LIQUIDS AND LIQUID CRYSTALS

THERMODYNAMICS
PROPERTIES OF GLYCEROL–WATER SOLUTION

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The influence of structural features of water on the thermodynamic properties of associated liquids has been studied, with the glycerol–water solutions being taken as an example. The $P - V - T$ data for those solutions are experimentally measured in the pressure interval 0.1–103.1 MPa and in the temperature range 293–380 K. The modulus of elasticity, the coefficient of thermal expansion, the increments of the entropy, Gibbs energy, and the enthalpy are calculated numerically. The temperature dependences of the parameters of the semiempirical Tait equation have been analyzed, and the recommendation to use this equation for the description of data obtained is made.

It is known that there is no theory of real solutions in molecular physics which adequately describes the relevant experimental thermal data. The existing theories of two-component liquid systems are developed in the case where the difference between the dimensions of molecules is small, as well as the energy of interaction between different components; in this case, the potential energy is an even additive function [1]. The development of the statistical theory of liquid solutions becomes substantially complicated if this difference grows and if the solution components are associated liquids, for which the potential of intermolecular interaction is not an even additive function any more.

We studied the solutions glycerol–water, where the molecules of their components substantially differ from one another by shape, dimensions, and interaction energy magnitude. Experimental researches of solutions are of fundamental and applied significance, because, on the one hand, they assist in the development of the statistical theory of molecular liquid solutions and, on the other hand, allow one to solve important engineering problems. For instance, glycerol–water solutions are used as a working liquid in hydrostatic pressure technologies for fabricating compact powders, because they preserve their liquid phase state up to pressures of the order of 5 GPa [2], as well as in cryomedicine.

We aimed at studying the thermodynamic properties of solutions glycerol–water by measuring $P - V - T$ data experimentally in the pressure interval 0.1–103.1 MPa and the temperature range 293–380 K making use of a bellows piezometer. We studied glycerol–water solutions with four concentrations: 0.27, 0.31, 0.33, and 0.35 mole fraction of glycerol (m.f. Gly). The results of our researches revealed that the concentration dependence of the solution density demonstrated a peculiarity, namely, a jump-like reduction at a concentration of about 0.33 m.f. Gly in the temperature interval concerned [3]. This concentration is close to the accepted threshold which divides glycerol–water solutions into two groups: glycerol-rich (the concentration from 0.4 to 1.0 m.f. Gly) and water-rich ones (the water concentration from 1.0 to 0.6 m.f.) [4,5].

The dependence of the solution density on pressure is monotonous within the whole studied interval of temperatures (Fig. 1). From this figure, one can see that adding 0.27 m.f. Gly to water at 0.1 MPa results in the increase of the solution density by approximately 18%. If the pressure grows under isothermal conditions, the density of water increases more rapidly than the density of solutions, which testifies that the glycerol–water solutions under investigation are less compressible and more dense-packed in comparison with water.

The method of numerical differentiation was applied to the measured $P - V - T$ data in order to calculate the following thermodynamic quantities:
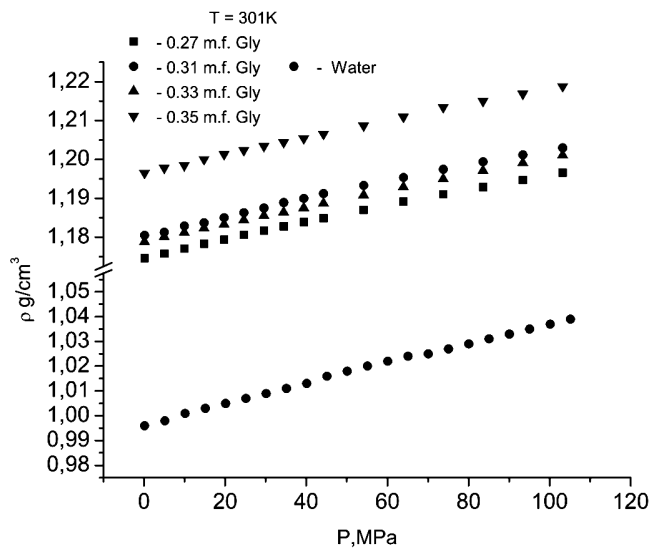
Fig. 1. Pressure dependences of the density for water and glycerol–water solutions with various glycerol concentrations and at a temperature of 301 K

