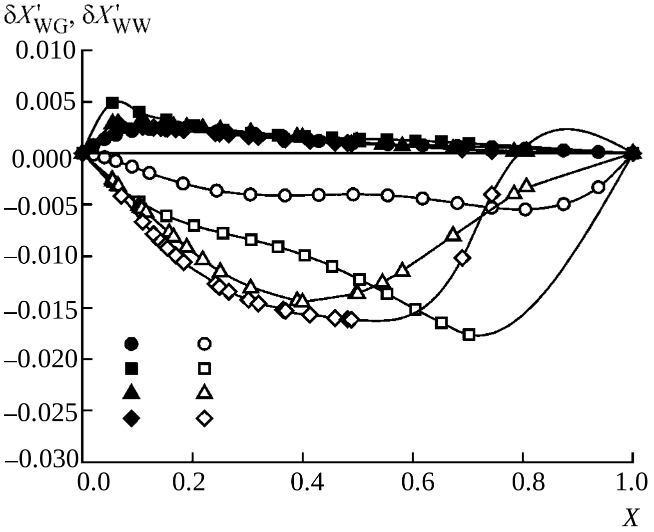


Fig. 5. Parameters of preferential solvation (*1–4*) $\delta X'_{WG}$ and (*5–8*) $\delta X'_{WW}$ in the first solvation shell of components of aqueous solutions of (*1, 5*) ethylene glycol, (*2, 6*) diethylene glycol, (*3, 7*) triethylene glycol, and (*4, 8*) tetraethylene glycol at 298.15 K.

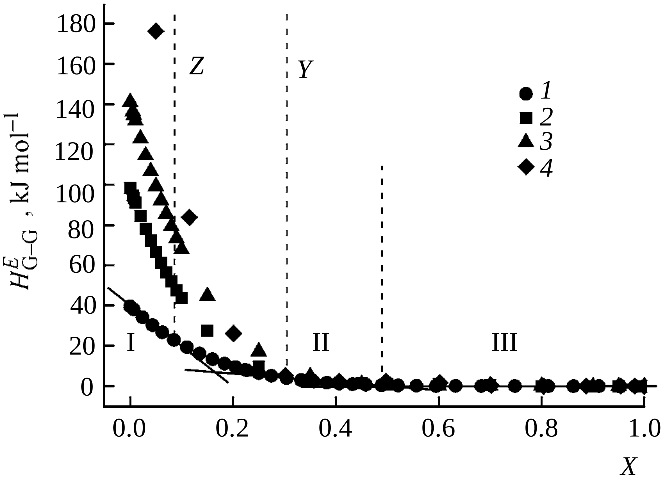


Fig. 6. Concentration dependence of the enthalpy function of interaction H^E_{G-G} in aqueous solutions of (*1*) ethylene glycol, (*2*) diethylene glycol, (*3*) triethylene glycol, and (*4*) tetraethylene glycol at 298.15 K.

The integrals G_{ij} allow estimation of the parameters of preferential solvation [Eqs. (9), (10)] characterizing the difference between the local concentration (superscript *L*) of water around both components and the molar concentration of water in the bulk of solution:

$$\delta X_{WW} = X^L_{WW} - X_W, \quad (9)$$

$$\delta X_{WG} = X^L_{WG} - X_W. \quad (10)$$

As shown by Matteoli [30], for correct estimation of these parameters it is necessary to use a reference system. Correspondingly, the refined parameters of preferential solvation $\delta X'_{WW}$ and $\delta X'_{WG}$ in water–glycol systems (Fig. 5) were calculated similarly to [27] using the relationships from [31].

The first additions of ethylene glycol to water (up to X ~0.1) do not give rise to appreciable deviations of $\delta X'_{WW}$ from zero. This is followed by a relatively wide range of compositions corresponding to the break-up of the water structure ($\delta X'_{WW} < 0$, minimum at X ~0.8), in which water preferentially solvates ethylene glycol ($\delta X'_{WG} > 0$, maximum at X ~0.2). This result is consistent with the results of computer simulation [37] according to which ethylene glycol weakly affects the H-bond network of water at $0 < X < 0.1$, and even at X 0.8 water in mixtures with ethylene glycol in small clusters preserves its tetrahedral H-bond network. An increase in the number of ether groups has no appreciable effect on the functions $\delta X'_{WG}(X)$ (in all the systems they have similar shape, Fig. 5), but is accompanied by more active break-up of the water structure ($\delta X'_{WW} < 0$). The coordinates of the minima of the functions $\delta X'_{WW}(X)$ correlate with the concentrations corresponding to the maxima in the $H^E_{W-W}(X)$ plots (Fig. 3). Despite the lack of experimental data for calculating $\delta X'_{WW}$ at $X > 0.8$, we can note a trend toward self-association of water ($\delta X'_{WW} > 0$) in this range of compositions with increasing number of ether groups, which also follows from the shape of the functions $H^E_{W-W}(X)$ (Fig. 3).

