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Thermodynamic Characteristics of Self-Associated Solvents

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Abstract—The thermodynamic characteristics of solvents differing by the type of molecular self-assembly through the hydrogen bonds were considered. In the framework of a model approach specific and nonspecific components of the total energy of intermolecular interaction were identified. The solvents with hydrogen bond network are found to belong to a class of liquids, where the strength of non-specific interactions increases with increasing temperature, while in the solvents with a chain of self-association contribution of these interactions is virtually independent of temperature. For this reason, the effect of increasing temperature on the internal pressure and its temperature coefficient were found to be different in these groups of solvents.

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The necessity to investigate oxyethylated glycols, diols, and monohydric alcohols is determined by their important role in science and modern technology. Despite the widespread use of these fluids in various industries [1], for example, in the production of cosmetic preparations, study of the thermodynamic parameters of these non-electrolytes, self-associated through hydrogen bonding, is still poor. In this connection, an urgent task is the investigation of the thermodynamic characteristics of liquid-phase systems reflecting effectively both the features of intermolecular interactions and the structural changes in the individual solvents.

It was shown in [2] that spatial network of hydrogen bonds determined the features of the thermodynamic properties of fluids, and a new class of solvents with H-bond network was singled out. For these solvents small values of the adiabatic and isothermal compressibility coefficients (β_T), as well as of the thermal volume expansion coefficient (α) are typical. Figure 1a, shows the dependence of $\beta_T(T)$ of organic solvents, mainly diols and oxyethylated glycols, and of water. Many of such solvents dissolve each other. The temperature dependences of molar coefficients of isothermal compressibility $\beta_{T,m}$ ($\beta_{T,m} = \beta_T V_m$) shown in Fig. 1b, behave differently, and their values grow from water to methanol and tetraethylene glycol, which, as will be shown below, do not belong to the solvents with H-bond network. Data on $\beta_T(T)$ of organic solvents are taken from [3–6], where also the polytherms of their internal pressure ($P_{int} = -T\alpha/\beta_T$) and density have been obtained.

Internal pressure as a thermodynamic characteristics of the individual solvents is rarely used in the study of fluids. In a study of the temperature dependence of $P_{int}(T)$ a difference was revealed in the behavior of the temperature coefficient of internal pressure ($\partial P_{int}/\partial T$) of the solvents of different classes [7]. It was found that coefficient was positive for the weakly associated liquids with the structure close to dense packing, for the solvents with H-bond chains like monohydric alcohols it was close to zero, and for the liquids with a network of hydrogen bonds it was negative. Figure 2 shows examples of the earlier obtained temperature dependences of internal pressure for *N*-methylpyrrolidone, formamide, and water [6, 8]. The dependences of $P_{int}(T)$ of the solvents have the opposite slope, which determines the difference of signs of the coefficient $\partial P_{int}/\partial T$ of these fluids (Fig. 2b). *N*-Methylpyrrolidone, which is a dipolar aprotic solvent, in accordance with [7] belongs to the group of weakly associated solvents with positive temperature coefficient of internal pressure. Water, formamide, and diols (not shown in Fig. 2) belong to the group of liquids with a negative coefficient $\partial P_{int}/\partial T$. However, it was noted later [9] that, although the temperature coefficient of internal pressure allowed distinguishing liquids with different molecular association (with and without participation of H-bonds), the use of internal pressure for the study of liquid systems was difficult

