Thermodynamic Properties of Water−Aliphatic Alcohol Systems in a Wide Range of Parameters

B. K. Karabekova*, E. A. Bazaev, and A. R. Bazaev

*Institute for Geothermic Problems, Dagestan Scientific Center, Russian Academy of Sciences,
Makhachkala, 367030 Russia*
*e-mail: badji@mail.ru

Abstract—The results of thermal and thermodynamic (phase diagram) property calculations of water−aliphatic alcohol (methanol, ethanol, *n*-propanol) systems in liquid and vapor phases, as well as supercritical fluid water−methanol systems have been presented. The calculations are based on the polynomial equation of state, represented by expansion of the compressibility factor into a power series of reduced density ($\omega = \rho/\rho_{cr}$ and reduced temperature ($\tau = T/T_{cr}$)

$$Z = \frac{p}{RT\rho_m} = 1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} \frac{a_{ij}\omega^i}{\tau^j},$$

which describes experimental p,ρ,T,x-dependencies with an average relative error of 1.2%.

Keywords: temperature, pressure, density, concentration, phase, fluid, equation of state, compressibility factor, reduced parameters

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INTRODUCTION

Reliable data on the thermodynamic behavior of water−alcohol systems in different states of matter are of interest for the development of engineering and technology, as well as for the theory of solutions.

Previously, we have shown [1] that the polynomial equation of state

$$Z = \frac{p}{RT\rho_m} = 1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} \frac{a_{ij}\omega^i}{\tau^j}, \text{ where}$$

$$p = RT\rho_m\left(1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} \frac{a_{ij}\omega^i}{\tau^j}\right)$$

(1)

(where p is the pressure; ρ_m, molar density, mol/m³; $\omega = \rho/\rho_{cr}$, ($\tau = T/T_{cr}$, reduced density and reduced temperature, respectively; ρ, density; T, temperature; ρ_{cr}, T_{cr}, critical density and critical temperature; $R = 8.314$ J/(mol K), universal gas constant; a_{ij}, coefficients) describes experimental p,ρ,T,x-dependencies of water−aliphatic alcohol (methanol, ethanol, *n*-propanol) systems in subcritical and supercritical states with an average relative error of 0.83%.

This paper is a continuation of the study [1] and devoted to the calculation of thermodynamic properties of the systems in a wide range of state parameters (liquid, vapor and supercritical fluid) using equation (1).

The equation coefficients (Table 1) were determined using experimental p,ρ,T,x-data [1−3] by the improved method of least squares [1, 4, 5] after agreeing on the function $p(\omega, \tau)_x$ and its derivatives $(\partial p/\partial \omega)_{\tau, x}$, $(\partial p/\partial \tau)_{\omega, x}$, $(\partial^2 p/\partial^2 \omega)_{\tau, x}$ at the boundaries of vapor and liquid phases with the supercritical region [4, 6, 7]. Although, this method of agreement slightly decreases the calculation accuracy (Table 2), it is warranted for the generalization of experimental p,ρ,T,x-dependencies in three states (Fig. 1), the vapor and liquid phases (VP and LP) and supercritical fluid (SCF).

CALCULATION OF THERMODYNAMIC PROPERTIES

Comparing the results of property calculations for water−methanol, water−ethanol, water−*n*-propanol using equation (1) we found that the thermodynamic behavior of these systems is identical within the investigated parameter range. Thus, the results of property calculations are presented only for the water−ethanol system.

The coefficient of isothermal compressibility [8]

$$K_T = -1/V(\partial V/\partial p)_T = 1/\rho(\partial p/\partial \rho)_T^{-1}. \quad (2)$$

Taking into account (1) and (2), we have the following expression:

Table 1. The coefficients of equation (1) (x is the molar fraction of alcohol)

Water–methanol, $x = 0.5$	
VP, LP	SCF
$a_{10} = -0.17428032946858987$	$a_{10} = 0.04384137260843783$
$a_{11} = 1.295238939814144$	$a_{11} = -1.2784707773275066$
$a_{12} = 4.888088935176604$	$a_{12} = 12.81527411254474$
$a_{13} = -9.971619880078844$	$a_{13} = -19.210297381919187$
$a_{14} = 11.550851585825754$	$a_{14} = 14.966046740511038$
$a_{15} = -8.086081771252706$	$a_{15} = -7.0613593728301245$
$a_{16} = 2.7252492258367824$	$a_{16} = 1.793163490248773$
$a_{17} = -0.3392516694194726$	$a_{17} = -0.1898215850191755$
$a_{20} = 4.935012959332709$	$a_{20} = 4.5821179541652866$
$a_{21} = -17.689241853303564$	$a_{21} = -13.290123308751983$
$a_{22} = 18.32124304242492$	$a_{22} = 4.128124528071543$
$a_{23} = -16.681657219707642$	$a_{23} = 1.0295119466442488$
$a_{24} = 8.315397462834062$	$a_{30} = -5.58277026166969$
$a_{25} = 0.01111738100004176$	$a_{31} = 11.25745774674846$
$a_{26} = -0.9311764515785476$	$a_{32} = -4.756578747094595$
$a_{27} = 0.14930076602466114$	
$a_{30} = -5.71753128918924$	
$a_{31} = 13.082627662175389$	
$a_{32} = -11.021243589560056$	
$a_{33} = 8.469475568259542$	
$a_{34} = -4.896430681868014$	
$a_{35} = 1.0110276636523527$	

Water–methanol, $x = 0.8$	
VP, LP	SCF
$a_{10} = -3.6495200616953016$	$a_{10} = -3.425540376400364$
$a_{11} = 20.236790095416524$	$a_{11} = 17.51337243492665$
$a_{12} = -33.86366799887383$	$a_{12} = -25.275911890074017$
$a_{13} = 35.90712430415449$	$a_{13} = 22.654797266099667$
$a_{14} = -25.6480329499842$	$a_{14} = -13.847502526266528$
$a_{15} = 10.798280103809825$	$a_{15} = 4.779049473755413$
$a_{16} = -2.2115374117692546$	$a_{16} = -0.6548120082163983$
$a_{17} = 0.14625964911649997$	$a_{20} = 10.188927105554043$
$a_{20} = 10.017343395827131$	$a_{21} = -39.43217014141236$
$a_{21} = -40.02885140247131$	$a_{22} = 46.95385035949933$
$a_{22} = 50.37572253689593$	$a_{23} = -34.39791094583388$
$a_{23} = -41.417861954558234$	$a_{24} = 19.079412993079778$
$a_{24} = 27.392834970810906$	$a_{25} = -6.463736773744575$
$a_{25} = -11.765919205358042$	$a_{26} = 0.8750967155024538$
$a_{26} = 2.432005624558386$	$a_{30} = -7.892225152218352$
$a_{27} = -0.1462862892060427$	$a_{31} = 20.16249790581525$
$a_{30} = -7.4966592629254345$	$a_{32} = -15.077062739848287$
$a_{31} = 18.035714345437235$	$a_{33} = 3.4955424738520247$
$a_{32} = -9.910931146313448$	
$a_{33} = -2.737422104136812$	
$a_{34} = 3.4878489546650133$	
$a_{35} = -0.7175600193302589$	

Table 1. (Contd.)