Figure 6 shows the concentration dependences of the second derivatives of the excess partial molar enthalpies of glycols in the mixtures under consideration at 298.15 K. The bending points in the corresponding dependences divide the whole concentration range into several parts. According to [28], in water–glycol systems there are three concentration ranges (I, II, III) and a transition range $Z < X < Y$. The corresponding ranges in Fig. 6 are indicated only for the enthalpy function of interaction $\mathrm{H}^{\mathrm{E}}_{G-G}(X)$ in aqueous solutions of ethylene glycol.

Belousov and Panov [38] showed that, when polyfunctional electrolytes are added to pure water, in the range $0 < X < X^*$ the perturbing effect of solute molecules on the water molecules is weak, and the upper boundary of this range, X^*, corresponds to the minima of the excess partial molar volumes of the solute molecules. The coordinates of the minima of the functions $V^E_2(X)$, determined from data of [4, 32], are

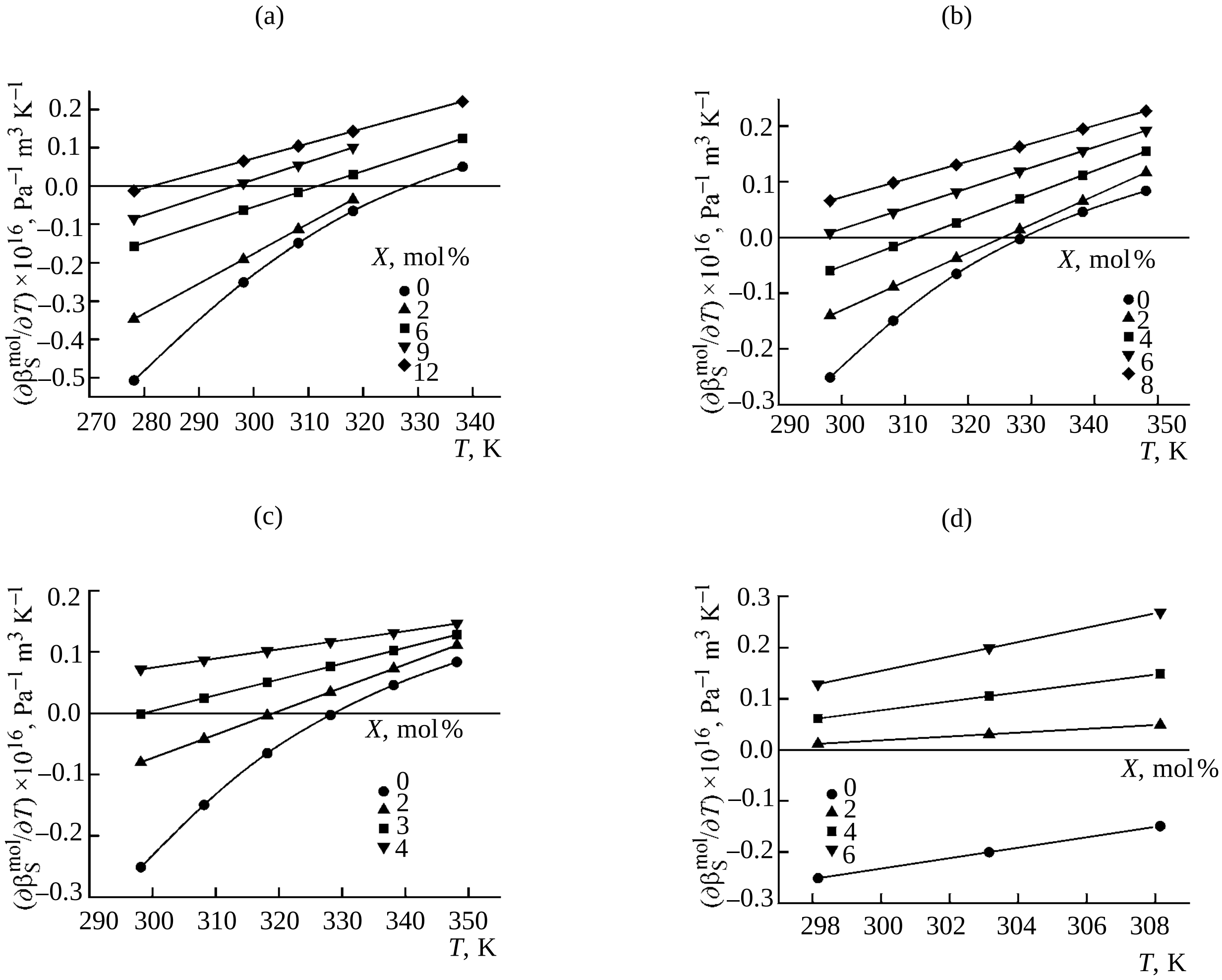


Fig. 7. Temperature dependence of the temperature coefficient of molar adiabatic compressibility $\partial\beta_S^{mol}/\partial T$ in aqueous solutions of (a) ethylene glycol, (b) diethylene glycol, (c) triethylene glycol, and (d) tetraethylene glycol.

given in Table 4. The concentration boundary Z of range I of aqueous solutions of glycols (Table 4) almost coincides with the coordinates of the minima of $V_2^E(X)$ and of the onset of the bend in the concentration dependence of the internal pressure. According to [37], in the range $0 < X < 0.1$, ethylene glycol does not noticeably affect the H-bond network of water. Table 4 shows that the concentration ranges with the minimally distorted structure of water in solutions of oxyethylated glycols are appreciably narrower than in solutions of ethylene glycols. The data of Table 4 on the limiting concentrations of glycols at which the hydrogen bond framework around the incorporated glycol molecules remains intact, according to estimations by different methods, refer only to 298.15 K. The preservation of such framework in aqueous solutions at other