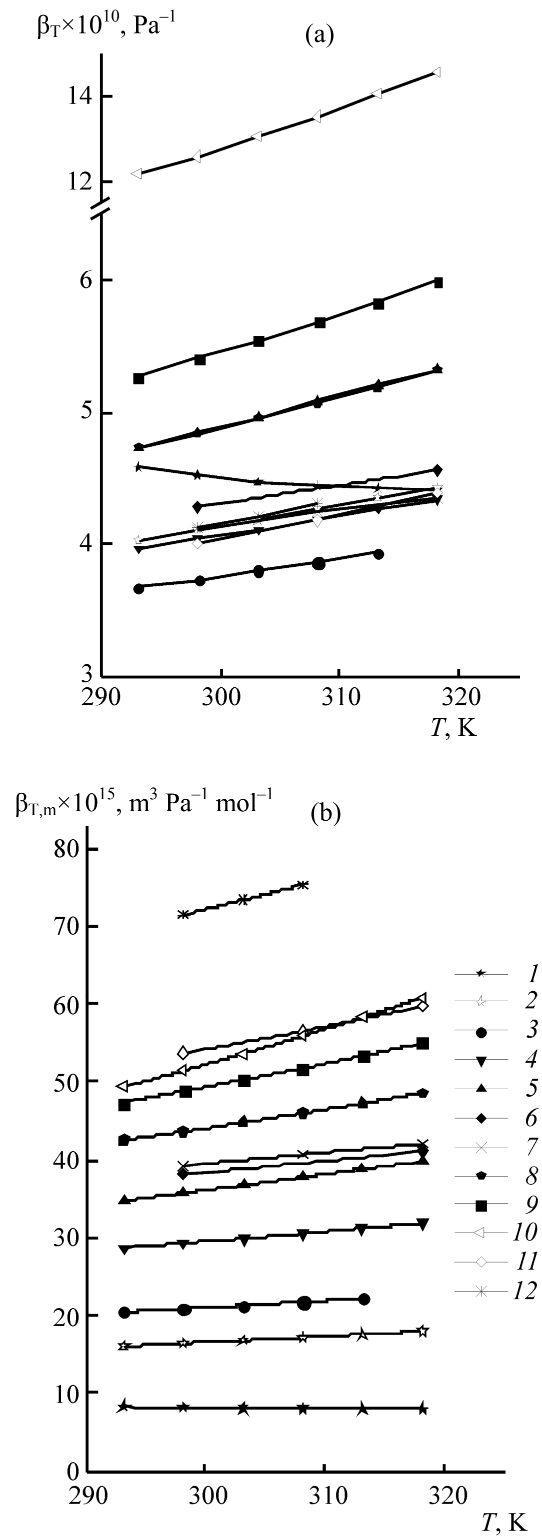

Fig. 1. Dependence of isothermal compressibility (a) and molar isothermal compressibility (b) on temperature: (*1*) water, (*2*) formamide, (*3*) ethanediol, (*4*) 1,3-propanediol, (*5*) 1,2-propanediol, (*6*) 1,4-butanediol, (*7*) diethylene glycol, (*8*) 1,3-butanediol, (*9*) 1,2-butanediol, (*10*) methanol, (*11*) triethylene glycol, (*12*) tetraethylene glycol.

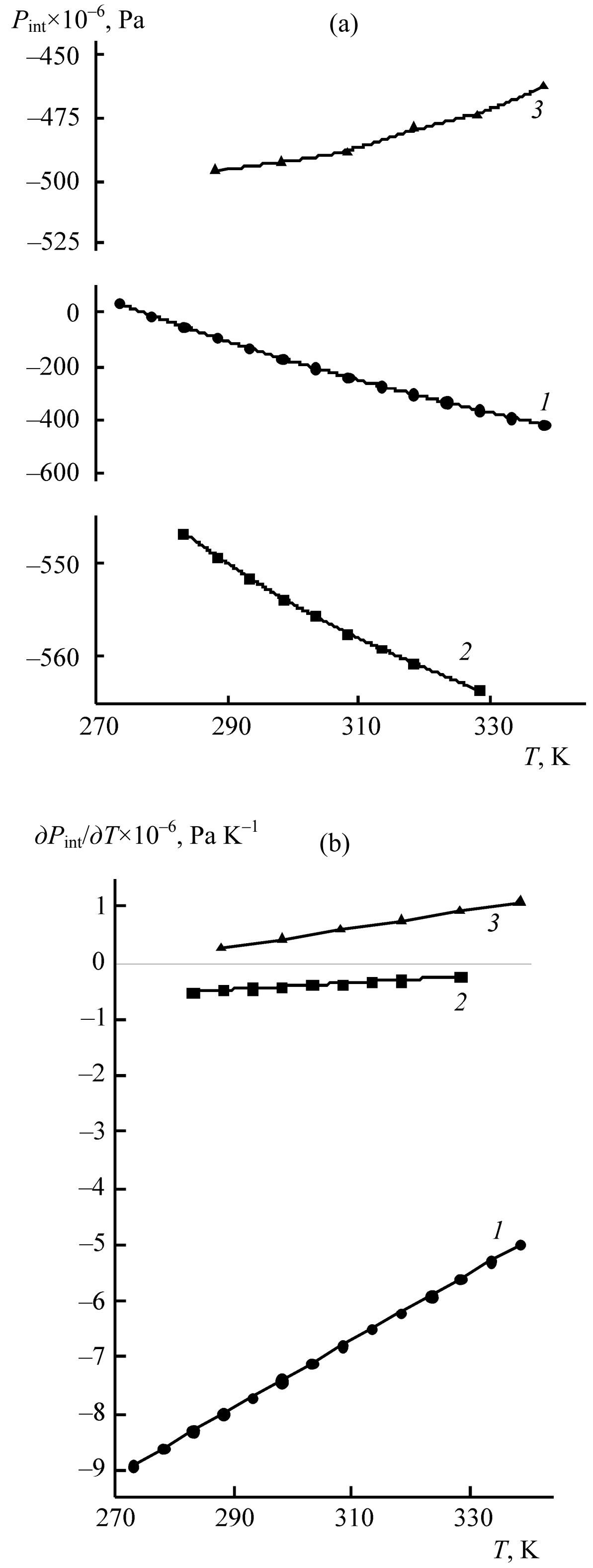

Fig. 2. Dependence of internal pressure (a) and temperature coefficient of internal pressure (b) on temperature: (*1*) water, (*2*) formamide, (*3*) *N*-methylpyrrolidone.