the isothermal modulus of elasticity

$$K_T = \rho \left(\frac{\partial P}{\partial \rho} \right)_T, \tag{1}$$

the isobaric coefficient of thermal expansion

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P, \tag{2}$$

and the isothermal increments of the isobaric-isothermal Gibbs potential,

$$\Delta G = \int_{P_0}^{P} \frac{1}{\rho} \, dP, \tag{3}$$

entropy,

$$T\Delta S = T \int_{P_0}^{P} \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T}, \right)_P dP \tag{4}$$

and enthalpy,

$$\Delta H = \int_{P_0}^{P} \left(\frac{1}{\rho} + \frac{T}{\rho^2} \left(\frac{\partial \rho}{\partial T} \right)_P \right) dP. \tag{5}$$

Figure 2 demonstrates the dependence of the isothermal modulus of elasticity K_T on pressure. It is evident that this quantity increases with the growing pressure, being approximately 2.5 times as large as that for water.
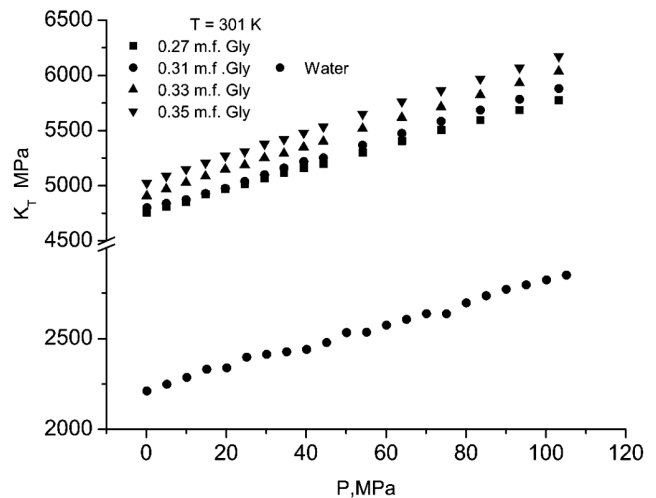

Fig. 2. The same as in Fig. 1, but for the isothermal modulus of elasticity

The temperature dependence of the elasticity modulus for water is known to have a maximum at the pressure $P = 0.1$ MPa and a temperature of 320 K. Similar temperature dependences of K_T are also observed for glycerol–water solutions with concentrations ranging from 0.27 to 0.31 m.f. Gly. At a solution concentration of 0.33 m.f. Gly, this maximum disappears (Fig. 3). In the case of water, the maximum in the temperature dependence of K_T at $P = 0.1$ MPa and near the temperature $T = 320$ K is associated with the disappearance of an ice-like water structure. It is natural to assume that this structural feature of water would manifest itself in the glycerol–water solutions with concentrations up to 0.31 m.f. Gly as well.