temperatures follows from the negative signs of the temperature derivative of the molar adiabatic compressibility $\partial\beta_S^{mol}/\partial T$ ($\beta_S^{mol} = V^{mol}/u^2\rho$, where V^{mol} is the molar volume) [39]. Figure 7 clearly shows that in dilute aqueous solutions the negative values of $\partial\beta_S^{mol}/\partial T$ become positive above certain temperature. In more concentrated solutions of the glycols under consideration, the derivative $\partial\beta_S^{mol}/\partial T$ is positive at all the examined temperatures (Fig. 7). All these data indicate that an increase in the number of ether groups in oxyethylated glycols is accompanied by more efficient break-up of the water structure

Table 4. Position of minima of functions $V_2^E(X)$ and concentration boundaries of structural ranges in aqueous solutions of glycols at 298.15 K

Glycol	min $V_2^E(X)$	Z	Y	II→III
Ethylene glycol	0.06	0.10	0.30	0.48
Diethylene glycol	0.04	0.05	0.27	0.45
Triethylene glycol	0.03	0.04	0.25	0.42
Tetraethylene glycol	0.02	0.03	0.21	0.37

and narrowing of range I of the solutions not only at 298.15 K but also at other temperatures.

In the water–ethylene glycol system, the concentration range $Z < X < Y$, determined in accordance with [28], is the widest among the examined systems (Fig. 6) and virtually coincides with the region in which the concentration dependence of $\Delta p_{\text{int}}/\Delta T$ has a bend. The boundaries of this range completely correspond to the transition range of compositions found in a comprehensive study of the water–ethylene glycol system [7]. The right boundary of the transition range of aqueous solutions of oxyethylated glycols (Table 4) is shifted relative to water–ethylene glycol mixtures toward pure water. Despite the fact that in this range the structural changes of water are the most significant, all the mixtures, on the whole, preserve the H-bond network, as indicated by negative values of their temperature coefficients (Fig. 1). This may be due to incorporation of glycol molecules into a hydrogen bond network of water, leading to its gradual change and formation of a common H-bond network.