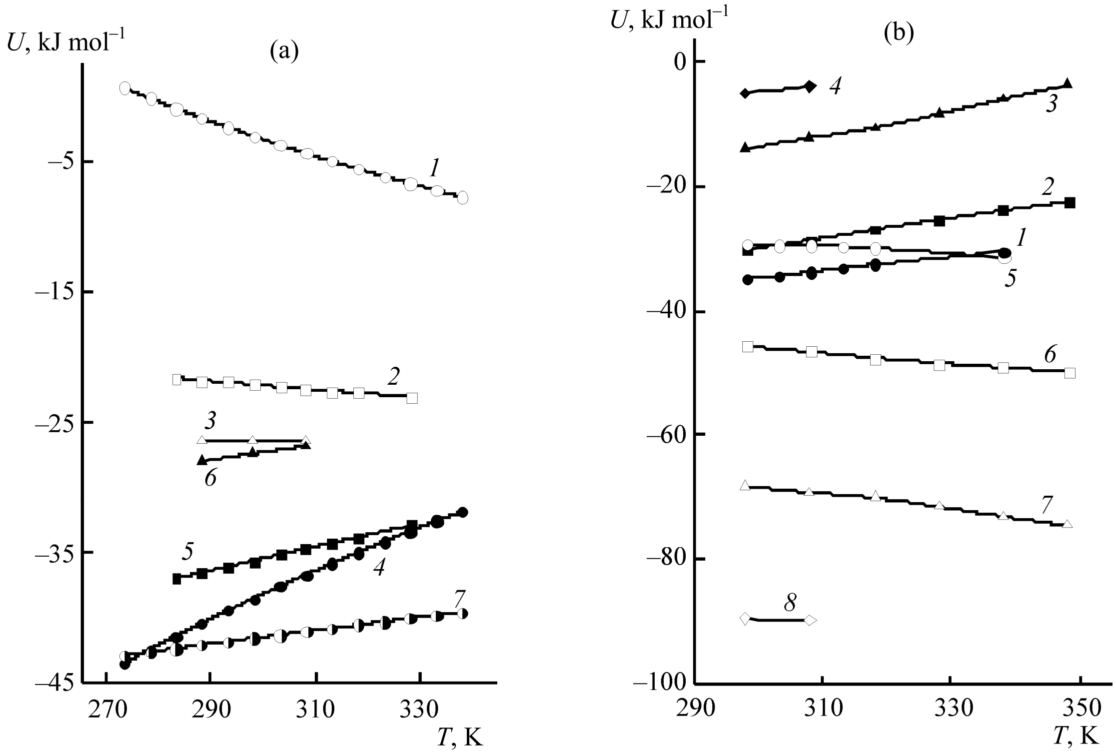

Fig. 3. Temperature dependence of (a) the contributions U_{nsp} (*1–3*) and U_{sp} (*4–6*) to the total energy of intermolecular interaction of water (*1, 4*), formamide (*2, 5*) and *N*-methylformamide (*3, 6*), (*7*, U_{tot} of water) and (b) contributions of U_{nsp} (*5–8*) and U_{sp} (*1–4*) to the total energy of intermolecular interaction in ethanediol (*1, 5*), diethylene glycol (*2, 6*), triethylene glycol (*3, 7*) and tetraethylene glycol (*4, 8*).

because of the ambiguous relationship between this parameter and the state of a system.

Recent studies [10, 11] showed that cohesive energy density contains a volume-independent part due to the presence of specific interactions, as well as the volume-dependent part, which results from the nonspecific interactions and for alkanes coincides with the P_{int}. It is obvious that the internal pressure is an important thermodynamic characteristic of a liquid. Therewith, the difference in the dependences $P_{int}(T)$ and the coefficients of $\partial P_{int}/\partial T$ for certain classes of solvents becomes clear after the calculation of molar specific and nonspecific components of the intermolecular interaction. The application of these quantities to the analysis of the thermodynamic properties of individual and mixed solvents is more correct.