Water−ethanol, $x = 0.2$	
VP, LP	SCF
$a_{10} = -9.891556082461635$	$a_{10} = -9.334566257341587$
$a_{11} = 28.79732265697415$	$a_{11} = 24.618590686097665$
$a_{12} = -34.589775301297955$	$a_{12} = -21.99007103508372$
$a_{13} = 24.027126065672245$	$a_{13} = 3.256511021830629$
$a_{14} = -6.226707317567696$	$a_{14} = 13.611165295277765$
$a_{15} = -1.6718433744641068$	$a_{15} = -12.67014463238952$
$a_{16} = 1.1757246158940158$	$a_{16} = 4.467105482981438$
$a_{17} = -0.1697558803379205$	$a_{17} = -0.5802147832620471$
$a_{20} = 20.033695818638993$	$a_{20} = 19.38148074598606$
$a_{21} = -49.01142920178437$	$a_{21} = -44.526032900437585$
$a_{22} = 51.903430293249045$	$a_{22} = 39.16857379728503$
$a_{23} = -41.4443340772981$	$a_{23} = -20.644672136547733$
$a_{24} = 20.387902732465314$	$a_{24} = 0.49980086579806493$
$a_{25} = -4.919029834458088$	$a_{25} = 6.118374209472086$
$a_{26} = 0.46730655551679806$	$a_{26} = -2.8385758809659998$
$a_{30} = -10.990613368578305$	$a_{27} = 0.4125341240606389$
$a_{31} = 16.804721522416802$	$a_{30} = -10.894476595611298$
$a_{32} = -5.422746013217094$	$a_{31} = 16.49450071645872$
	$a_{32} = -5.290442914246538$

Water−ethanol, $x = 0.5$	
VP, LP	SCF
$a_{10} = -1.895432761783083$	$a_{10} = -1.7144678962941937$
$a_{11} = -5.675080101926052$	$a_{11} = -5.9482158179382845$
$a_{12} = 36.45248980424302$	$a_{12} = 30.568696311490765$
$a_{13} = -57.57539626224303$	$a_{13} = -31.341891467827395$
$a_{14} = 46.235602203628574$	$a_{14} = -2.4063559076151404$
$a_{15} = -20.233528225531522$	$a_{15} = 27.60285597474392$
$a_{16} = 4.575409594798052$	$a_{16} = -21.435945129928427$
$a_{17} = -0.4245210187227502$	$a_{17} = 6.952985246443128$
$a_{20} = 9.289057660916331$	$a_{18} = -0.8518072039536455$
$a_{21} = -10.099006984822179$	$a_{20} = 9.089265092088741$
$a_{22} = -20.640133063051078$	$a_{21} = -9.683270430574225$
$a_{23} = 40.135428291839744$	$a_{22} = -15.011804623267722$
$a_{24} = -32.183288879184154$	$a_{23} = 14.06283716731776$
$a_{25} = 13.710686032721252$	$a_{24} = 16.426646930277528$
$a_{26} = -2.9452561823762697$	$a_{25} = -34.12668529048757$
$a_{27} = 0.2551548670801756$	$a_{26} = 23.06663289704867$
$a_{30} = -8.12747303799188$	$a_{27} = -7.122508082435366$
$a_{31} = 12.083106727187369$	$a_{28} = 0.851826376768127$
$a_{32} = -3.6699665719841374$	$a_{30} = -8.108643299635018$
	$a_{31} = 11.940464629782468$
	$a_{32} = -3.4142575148288343$
	$a_{33} = -0.16159781616115376$
	$a_{34} = 0.03309194778376266$

Table 1. (Contd.)

Water–ethanol, $x = 0.8$	
VP, LP	SCF
$a_{10} = -7.122610701397848$	$a_{10} = -6001.180157873362$
$a_{11} = 19.99759500408091$	$a_{11} = 9688.371846726623$
$a_{12} = -22.42920161749221$	$a_{12} = 7272.578428070782$
$a_{13} = 16.511410942222177$	$a_{13} = -24685.228373591628$
$a_{14} = -7.826329948649879$	$a_{14} = 23293.92328507435$
$a_{15} = 3.207031685910666$	$a_{15} = -10221.483061603882$
$a_{16} = -1.6521682957399526$	$a_{16} = 1924.14869440344$
$a_{17} = 0.6226313970078434$	$a_{17} = -96.86569402432974$
$a_{18} = -0.09879080446975373$	$a_{20} = 16685.72408744692$
$a_{20} = 17.82629489291787$	$a_{21} = -32970.2765287873$
$a_{21} = -43.419001634831915$	$a_{22} = 19482.938997911817$
$a_{22} = 50.519112235792505$	$a_{23} = -4062.7889790986815$
$a_{23} = -47.869513835985906$	$a_{24} = -538.3224322248219$
$a_{24} = 30.703352347526597$	$a_{25} = -1295.5474214340059$
$a_{25} = -11.382934103047312$	$a_{26} = 1581.5400279509122$
$a_{26} = 2.2101237369390647$	$a_{27} = -381.41697563914926$
$a_{27} = -0.1561881779785253$	$a_{30} = -10849.709605056758$
$a_{30} = -10.869433284141355$	$a_{31} = 14978.54646804922$
$a_{31} = 15.628030175692222$	$a_{32} = -759.7377729485386$
$a_{32} = -5.140510595856636$	$a_{33} = -10229.544400297851$
	$a_{34} = 10440.940147890851$
	$a_{35} = -4825.787070335282$
	$a_{36} = 828.0759078888719$

Water–n-propanol, $x = 0.2$	
VP, LP	SCF
$a_{10} = -2.4888194084283968$	$a_{22} = 21.130633260389434$
$a_{11} = 12.55667367106596$	$a_{23} = -12.461022124907505$
$a_{12} = -15.772485627192498$	$a_{24} = 4.1796764377442095$
$a_{13} = 10.705931134533728$	$a_{25} = -0.45803554271701624$
$a_{14} = -3.452930170214876$	$a_{30} = -5.4625554841482105$
$a_{15} = 0.35074136836266057$	$a_{31} = 9.920785042458956$
$a_{20} = 6.758085510949736$	$a_{32} = -3.5863638314774318$
$a_{21} = -22.65563200567523$	

Table 1. (Contd.)