Range III of glycol-rich solutions is the widest (Table 4). In the water–ethylene glycol system (Fig. 6), it covers more than a half of the whole concentration range, in agreement with [40]. Calculations show that the excess partial molar enthalpies of ethylene glycol (H^E_G) are small and negative even at X ~0.95, which is caused by the presence of free OH groups of water even at these concentrations. Computer simulation of ethylene glycol rich mixtures with water showed that only small amount of water molecules form self-associates (dimers and small clusters [37]). These facts suggest that in composition range III water is predominantly dispersed into separate molecules and forms heteroassociates with ethylene glycol which is in excess in solution. For oxyethylated glycols, range III is wider than in the water–ethylene glycol system (Table 4). An increase in the number of ether groups in their molecules is accompanied by the shift of the left boundary of this range, as compared to ethylene glycol solutions, toward pure water. Among the systems we examined, the water–tetraethylene glycol system is the only system in which there is no network structure in range III, because there is no H-bond network in pure tetraethylene glycol.

The shift toward water-rich solutions with increasing length of the backbone is also observed for composition range II (Table 4). In this range, negative values of $H^E_G(X)$ appear, suggesting the presence of free OH groups of water molecules, which can form not only heteroassociates but also clusters consisting exclusively of water molecules. Also, in this composition range the interaction between glycol molecules becomes less preferable than in the pure liquid (Fig. 6).

Thus, analysis of the thermodynamic characteristics of aqueous solutions of glycols at various temperatures reveals three concentration ranges with specific predominant structural organization and a transition range. In solutions of all the glycols, there is the composition range $0 < X < Z$ in which glycols affect the water structure insignificantly. This range becomes narrower with increasing number of ether groups and temperature. With a further increase in the glycol concentrations, the three-dimensional structure of hydrogen bonds of water undergoes transformations, and only in the water–tetraethylene glycol system it is apparently broken. All the other systems remain three-dimensionally associated throughout the composition range. A sharp decrease in the specific term and an increase in the nonspecific term of the total energy of intermolecular interactions in the range $X < 0.35$ additionally support the assumption that specifically in this concentration range changes in the water structure are the most dramatic. In range II, apparently, the structural formations of both components and various heteroassociates are present simultaneously. An increase in the number of oxyethyl groups leads to widening of composition range III in which water is predominantly dispersed into monomeric molecules and forms heteroassociates with glycol molecules (although self-association of a part of water molecules is still possible).

EXPERIMENTAL

Tetraethylene glycol (Aldrich) was double-distilled in a vacuum with collection of the middle fractions. The calorimetric experiment was performed with double-distilled water. The water content of tetraethylene glycol, determined by Fischer titration, did not exceed 0.03 wt %, and its density was in good agreement with published data [6]. The enthalpies of mixing of tetraethylene glycol with water were measured on a rocking calorimeter with an isothermal shell [41]. The relative error of measuring enthalpies did not exceed 1%.

REFERENCES

1. Kartsev, V.N., Rodnikova, M.N., Shtykov, S.N., and Bartel, J., *Zh. Fiz. Khim.*, 2003, vol. 77, no. 8, p. 1456.
2. Kartsev, V.N., Rodnikova, M.N., Bartel, J., and Shtykov, S.N., *Zh. Fiz. Khim.*, 2002, vol. 76, no. 6, p. 1016.
3. Ivanov, E.V. and Abrosimov, V.K., *Zh. Strukt. Khim.*, 2005, vol. 46, no. 5, p. 889.