According to the known theoretical concepts [12] the nonspecific contribution to the energy of the total intermolecular interaction per one mole of solvent can be calculated using relation (1):

$$U_{nsp} = P_{int}V_m = -TV_m\alpha/\beta_T, \qquad (1)$$

where V_m is the molar volume. Specific component with accounting for Eq. (1) is calculated from relation (2):

$$U_{sp} = U_{tot} - U_{nsp} = -\Delta_V H + RT + TV_m\alpha/\beta_T, \qquad (2)$$

where $\Delta_V H$ is the molar enthalpy of vaporization of the solvent, and R is universal gas constant. The appropriateness of using these concepts to obtain reliable information on the nature of intermolecular interactions and structural changes was confirmed in a study of thermodynamic properties of monohydric alcohols [13].

Figure 3 shows the temperature dependence of the non-specific and specific contributions U_{nsp} and U_{sp} to the total energy of intermolecular interaction (U_{tot}) in the studied solvents. The U_{sp} contribution for propanediol, 1,2- and 1,3-butanediols were evaluated attracting the dependences $\Delta_V H(T)$ [14, 15]. For the calculation of U_{sp} in ethanediol and 1,4-butanediol the data of [16, 17] were used. The functions $\Delta_V H(T)$ of formamide, diethylene glycol, and tetraethylene glycol were obtained by us [5, 6, 18], and the data for triethyleneglycol were taken from [19].

The presence of H-bond networks in water, formamide, and ethanediol was proved mainly using computer simulation techniques [20, 21, 22]. In formamide and water (Fig. 3a) the dominant role belongs to specific interactions. However, in these solvents the $|U_{\mathrm{sp}}|$ contribution decreases with increasing temperature, while simultaneously the contribution from $|U_{\mathrm{nsp}}|$ to the intermolecular interaction increases, which requires more detailed consideration.

Water is the most studied solvent with H-bond network. It forms weak H-bonds with an energy ~ -21 kJ mol^{-1} [23]. With increasing temperature, the hydrogen bonds between its molecules begin to disrupt that decreases the average number of H-bonds formed by water [24]. This leads to a decrease in the degree of ordering in the arrangement of its molecules and a decrease in the distance at which this ordering is preserved, as confirmed by experimental data on thermodynamic, kinetic, spectroscopic, and diffraction characteristics of water [25]. In addition, the average energy of the hydrogen bond becomes weaker [24], and the increase in temperature leads to a decrease in the overall contribution of U_{sp} (Fig. 3a). It was pointed out in [25] that despite the decrease in the contribution of H-bonds to the total energy of intermolecular interactions, even at 300°C they still contribute about 50%, in consistence with the results of studies of high-temperature infrared spectra of water. However, the degree of bonding of water molecules in the H-bond network falls while temperature rises. This leads to the opposite effect on non-specific interactions: the latter on the contrary increases with increasing temperature. The increase in the contribution of $|U_{\mathrm{nsp}}|$ (Fig. 3a) partially compensates a decrease in the contribution of $|U_{\mathrm{sp}}|$, which resulted only in a weak decrease in the total energy of intermolecular interactions in water $|U_{\mathrm{tot}}|$ with increasing temperature. Data in Fig. 3a confirms the findings [25, 26] that with increasing temperature the contribution of nonspecific (van der Waals) interactions in water grows, which, along with specific interactions, play a significant role in the structural organization and intermolecular interactions in water–organic mixtures [8, 27]. The value of non-specific contribution in water estimated by simulation [12] correlates with its numerical estimates obtained in [28, 29]. The low contribution of $|U_{\mathrm{nsp}}|$ in water is caused, in terms of Eq. (1), by abnormally low values of the coefficient α and the values of V_{m}.

From Fig. 3b, we can see that in ethanediol the contributions of U_{nsp} and U_{sp} become identical even at ~335 K (to increase the temperature range, the calculation for this diol was carried out using the data [5, 9, 18]). At higher temperatures, the balance between the U_{nsp} and U_{sp} contributions changes in favor of non-specific interactions. Data in Fig. 3 indicate that in water the $|U_{\mathrm{nsp}}|$ increases fastest with increasing temperature among all the above solvents with H-bond network. This is caused by anomalous behavior of the coefficients α and β_{T} of water [20, 30] that determines a significant increase in the nonspecific interactions in it with increasing temperature. In organic solvents with H-bond network the coefficient α varies only slightly, while their compressibility β_{T} increases rapidly. For this reason, the corresponding raise in the contributions of $|U_{\mathrm{nsp}}|$ in these solvents is much less than in water (Fig. 3). As shown below, upon increase in the molar volume of diols from ethanediol to butanediol the contribution of $|U_{\mathrm{nsp}}|$ grows in succession. The non-specific contribution increases more in oxyethylated glycol (Fig. 3b) which correlates with data [31] indicating the growth of non-specific component from ethylene glycol to tetraethylene glycol. A reason for this is that in oxyethylated glycols of general formula $HOCH_2\cdot(CH_2CH_2O)_nCH_2OH$, where n varies from 0 (ethylene glycol) to 3 (tetraethylene glycol), the molar volume of the ether group exceeds more than twice that of the CH_2 radical (Fig. 3b).