Water—n-propanol, $x = 0.5$	
VP, LP	SCF
$a_{10} = -28.665997996319454$	$a_{10} = -28.956699659072857$
$a_{11} = 80.18297661376324$	$a_{11} = 83.86986489753869$
$a_{12} = -73.8856885567051$	$a_{12} = -87.79570206247506$
$a_{13} = 34.39007484984551$	$a_{13} = 58.97012740963951$
$a_{14} = -7.9312933320373$	$a_{14} = -31.29293798294783$
$a_{15} = -0.38514958246623476$	$a_{15} = 11.89992560592291$
$a_{16} = 0.6321317252275807$	$a_{16} = -2.732480355458365$
$a_{17} = -0.08332842974220345$	$a_{17} = 0.29101277116411367$
$a_2 0 = 57.2369510670547$	$a_{20} = 57.52725696060067$
$a_{21} = -148.8913395054257$	$a_{21} = -152.57989493339701$
$a_{22} = 123.97302306941417$	$a_{22} = 137.88767548006948$
$a_{23} = -53.35339273292083$	$a_{23} = -77.93542727095274$
$a_{24} = 16.004212799681113$	$a_{24} = 39.36590605487814$
$a_{25} = -3.1284571634416274$	$a_{25} = -15.413564759459627$
$a_{26} = 0.2042254786510212$	$a_{26} = 3.5688485766752773$
$a_{30} = -29.285049824393457$	$a_{27} = -0.3743426928955127$
$a_{31} = 65.92004609987882$	$a_{30} = -29.284653911674265$
$a_{32} = -41.75377124816656$	$a_{31} = 65.92171024800084$
$a_{33} = 8.098461778403344$	$a_{32} = -41.758393718352636$
	$a_{33} = 8.100404452497353$

Water—n-propanol, $x = 0.8$	
VP, LP	SCF
$a_{10} = -6.074833978040517$	$a_{10} = -5.375135304091933$
$a_{11} = 23.557565858956757$	$a_{11} = 14.871173233567095$
$a_{12} = -31.694665443237536$	$a_{12} = 0.04762017760706238$
$a_{13} = 33.618005538832094$	$a_{13} = -19.60716648505662$
$a_{14} = -24.752841455258345$	$a_{14} = 20.85923410881033$
$a_{15} = 7.09238749309098$	$a_{15} = -11.51296548279312$
$a_{16} = 2.233287912765521$	$a_{16} = 3.785535745485976$
$a_{17} = -1.8604955221599055$	$a_{17} = -0.6773300207245107$
$a_{18} = 0.3229174902032032$	$a_{18} = 0.05074852042729263$
$a_{20} = 16.591020161384826$	$a_{20} = 15.890465596750987$
$a_{21} = -55.93863585940664$	$a_{21} = -47.24552598863147$
$a_{22} = 66.33536160119813$	$a_{22} = 34.58238527013528$
$a_{23} = -60.890997699538644$	$a_{23} = -7.659732650944068$
$a_{24} = 45.615856667609954$	$a_{30} = -11.27825789851896$
$a_{25} = -18.608949848637938$	$a_{31} = 28.26880121291681$
$a_{26} = 1.5542473807540456$	$a_{32} = -20.082213960554824$
$a_{27} = 1.1825654922723328$	$a_{33} = 4.345078462893158$
$a_{28} = -0.27209409632246245$	
$a_{30} = -11.27910792012049$	
$a_{31} = 28.27539006739706$	
$a_{32} = -20.092105163465444$	
$a_{33} = 4.348835859001257$	

$$K_T(\rho, T) = -\frac{1}{\rho}\left(RT\left(1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\frac{T_{cr}^j \rho^i(i+1)}{\rho_{cr}^i T^j}\right)\right)^{-1}. \quad (3)$$

As can be seen from Fig. 2, K_T of the systems increases while the density rises, achieves its maximum near the critical point, and then decreases. K_T increases while the concentration rises and decreases while temperature rises; the latter is weakly expressed for water, and significantly for alcohol (Fig. 3).

The coefficient of volume thermal expansion [8]

$$\alpha = 1/V(\partial V/\partial T)_p = 1/\rho(\partial p/\partial T)_\rho(\partial p/\partial \rho)_T^{-1}. \quad (4)$$

Taking into account (1) and (4), we have the following expression:

$$\alpha(\rho, T) = -\frac{1}{\rho}\left(R\rho\left(1 + \sum_{i=1}^{n}\sum_{j=0}^{S_i} a_{ij}\frac{T_k^j \rho^i(i-j)}{\rho_k^i T^j}\right)\right)$$
$$\times \left(RT\left(1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\frac{T_{cr}^j \rho^i(i+1)}{\rho_{cr}^i T^j}\right)\right)^{-1}. \quad (5)$$

The character of the dependence of α on density and temperature is similar to the one for K_T; it is nearly independent of concentration up to a molar fraction of alcohol $x = 0.4$, and rises with high concentrations (Fig. 5).

The pressure coefficient [8]

$$\beta = (\partial p/\partial T)_\rho. \quad (6)$$

Taking into account (1) and (6), we have the following expression:

Table 2. The average relative deviation between the experimental and calculated pressure values (δ, %)

System	Vapor and liquid phases	Supercritical fluid
	δ, %	δ, %
Water–methanol, $x = 0.5$	3.3	0.6
Water–methanol, $x = 0.8$	2.2	0.6
Water–ethanol, $x = 0.2$	0.5	0.9
Water–ethanol, $x = 0.5$	2.0	1.0
Water–ethanol, $x = 0.8$	0.6	2.1
Water–n-propanol, $x = 0.2$	1.0	1.0
Water–n-propanol, $x = 0.5$	1.0	1.6
Water–n-propanol, $x = 0.8$	1.9	0.7

$$\beta(\rho, T) = R\rho\left(1 + \sum_{i=1}^{n}\sum_{j=0}^{S_i} a_{ij}\frac{T_k^j \rho^i(i-j)}{\rho_k^i T^j}\right). \quad (7)$$

β increases while density rises for all the isotherms, and up to the critical density nearly independent of temperature; at high values of density, it insignificantly increases with a rise in temperature (Fig. 6). β decreases gradually when the concentration of alcohol rises (Fig. 7).