Dielectric spectroscopy of water-rich solutions glycerol–water showed that they are characterized by a high degree of inhomogeneity. This is connected with the fact that some part of water molecules can be included into glycerol–water domains, another part can form aggregates with loosen packing of the Ice I type, and the rest of them remains free to form interphase water. Using data on the latent heat of ice melting, it was shown that, in the glycerol–water solution with a concentration of 0.1 m.f. Gly, water is distributed among those states as follows: 0.5 m.f. is in the ice-like structure, 0.15 m.f. in "domains", and 0.25 m.f. forms interphase water [5]. One may expect that the variation of pressure would change this relationship for the water molecule distribution among "various states", which would manifest itself in the thermodynamic properties of glycerol–water solutions.
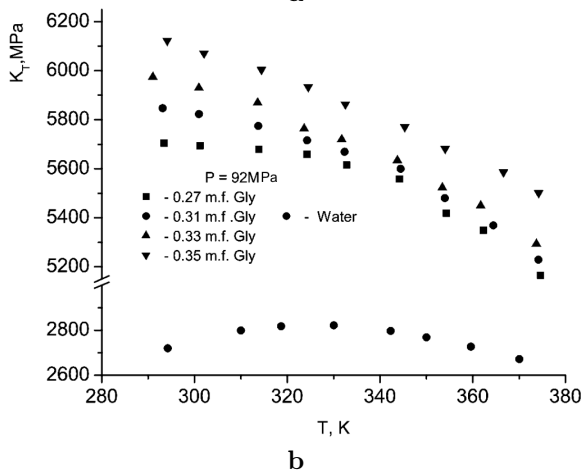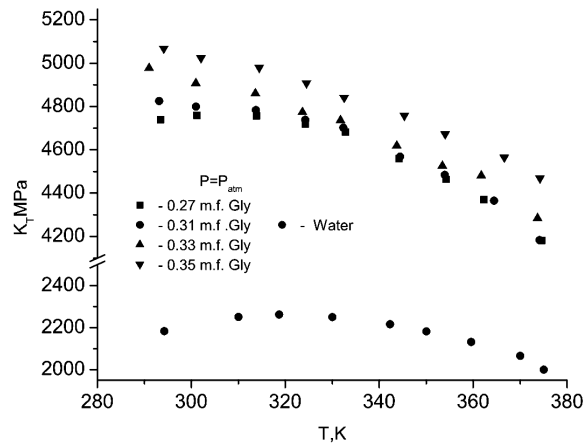
Fig. 3. Temperature dependences of the isothermal modulus of elasticity for water and glycerol–water solutions with various glycerol concentrations at atmospheric pressure (a) and at $P = 98.1$ MPa (b)
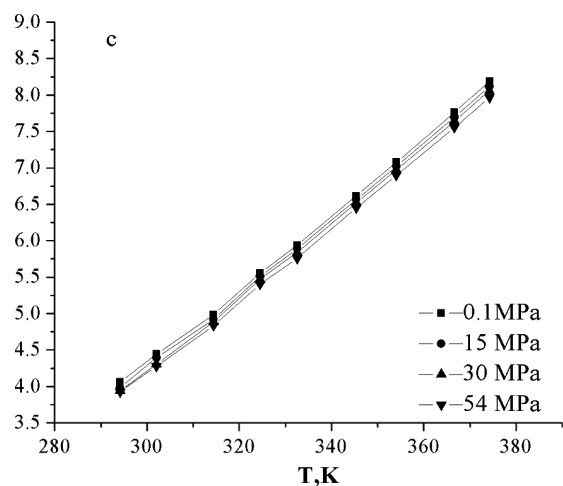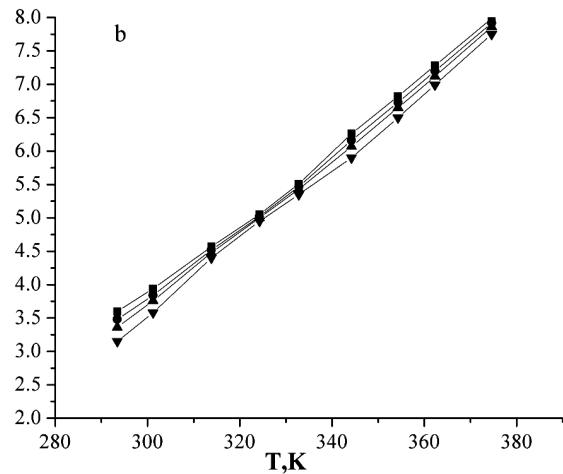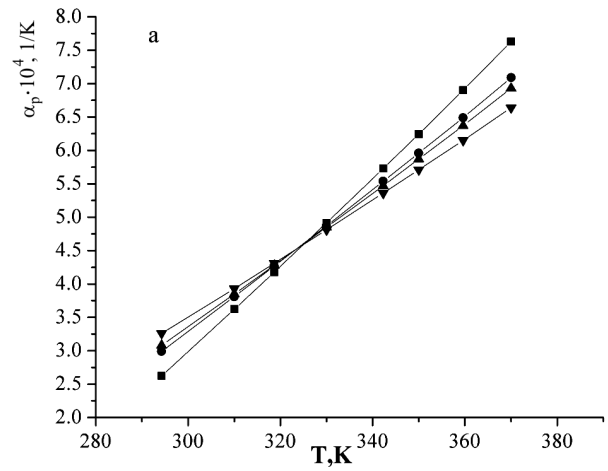