Now it is well known that the elongation of the hydrocarbon chain of alkane molecules consistently increases their packing ratio, reflecting the ratio of the proper volume of solvent molecules to the solvent molar volume ($y = V/V_{\mathrm{m}}$). As shown, for example, in [32], the packing coefficient does not characterize the specific interactions due to self-association through H-bonds. It reflects the interaction of a universal nature growing in alkanes in line with the increase in this ratio. It is interesting to trace the changes in this ratio in oxyethylated glycols and diols relative to the contributions of $|U_{\mathrm{nsp}}|$. There are several ways to calculate this ratio [32]. In the present study it was calculated from the data on isothermal compressibility coefficient in the framework of the theory of large-scale particles [33]. The calculations indicate (Fig. 4) that with an increase in the number of CH_2CH_2O fragments in the molecules of oxyethylated glycol the packing ratio increases significantly, which correlates with data of simulation [34]. On the other hand, with an increase in this ratio the contribution of nonspecific interactions consistently increases. In general, note that

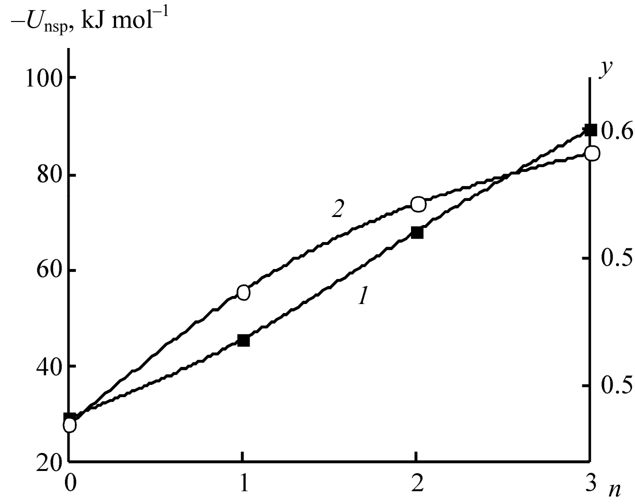

Fig. 4. The dependence of the contributions of U_{nsp} and packing coefficient (y) on the number of (CH_2CH_2O) groups in the molecules of oxyethylated glycols.

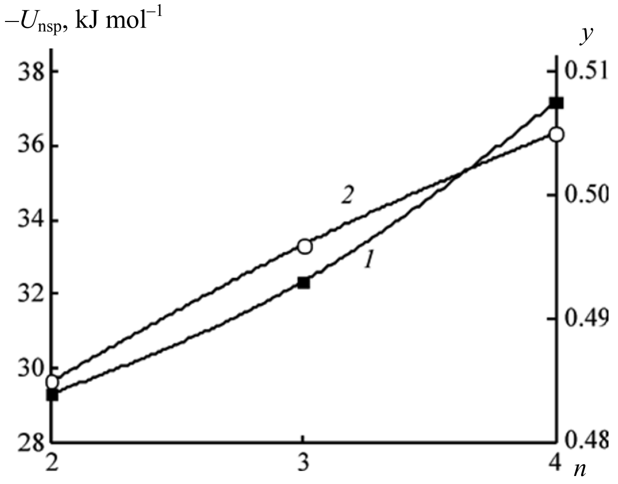

Fig. 5. The dependence of the contributions of U_{nsp} and packing coefficient (y) on the number of CH_2 groups in the molecules of diols.

increase in the number of ether fragments in the molecules of oxyethylated glycol reduces the contribution of $|U_{sp}|$, as well as increases substantially the packing factor and the contribution of $|U_{nsp}|$.

Figure 5 shows a dependence between the calculated packing coefficient of 1,2-diols and the number of CH_2 groups in their molecules. For these diols it should be noted that the packing factor, as well as the contribution of $|U_{nsp}|$, grow slowly with increasing n. Therewith, the value of $|U_{sp}|$ contribution varies considerably less than in the oxyethylated glycols that should be addressed in more detail.

In organic solvents with H-bond network, as especially noticeable in formamide (Fig. 6a) and diols (Fig. 6b), the weakening of specific contributions of $|U_{sp}|$ with increasing temperature occurs more slowly than in water. It is found that the number of H-bonds in formamide decreases slowly with increasing temperature [35]. For ethanediol this may be caused, as stated in [2], by the fact that its H-bond network is more uniform, less mobile and less labile than in water. At 298 K in ethanediol, like both in water and formamide, the specific interactions dominante in the intermolecular interactions. The U_{nsp} and U_{sp} contributions obtained in this work for ethanediol and formamide in the framework of approach [2], correlate with their numerical estimates obtained in [22, 36], as well as for *N*-methylformamide and methanol [36, 37].