4. Sakurai, M., *J. Chem. Eng. Data*, 1991, vol. 36, no. 4, p. 424.
5. George, J. and Sastry, N.V., *Fluid Phase Equil.*, 2004, vol. 216, no. 1, p. 307.
6. Muller, E.A. and Rasmussen, P., *J. Chem. Eng. Data*, 1991, vol. 36, no. 2, p. 214.
7. Huot, J.Y., Battistel, E., Lumry, R., Villeneuve, G., Lavallee, J.F., Anusem, A., and Jolicoeur, C., *J. Solution Chem.*, 1988, vol. 17, no. 7, p. 601.
8. Pal, A. and Singh, W., *J. Chem. Eng. Data*, 1997, vol. 42, no. 2, p. 234.
9. Douheret, G., Davis, M.I., Fjellanger, I.J., and Hoiland, H., *J. Chem. Soc., Faraday Trans. 1*, 1997, vol. 93, no. 10, p. 1943.
10. Nan, Z., Liu, B., and Tan, Z., *J. Chem. Thermodyn.*, 2002, vol. 34, no. 6, p. 915.
11. Dyment, O.N., Kazanskii, K.S., and Miroshnikov, A.M., *Glikoli i drugie proizvodnye okisei etilena i propilena* (Glycols and Other Derivatives of Ethylene and Propylene Oxides), Moscow: Khimiya, 1976.
12. Uosaki, Y., Kitaura, S., and Moriyoshi, T., *J. Chem. Eng. Data*, 2006, vol. 51, no. 2, p. 423.
13. Mikhailov, V.A. and Kirgintsev, A.N., *Zh. Fiz. Khim.*, 1962, vol. 36, no. 9, p. 2085.
14. Dack, M.R., *Aust. J. Chem.*, 1975, vol. 28, no. 8, p. 1643.
15. Holtzer, A. and Emerson, M.F., *J. Phys. Chem.*, 1969, vol. 73, no. 1, p. 26.
16. Vargaftik, N.B., *Spravochnik po teplofizicheskim svoistvam gazov i zhidkostei* (Handbook of Thermal Properties of Gases and Liquids), Moscow: Nauka, 1972.
17. Knauth, P. and Sabbah, R., *Bull. Soc. Chim. Fr.*, 1988, vol. 53, no. 6, p. 834.
18. Steel, W.V., Chirico, R.D., Knipmeyer, S.E., and Nguen, A., *J. Chem. Eng. Data*, 2002, vol. 47, no. 4, p. 689.
19. Zaichikov, A.M., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 8, p. 1320.
20. Matsumoto, Y., Touhara, H., Nakanishi, K., and Watanabe, N., *J. Chem. Thermodyn.*, 1977, vol. 9, no. 8, p. 801.
21. Hamam, S.E.M., Benson, G.C., and Kumaran, M.K., *J. Chem. Thermodyn.*, 1985, vol. 17, no. 10, p. 973.
22. Atovmyan, E.G., Baturin, S.M., and Fedotova, T.N., *Vysokomol. Soedin., Ser. A*, 1989, vol. 31, no. 8, p. 1685.
23. Rudan-Tasic, D. and Klofutar, C., *J. Mol. Liq.*, 2004, vol. 111, no. 1, p. 125.
24. Krasnoperova, A.P., Surov, Yu.N., and Pivnenko, N.S., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 12, p. 2053.
25. Ginzburg, I.M., Strelkova, L.F., and Ragozina, T.N., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 5, p. 1116.
26. Schrodle, S., Buchner, R., and Kunz, W., *J. Phys. Chem. (B)*, 2004, vol. 108, no. 20, p. 6281.
27. Zaichikov, A.M., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 4, p. 660.
28. Koga, Y., *J. Phys. Chem.*, 1996, vol. 100, no. 13, p. 5172.
29. Kirkwood, J.G. and Buff, F.P., *J. Chem. Phys.*, 1951, vol. 19, no. 6, p. 774.
30. Matteoli, E., *J. Phys. Chem. B*, 1997, vol. 101, no. 47, p. 9800.
31. Marcus, Y., *Monatsh. Chem.*, 2001, vol. 132, no. 12, p. 1387.
32. Dethlefsen, C. and Hvidt, A., *J. Chem. Thermodyn.*, 1985, vol. 17, no. 2, p. 193.
33. Villamanan, M.A., Gonzalez, C., and Van Ness, H.C., *J. Chem. Eng. Data*, 1984, vol. 29, no. 4, p. 427.
34. Herskowitz, M. and Gottlieb, M., *J. Chem. Eng. Data*, 1984, vol. 29, no. 2, p. 173.
35. Herskowitz, M. and Gottlieb, M., *J. Chem. Eng. Data*, 1984, vol. 29, no. 4, p. 450.
36. Marcus, Y., *J. Mol. Liq.*, 2003, vol. 107, nos. 1–3, p. 109.
37. Gubskaya, A.V. and Kusalik, P.G., *J. Phys. Chem. A*, 2004, vol. 35, no. 108, p. 7165.
38. Belousov, V.P. and Panov, M.Y., *Thermodynamic Properties of Aqueous Solutions of Organic Substances*, Boca Raton: CRC, 1994.
39. Grineva, O.V., *Zh. Strukt. Khim.*, 2006, vol. 47, no. 1, p. 185.
40. Douheret, G., Pal, A., Hoiland, H., and Davis, M.I., *J. Chem. Thermodyn.*, 1991, vol. 23, no. 5, p. 569.
41. Zaichikov, A.M., Nogovitsyn, E.A., Zheleznyak, N.I., and Krestov, G.A., *Zh. Fiz. Khim.*, 1988, vol. 62, no. 11, p. 3118.