Fig. 4. Temperature dependences of the isobaric coefficients of thermal expansion for water (a) and the glycerol–water solutions with concentrations of 0.27 (b) and 0.35 m.f. Gly (c)

In particular, the maximum in the temperature dependences of the isothermal elasticity moduli of water and aqueous solutions of glycerol under consideration diminishes as the pressure grows and, at a pressure of 98.1 MPa, practically disappears in the 0.31-m.f. Gly solution.

The dependence of the thermal expansion coefficient α_P on temperature is ascending for pure water (Fig. 4,a). At the same time, the isobars of the thermal expansion coefficient of water intersect one another: if the pressure grows, the parameter α_P of water increases at temperatures below 325 K but decreases at $T > 325$ K, as α_P's of all other associated and non-associated liquids do. The coefficient of thermal expansion for solutions with concentrations of 0.27 and 0.35 m.f. Gly also increases as the temperature grows, but the α_P-isobars
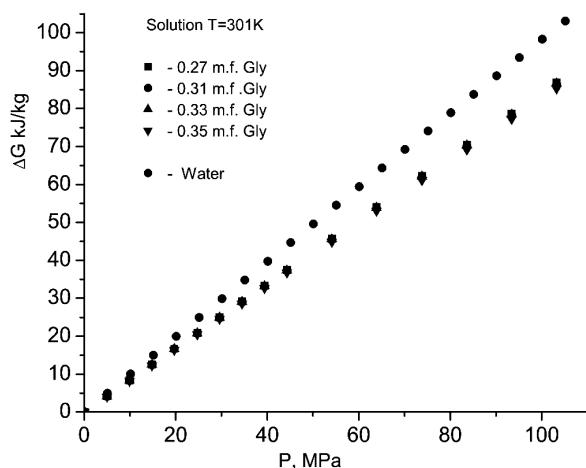
Fig. 5. Baric dependences of the Gibbs potential increment at $T = 301$ K for water and glycerol–water solutions with various glycerol concentrations

Fig. 6. Temperature dependences of the parameter B for water and glycerol–water solutions with various glycerol concentrations

do not intersect (Fig. 4,b and c). The isobars of the thermal expansion coefficient of the 0.27-m.f. Gly solution glycerol–water have a characteristic feature of the small-cusp type at about $T = 325$ K. However, if the concentration of glycerol in the solution grows further, this feature disappears (Fig. 4,c).

The isothermal increment of the isobaric-isothermal Gibbs potential for both water and the solutions concerned increases in the investigated temperature interval (Fig. 5), with the corresponding increments of the Gibbs potential for solutions growing more slowly with the increasing pressure than that for water. For the solutions, the increment of the Gibbs potential does not depend on the concentration within the limits of calculation errors.

The isothermal increments of the entropy for water and glycerol–water solutions are identical to each other within the error limits of their determination, while the isothermal increment of the enthalpy for water is larger than those for glycerol–water solutions.