If only one ether group is introduced in the ethanediol molecule even in diethylene glycol the specific interaction no more dominates in the total intermolecular interaction (Fig. 3b). This is largely due to the partial replacement of strong H-bonds between hydrogen and oxygen of the hydroxy groups in ethylene glycol by less stable H-bonds between the oxygen of ether groups and the hydroxy hydrogen of oxyethylated glycols. For example, in triethylene glycol a one third part of all the hydrogen bonds is formed with participation of oxygen of ether groups [38]. In accordance with the data [39] on the IR spectroscopy of oxyethylated glycols, the strength of intermolecular hydrogen bond is markedly reduced from ethylene glycol to tetraethylene glycol. In addition, due to the strong elongation of the molecular backbone the process of association of these glycols, which is very sensitive to steric effects, becomes significantly complicated that also contributes to the consistent decrease in the absolute value of the contributions due to the specific interactions in oxyethylated glycols. Indirectly, this is confirmed by the results of simulation of tetraethylene glycol [34] showing that at higher temperatures the H-bonds with the ether oxygen are not practically formed. All this leads to the fact that tetraethylene glycol, unlike diethylene glycol and triethylene glycol, no longer corresponds to a solvent with a net structure. Together with methanol (Figs. 6a and 6b) and *N*-methylformamide (Fig. 3a), it falls into the group of solvents with the chain self-association through H-bonds. For these solvents it is typical that upon increase in temperature the specific interactions are weakened due to the breaking of H-bonded chains, while the

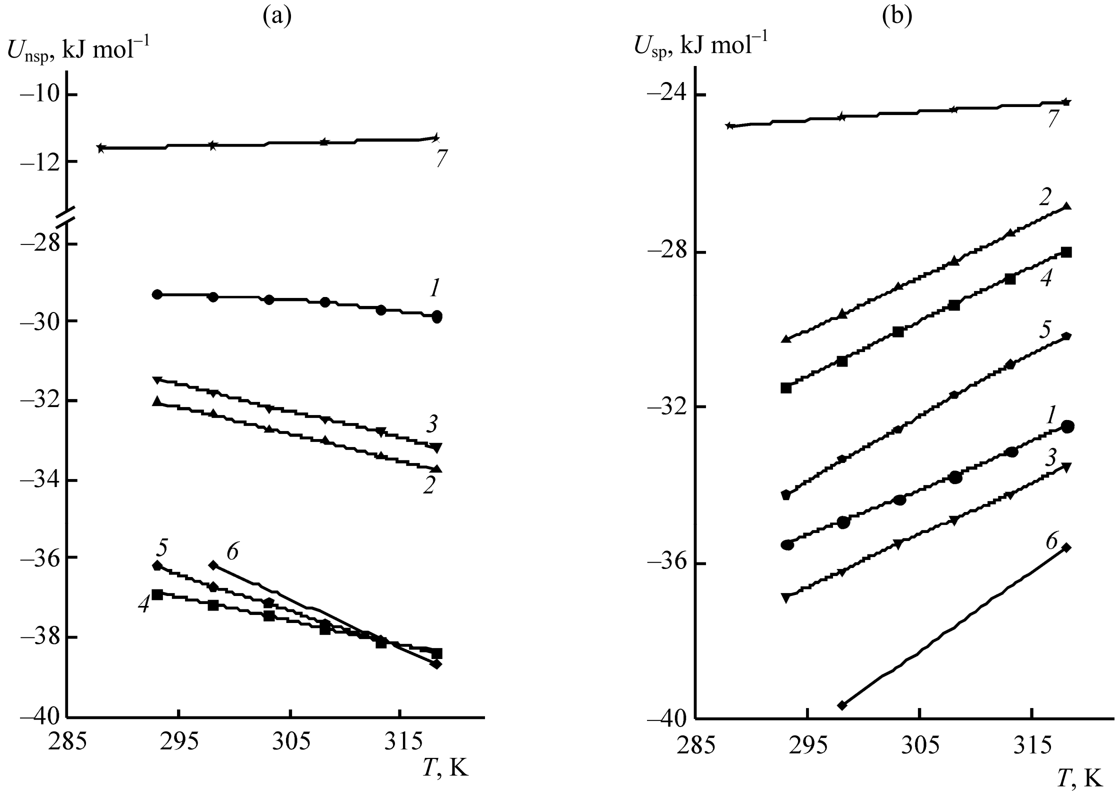

Fig. 6. Temperature dependence of the nonspecific (a) and specific (b) contributions to the total energy of intermolecular interaction in ethanediol (*1*), 1,2-propanediol (*2*), 1,3-propanediol (*3*), 1,2-butanediol (*4*), 1,3-butanediol (*5*), 1,4-butanediol (*6*) and methanol (*7*).

nonspecific interactions are almost independent of temperature. Therefore, the internal pressure in the solvents with chain H-bonds does not change with increasing temperature, and the temperature coefficient of internal pressure for this class of solvents is close to zero.