The internal pressure. The total pressure in the real system depends on the intensity of molecular thermal
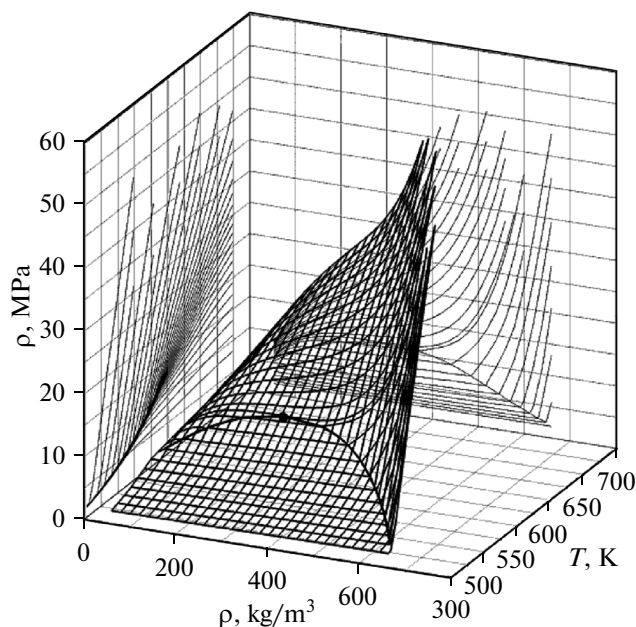
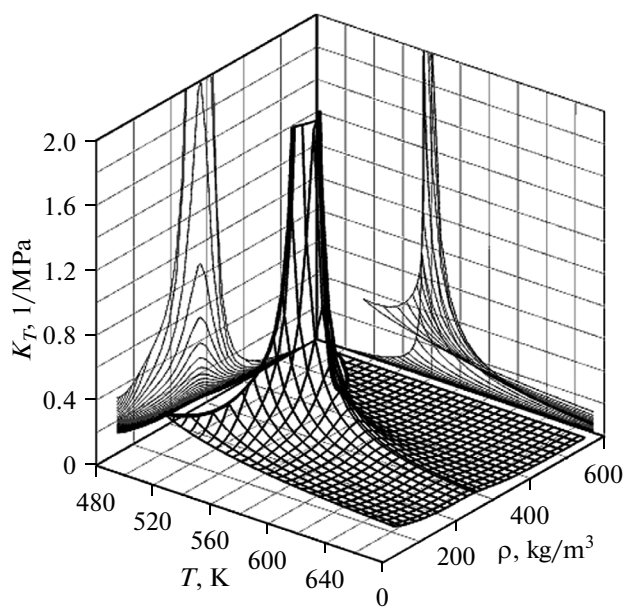**Fig. 1.** p,ρ,T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p,T-plane and p,ρ-plane.

Fig. 2. K_T,ρ,T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p,T-plane and p,ρ-plane.
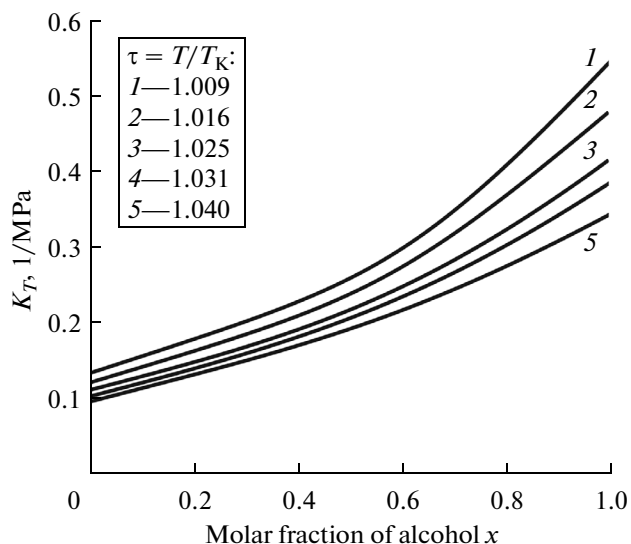
Fig. 3. Isotherms of water–ethanol system, which show dependence of K_T on concentration for reduced density $\omega = 0.4$.
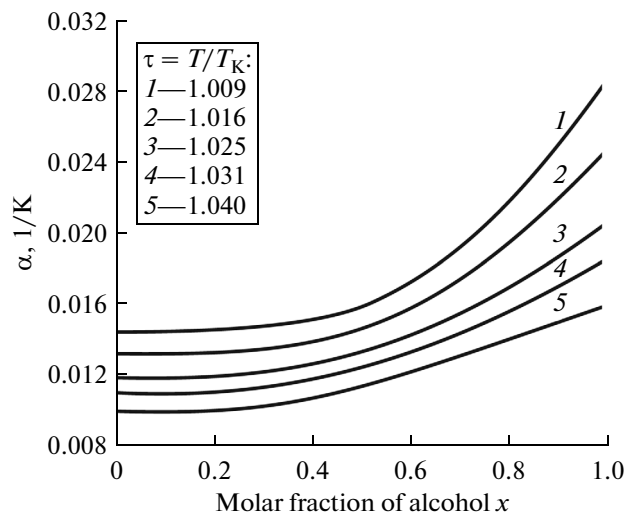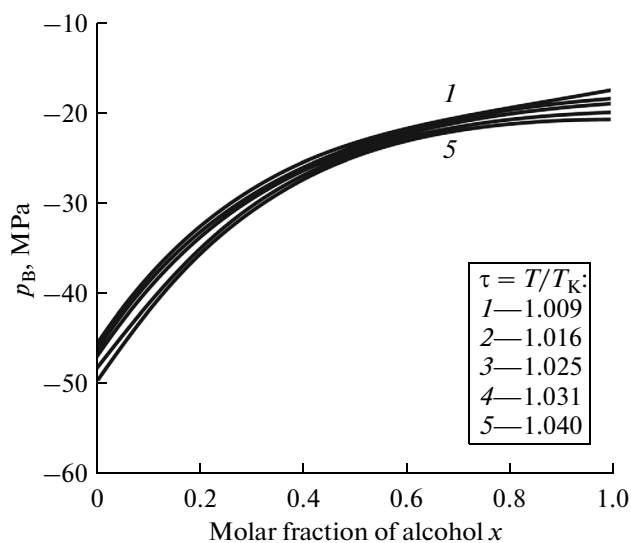

Fig. 4. α, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

Fig. 5. Isotherms of water–ethanol system, which show dependence of α on concentration for reduced density $\omega = 0.4$.

Fig. 6. β, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

motion p_K (kinetic pressure) and intermolecular interaction p_I (internal pressure) [9, 10], i.e.,

$$p_I = p - p_K, \text{ or } p_I = p - T(\partial p / \partial T)_\rho. \qquad (8)$$

Taking into account (1) and (8), we have the following expression:

$$p_I(\rho, T) = R \sum_{i=1}^{n} \sum_{j=0}^{n_i} a_{ij} \frac{T_{cr}^j \rho^{i+1} j}{\rho_{cr}^i T^{j-1}}. \qquad (9)$$