To describe the $P - V - T$ data obtained for water and glycerol–water solutions, we took the semiempirical Tait equation of state which includes a small number of parameters and can be substantiated statistically [6]:

$$\frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial P}\right) = \frac{A}{B + P}. \tag{6}$$

The choice of this equation was caused by the fact that the character of the dependence of the isothermal derivative $\rho^2(\partial P/\partial \rho)_T$ on pressure turned out linear for the studied solutions.
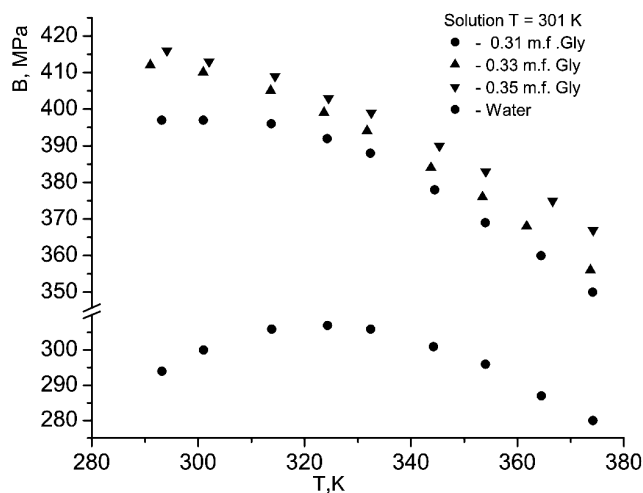
We calculated the values of the constants A and B in the Tait state equation for water and glycerol–water solutions. The values obtained for the constant A are as follows: 0.136 for water, 0.091 for the 0.27-m.f. Gly solution, and 0.082 for the 0.35-m.f. Gly solution; i.e. the increase of the glycerol content in the solutions studied gives rise to a reduction of the A value.

At the same time, the increase of the glycerol content in the solutions is accompanied by the growth of the constant B (Fig. 6). The values of the parameter B for solutions are larger than that for water, which testifies that the energy of intermolecular interactions in solutions is greater than that in pure water.

Basing on the physical meaning of the Tait constants A and B, one may assert that the addition of glycerol to water-rich glycerol–water solutions increases the energy of interaction and the steepness of the intermolecular repulsion potential.

The value of constant B depends on the temperature (Fig. 6). In the case of water, the $B(T)$ dependence has a maximum. The same behavior is also observed for the temperature dependence of B in the solutions with concentrations of 0.27 and 0.31 m.f. Gly. If the concentration of glycerol increases further, the maximum in the temperature dependence $B(T)$ diminishes, and this dependence becomes monotonously descending, as it occurs for non-associated liquids.

The increase of quantities K_T and B with the temperature growing in the interval 293–325 K is not typical of a wide class of liquids, being inherent to aqueous liquid systems only.

The researches carried out for glycerol–water solutions showed that, for water-rich solutions, there exists the threshold concentration, at which the temperature dependences of the isothermal elasticity modulus K_T and the Tait constant B change their behavior. If the glycerol concentration is lower than the threshold one, the temperature dependences of K_T and B have maxima. At higher concentrations of glycerol, the maxima in the temperature dependences of K_T and B are not observed. Therefore, one may assert that, if the glycerol concentration in glycerol–water solutions is equal to or lower than the threshold one, the appearance of structural skeleton formations of the "Ice I" type made up of water molecules becomes possible. At higher glycerol concentrations, such structural formations do not exist. Our researches demonstrated that the increase of pressure gives reduction of the threshold concentration and, therefore, favors the destruction of such structural skeleton formations of water molecules of the "Ice I" type in glycerol–water solutions.

The analysis of the results of our calculations also showed that, for water and the glycerol–water solutions concerned, the Tait equation describes the temperature and baric dependences of the solution density with an error of 0.5%.

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ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ РОЗЧИНІВ ГЛІЦЕРИН–ВОДА

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Р е з ю м е

Досліджено вплив структурних особливостей води на термодинамічні властивості асоційованих рідин на прикладі розчинів гліцерин–вода. Експериментально отримані P–V–T-дані для цих розчинів в інтервалі тисків 0,1–103,1 МПа та температур 293–380 K. Розраховано пружний модуль, коефіцієнт теплового розширення, прирости ентропії, ізобаро-ізотермічного потенціалу Гіббса та ентальпії. Рекомендовано рівняння стану Тейта та проаналізовано залежність його параметрів від температури.