Data in Fig. 6b show that the contributions of $|U_{sp}|$ increases in the series: 1,2-butanediol < 1,3-butanediol < 1,4-butanediol. Recently it was found by two different methods [40, 41] that the strength of hydrogen bonds increased in the same sequence. The calculation of the average number of hydrogen bonds per a molecule of a diol [40] indicates their increase in the order of 1,2-butanediol (3.45) < 1,3-butanediol (3.61) < 1,4-butanediol (3.65). All this in general is perfectly consistent with the data in Fig. 6b, where we showed that the absolute value of the contributions due to specific interaction consistently increases from 1,2-butanediol to 1,4-butanediol. Boiling points and vaporization enthalpies of butanediols rise in the same direction [14–16]. Calculations in [40] confirm the a priori assumption that the average number of hydrogen bonds per a molecule of butanediol decreases with increasing temperature. The simulation [40] showed that 1,4-butanediol with its hydroxy groups located at the ends of the hydrocarbon chain forms a very strong intermolecular hydrogen bonds due to the absence of steric hindrances to their formation. We can assume that a substantial increase in specific interactions in 1,3-propanediol compared to 1,2-propanediol (Fig. 6b), as well as in the related butanediol is due to a decreased steric hindrances for the intermolecular interactions in the diol with the hydroxy groups located at the ends of the hydrocarbon chain.

Thus, the analysis of the results obtained allows an unambiguous conclusion that the solvents with H-bond network are classified as liquids in which strengthening of non-specific interactions occurs upon increase in temperature, while in the solvents with a chain self-association through H-bond the contribution of such interactions is almost independent of temperature. For this reason, the effect of increasing temperature on the internal pressure and its temperature coefficient is different in these two groups of solvents. Moreover, each group of liquids is characterized by weakening of specific interactions with increasing temperature. The results obtained in the model approach are consistent with published data which have been found for the studied solvents.