The p_I value of the system does not nearly depend on temperature; it decreases while density rises (Fig. 8) and increases while concentration rises (Fig. 9).
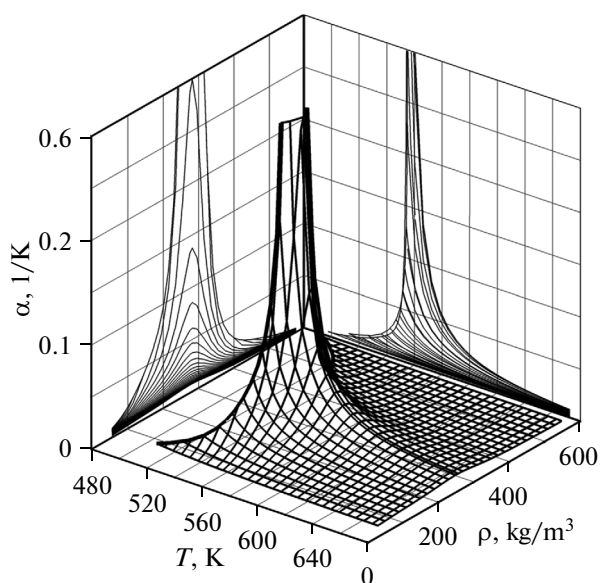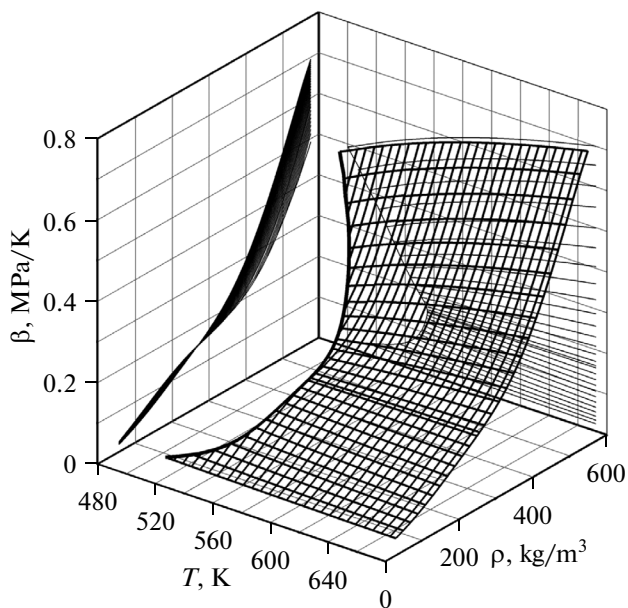
The internal pressure of the system p_I can be expressed through the coefficient of isothermal compressibility (2) and the coefficient of volume thermal expansion (4):

$$p_I = p - (\alpha T / K_T). \qquad (10)$$

Basic thermodynamic properties of the systems can be calculated as their difference from the ideal gas state at a pressure of 0.1 MPa in the investigated temperature range.

The isochoric heat capacity. To calculate the isochoric heat capacity of the systems [8]
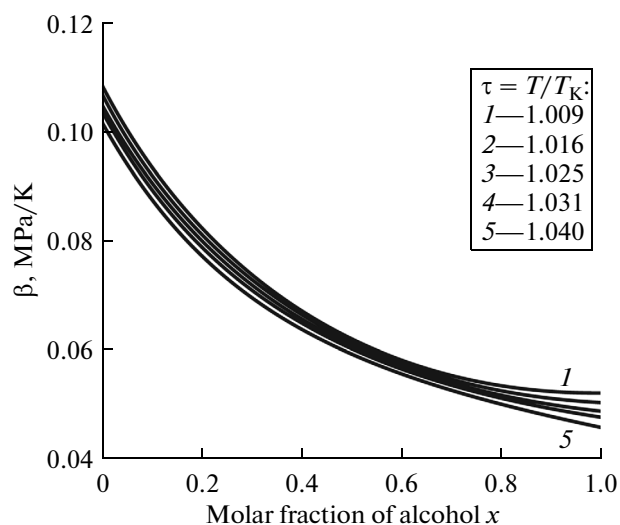
Fig. 7. Isotherms of water–ethanol system, which show dependence of β on concentration for reduced density ω = 0.4.

Fig. 8. p_I, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

Fig. 9. Isotherms of water–ethanol system, which show dependence of p_B on concentration for reduced density ω = 0.4.

Fig. 10. C_v, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

$$C_v - C_{v_0} = -\int_{\rho_0}^{\rho} T\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho \frac{d\rho}{\rho^2} \quad (11)$$

we need to know its value for the ideal gas state C_{v_0}. So, we can write the expression for isobaric heat capacity of the systems in the ideal gas state [11]:

$$C_{p_0}(T, x) = (1-x)C_{p_0}^W(T) + xC_{p_0}^A(T), \quad (12)$$
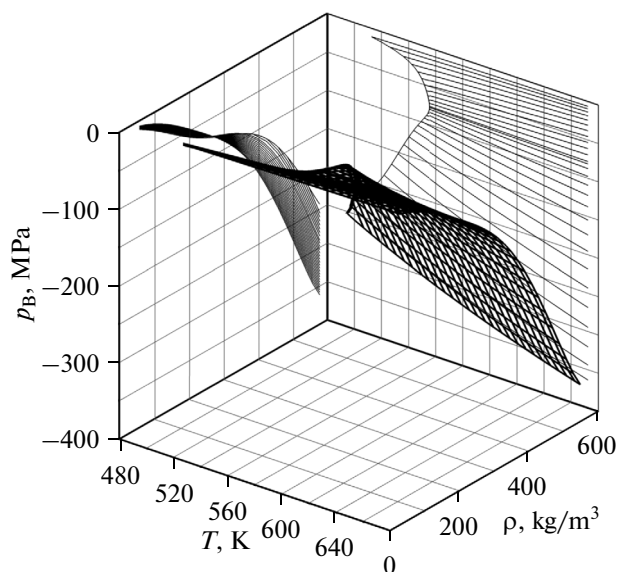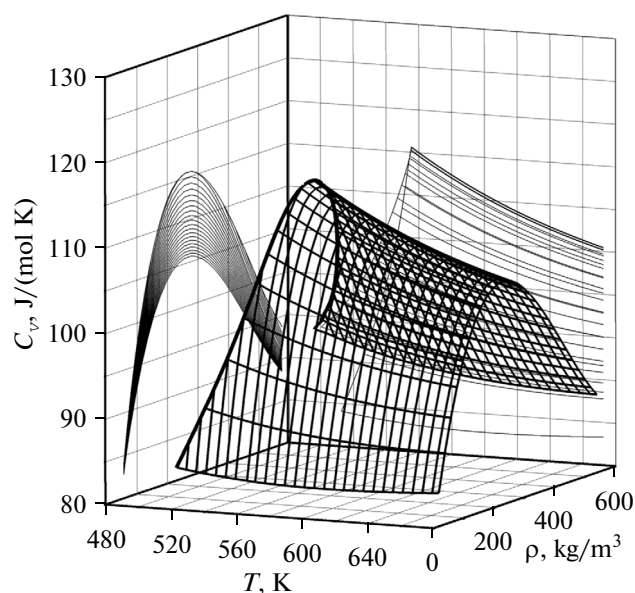
where $C_{p_0}^W(T)$ and $C_{p_0}^A(T)$ are the isobaric heat capacities of water and alcohol in the ideal gas state, respectively, which are determined according the empirical equation [11]

$$C_{p_0}^0(T) = A + BT + CT + DT^3. \quad (13)$$

The coefficients of equation (13), taken from [11], are given in Table 3.