REFERENCES

1. *Poly(Ethylene Glycol) Chemistry: Biotechnical and Biomedical Applications*, Harris, J.M., Ed., Heidelberg: Springer Verlag, 1992.
2. Rodnikova, M.N., *Strukturnaya samoorganizatsiya v rastvorakh i na granitse razdela faz* (Structural Self-Organization in Solutions and Interphase), Moscow: LKI, 2008, p. 151.
3. Zorebski, E., Dzida, M., and Piotrowska, M., *J. Chem. Eng. Data*, 2008, vol. 53, no. 1, p. 136.
4. Zorebski, E. and Dzida, M., *J. Chem. Eng. Data*, 2007, vol. 52, no. 3, p. 1010.
5. Zaichikov, A.M. and Krest'yaninov, M.A., *Zh. Obshch. Khim*., 2007, vol. 77, no. 7, p. 1134.
6. Zaichikov, A.M. and Krest'yaninov, M.A., *Zh. Strukt. Khim*., 2008, vol. 49, no. 2, p. 299.
7. Kartsev, V.N., Rodnikova, M.N., Bartel, I., and Shtykov, S.N., *Zh. Fiz. Khim*., 2002, vol. 76, no. 6, p. 1016.
8. Zaichikov, A.M., *Zh. Obshch. Khim*., 2006, vol. 76, no. 4, p. 660.
9. Kartsev, V.N., Rodnikova, M.N., and Shtykov, S.N., *Zh. Strukt. Khim*., 2004, vol. 45, no. 1, p. 99.
10. Kolker, A.M., Korolevv, V.P., and Batov, D.V., *Zh. Strukt. Khim*., 2005, vol. 46, no. 5, p. 959.
11. Rai, N., Siepmann, J.I., Schultz, N.E., and Ross, R.B., *J. Phys. Chem., C*, 2007, vol. 111, no. 43, p. 15634.
12. Dack, M.R.J., *Chem. Soc. Rev*., 1975, vol. 4, no. 1, p. 211.
13. Ivanov, E.V. and Abrosimov, V.K., *Zh. Strukt. Khim*., 2005, vol. 46, no. 5, p. 889.
14. Verevkin, S.P., *Fluid Phase Equil*., 2004, vol. 224, no. 1, p. 23.
15. Verevkin, S.P., *J. Chem. Eng. Data*., 2007, vol. 52, no. 1, p. 301.
16. Eusebio, M.E., Jesus, A.J.L., Cruz, M.S.C., Leitao, M.L.P., and Redinha, S., *J. Chem. Thermodyn*., 2003, vol. 35, no. 1, p. 123.
17. Knauth, P. and Sabbah, R., *Bull. Soc. Chim. Fr*., 1988, vol. 53, no. 6, p. 834.
18. Zaichikov, A.M. and Krest'yaninov, M.A., *Zh. Obshch. Khim*., 2004, vol. 74, no. 11, p. 1789.
19. Steel, W.V., Cirico, R.D., Knipmeyer, S., E., and Nguen, A., *J. Chem. Eng. Data*., 2002, vol. 47, no. 4, p. 689.
20. Malenkov, G.G., *J. Phys. Condens. Matter*, 2009, vol. 21, no. 28, p. 283101.
21. Bushuev, Yu.G. and Zaichikov, A.M., *Izv. Ros. Akad. Nauk, Ser. Khim*., 1998, vol. 47, no. 10, p. 1911.
22. Gubskaya, A.V. and Kusalik, P.G., *J. Phys. Chem., A*., 2004, vol. 108, no. 35, p. 7151.
23. Kessler, Yu.M. and Petrenko, V.E., *Voda: struktura, sostoyanie, sol'vatatsiya* (Water: Structure, State, and Solvation), Moscow: Nauka, 2003, p. 6.
24. Jorgensen, W.L., Madura, J.D., *Mol. Phys*., 1985, vol. 56, no. 6, p. 1381.
25. Valyashko, V.M., *Fazovye ravnovesiya i svoistva gidrotermal'nykh sistem* (Phase Equilibria and Properties of Hydrothermal Systems), Moscow: Nauka, 1990.
26. Gorbatyi, Yu.E. and Bondarenko, G.V., *Sverkhkritich. Flyuidy: Teor. i Prakt*., 2007, vol. 2, no. 2, p. 5.
27. Zaichikov, A.M. and Krest'yaninov, M.A., *Zh. Obshch. Khim*., 2008, vol. 78, no. 4, p. 560.
28. Skits, M.G. and Rais, S.A., *Voda i vodnye rastvory pri temperaturakh nizhe 0ºC* (Water and Aqueous Solutions at the Temperature below 0ºC), Kiev: Naukova Dumka, 1985, p. 76.
29. Guillot, B. and Guissani, Y., *J. Chem. Phys*., 2001, vol. 114, no. 15, p. 6720.
30. Stanley, H.E., Kumar, P., Xu, L., Yan, Z., Mazza, M.G., Buldyrev, S.V., Chen, S.-H., and Mallamace, F., *Physica, A*, 2007, vol. 386, no. 2, p. 729.
31. Atovmyan, E.G., Baturin, S.M., and Fedotova, T.N., *Vysokomol. Soed*., *A*, 1989, vol. 31, no. 8, p. 1685.
32. Balankina, E.S. and Lyashchenko, A.K., *J. Mol. Liq*., 2006, vols. 103–104, no. 1, p. 211.
33. Stolypin, V.F. and Mishustin, A.I., *Zh. Fiz. Khim*., 1987, vol. 61, no. 12, p. 3226.
34. Tritopoulou, E.A. and Economou, I.G., *Fluid Phase Equil*., 2006, vol. 248, no. 1, p. 134.
35. Radnai, T., Megyes, T., Bako, I., Kosztolanyi, T., Palinkas, G., and Ohtaki, H., *J. Mol. Liq*., 2004, vol. 110, no. 1, p. 123.
36. Gao, J., Pavelities, J.J., and Habibolasadeh, D., *J. Phys. Chem*., 1996, vol. 100, no. 7, p. 2689.
37. Durov, V.A. and Shilov, I.Yu., *Zh. Fiz. Khim*., 2007, vol. 81, no. 2, p. 249.
38. Stubbs, J.M., Potoff, J.J., and Siepmann, J.I., *J. Phys. Chem., B*, 2004, vol. 108, no. 45, p. 17596.
39. Krasnoperova, A.P., Surov, Yu.N., and Pivnenko, N.S., *Zh. Obshch. Khim*., 1995, vol. 65, no. 12, p. 2053.
40. Kelkar, M.S., Rafferty, J.L., Maginna, E.J., and Siepmann, J.I., *Fluid Phase Equil*., 2007, vol. 260, no. 1, p. 218.
41. Lopes Jesus, A.J., Rosado, M.T.S., Leitao, M.L.P., and Redinha, J.S., *J. Phys. Chem., A*, 2003, vol. 107, no. 19, p. 3891.