Table 3. The coefficients of equation (13)

Gas	A	B	C	D
Water	7.701	4.595×10^{-4}	2.521×10^{-6}	-0.859×10^{-9}
Methanol	5.052	1.694×10^{-2}	6.179×10^{-6}	-6.811×10^{-9}
Ethanol	2.153	5.113×10^{-2}	-2.004×10^{-5}	0.328×10^{-9}
n-Propanol	2.153	5.113×10^{-2}	-2.004×10^{-5}	0.328×10^{-9}

Thus, the isochoric heat capacity of the systems in the ideal gas state is equal to

$$C_{v_0}(T, x) = C_{p_0}(T, x) - R. \qquad (14)$$

We can derive the expression for calculation of isochoric heat capacity of the systems from equation (1), considering equations (11) and (14):

$$C_v(\rho, T) = R \sum_{i=1}^{m} \sum_{j=0}^{n_i} a_{ij} \frac{T_{cr}^j(i-j)j}{\rho_{cr}^i T^j i} \qquad (15)$$
$$\times (\rho^i - \rho_0^i) + C_{v_0}(T)_x.$$

As we can see in the projection on p, ρ-plane (Fig. 10), C_v has a maximum on the critical isochore of the system ($\rho = 282$ kg/m³) at all temperatures, having the highest value at the critical point ($T = 556.15$ K; $p = 10.9$ MPa; $\rho = 282$ kg/m³). C_v slightly depends on temperature in this range (projection on p, T-plane). Figure 11 demonstrates the dependence of C_v on concentration; C_v substantially remains a constant for the molar fraction of alcohol from 0.2 to 0.5, and then increases while concentration rises.

The isobaric heat capacity. The dependencies of the isobaric heat capacity of the systems on temperature, density and mole fraction, which are calculated using the expression [8]

$$C_p = C_v + T \frac{(\partial p/\partial T)_\rho^2}{\rho^2 (\partial p/\partial \rho)_T}, \qquad (16)$$

are illustrated in Figs. 12 and 13.

The isobaric heat capacity, like the isochoric one, also has maxima for the subcritical density of the system at all temperatures, but its value tends to infinity at the critical point. Unlike C_v, the isobaric heat capacity significantly decreases while the temperature rises (Fig. 12), and its concentration dependence is similar to that for the isochoric heat capacity (Fig. 13).

The speed of sound. The data on sound propagation in the system together with data on its density can be used for construction of thermodynamic entropy diagrams, which are needed for the calculation of thermal processes that take place in extraction and power plants. The dependence of the speed of sound in a
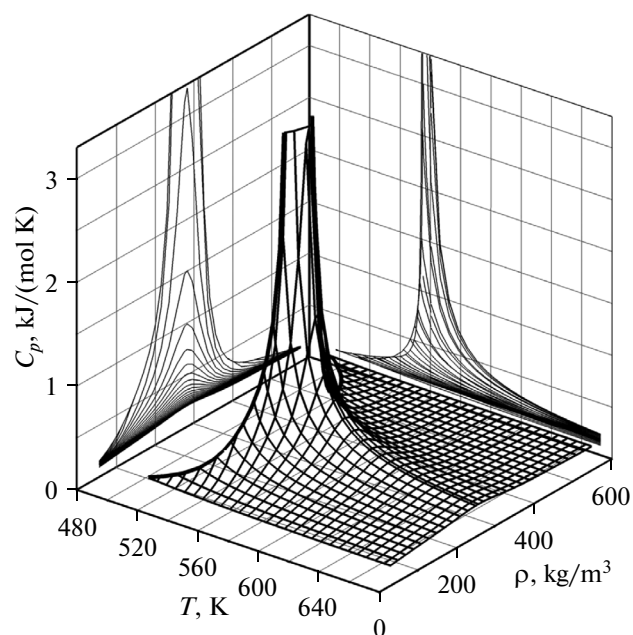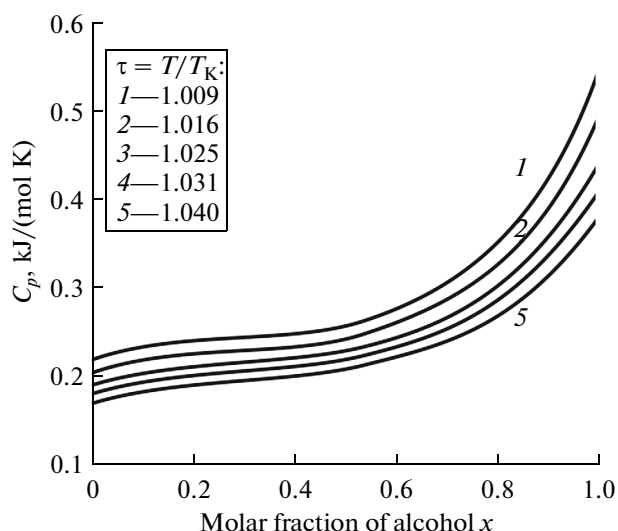

Fig. 11. Isotherms of water–ethanol system, which show dependence of C_v on concentration for reduced density $\omega = 0.4$.

Fig. 12. C_p, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

Fig. 13. Isotherms of water–ethanol system, which show dependence of C_p on concentration for reduced density $\omega = 0.4$.
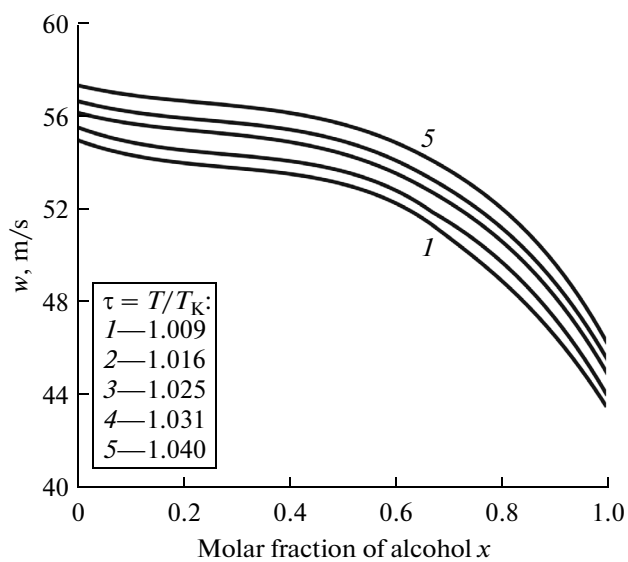

Fig. 14. w, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

Fig. 15. Isotherms of water–ethanol system, which show dependence of w on concentration for reduced density $\omega = 0.4$.

Fig. 16. k, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

medium on density and temperature defined is by the expression [8]

$$w^2(\rho, T) = \frac{C_p(\rho, T)}{C_v(\rho, T)}\left(\frac{\partial p}{\partial \rho}\right)_T. \qquad (17)$$

The value of the speed of sound ω in the system decreases while density rises, has a minimum on the critical isochore and further increases while density rises (Fig. 14). ω increases with rising temperature, and decreases with rising concentration (Fig. 15).
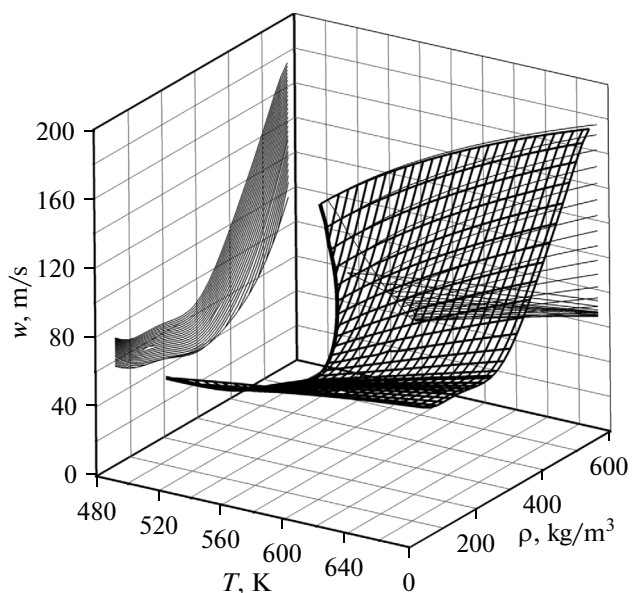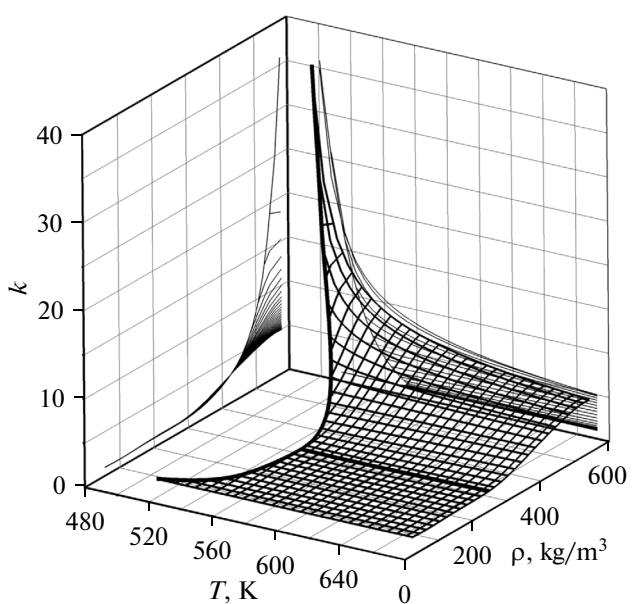
The adiabatic index [7]

$$k(\rho, T) = \frac{\rho}{p(\rho, T)}\frac{C_p(\rho, T)}{C_v(\rho, T)}\left(\frac{\partial p}{\partial \rho}\right)_T. \qquad (18)$$

The adiabatic index k of the system increases insignificantly while density rises up to the critical value and increases dramatically for high values of density; k decreases gradually while temperature rises (Fig. 16). k of the systems with the molar fraction of alcohol
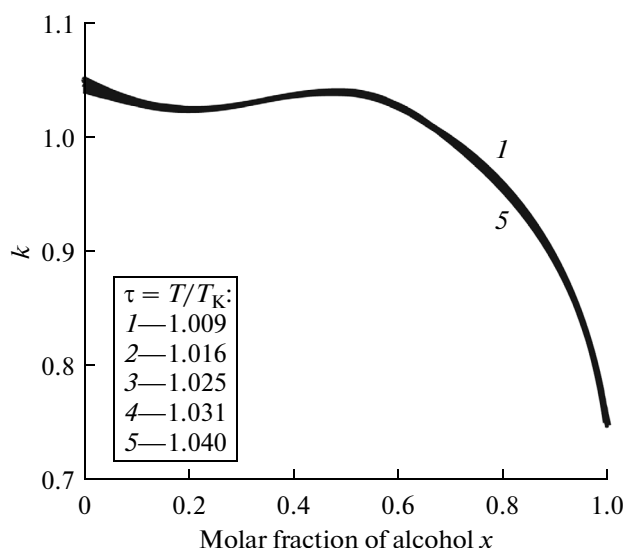
Fig. 17. Isotherms of water–ethanol system, which show dependence of k on concentration for reduced density $\omega = 0.4$.
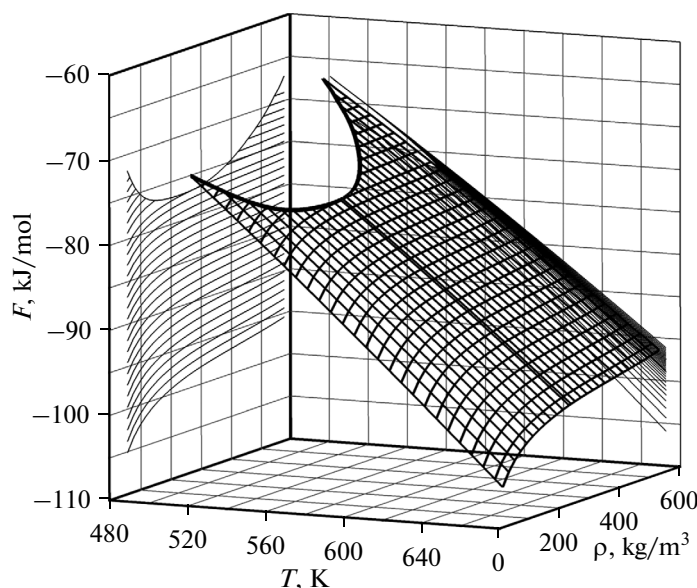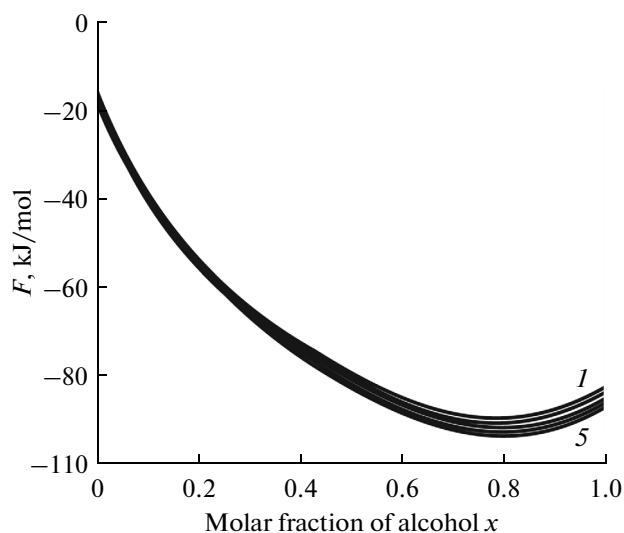

Fig. 18. F, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

from 0 to 0.5 hardly varies and decreases under further rise in concentration (Fig. 17).

The Helmholtz free energy. The expression for calculation of the difference of the Helmholtz free energy for the pure substance relative to the ideal gas state [11]

$$F - F_0 = -\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV - RT\ln\frac{V}{V^0}$$
$$= \int_{0}^{\rho}\left(\frac{p - RT\rho}{\rho^2}\right)d\rho + RT\ln\frac{\rho}{\rho_0} \qquad (19)$$

can be applied to a system of constant composition. The Helmholtz free energy of the system in the ideal gas state is equal to:

$$F_0(T) = H_0(T) - S_0(T)T - R_T, \qquad (20)$$

where the dependence of enthalpy H_0 and entropy S_0 on temperature is defined as

$$H_0(T) = H_0(T_0) + \int_{T_0}^{T}C_{p_0}(T)dT, \qquad (21)$$

$$S_0(T) = S_0(T_0) + \int_{T_0}^{T}\frac{C_{p_0}(T)}{T}dT. \qquad (22)$$

The values of enthalpy H_0 at $T_0 = 100$ K and entropy at $T_0 = 298$ K for pure substances in ideal gas state, taken from the papers [12, 13], are given in Table 4.

We can derive the expression for calculation of the Helmholtz free energy for the system of constant composition depending on the density and temperature from equation (1), considering equations (19)–(22):

$$F(\rho, T) = RT\sum_{i=1}^{n}\sum_{j=0}^{S_i} a_{ij}\frac{T_{cr}^j \rho^i}{\rho_{cr}^i T^j i}$$
$$+ RT\ln\frac{\rho}{\rho_0} + F_0(T). \tag{23}$$

Table 4. The values of enthalpy and entropy in standard state

Substance	$H_0(T_0)$, J/mol, $T_0 = 100$ K	$S_0(T_0)$, J/(mol K), $T_0 = 298$ K
Water	3289	188.74
Methanol	3509	239.76
Ethanol	3841	281.38
n-Propanol	4156	324.8

The Helmholtz free energy of an equimolar water–ethanol ($x = 0.5$) system decreases while the temperature rises and insignificantly increases with a rise in

Fig. 19. Isotherms of water–ethanol system, which show dependence of F on concentration for reduced density $\omega = 0.4$.
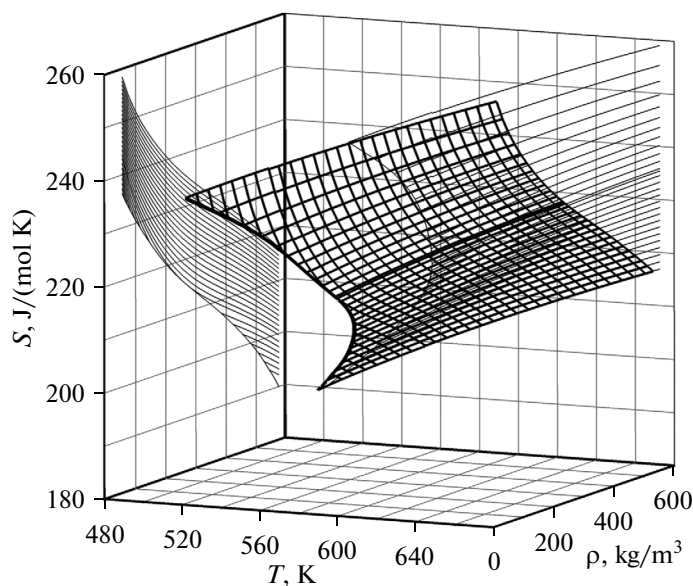

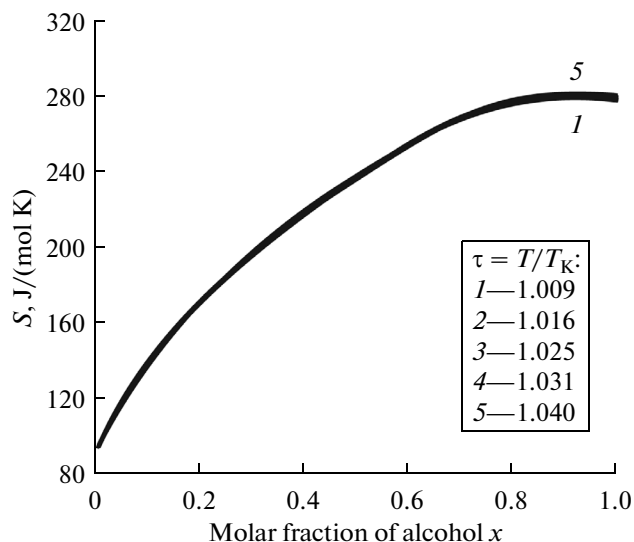**Fig. 20.** S,ρ,T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p,T-plane and p,ρ-plane.

Fig. 21. Isotherms of water−ethanol system, which show dependence of S on concentration for reduced density $\omega = 0.4$.
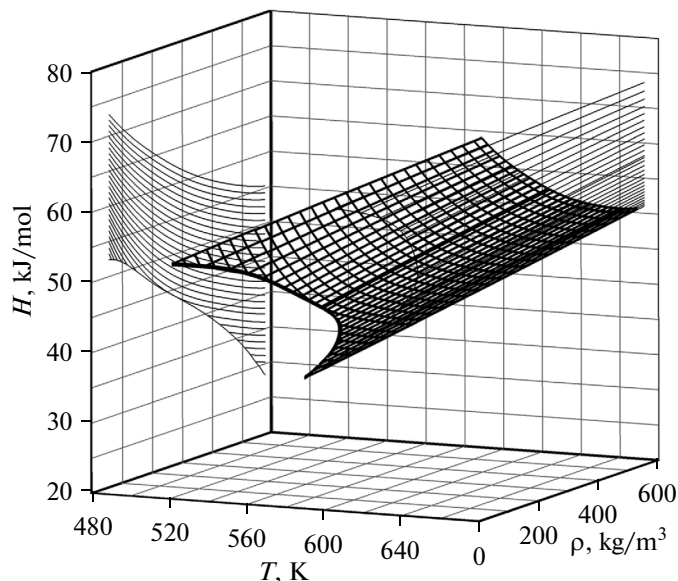

Fig. 22. H, ρ, T-surface of equimolar water−ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

density, especially at high density values (Fig. 18). The value of the Helmholtz free energy decreases while ethanol concentration rises, has a minimum at $x = 0.8$, and after that increases a little (Fig. 19).

The entropy. The difference of the entropy for the system of constant composition in the ideal gas state can be calculated according the expression [11]

$$S - S_0 = \int\limits_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{R}{V}\right]dV + R\ln\frac{V}{V_0}$$

$$= -\int\limits_{0}^{\rho}\left[\left(\frac{\partial p}{\partial T}\right)_\rho - R\rho\right]\frac{d\rho}{\rho^2} - R\ln\frac{\rho}{\rho_0}. \tag{24}$$

Taking into account (1), (22) and (24), we have the following expression:

$$S(\rho, T)$$

$$= -R\left[\sum_{i=1}^{n}\sum_{j=0}^{S_i}a_{ij}\frac{T_k^j\rho^i(i-j)}{\rho_k^i T^j i} + \ln\frac{\rho}{\rho_0}\right] + S_0(T). \tag{25}$$

The entropy of equimolar water−ethanol ($x = 0.5$) system in all the states (vapor and liquid phases, supercritical fluid) decreases while density rises and increases while temperature rises (Fig. 20). The dependence of the entropy on concentration is illustrated in Fig. 20. The value of the entropy increases
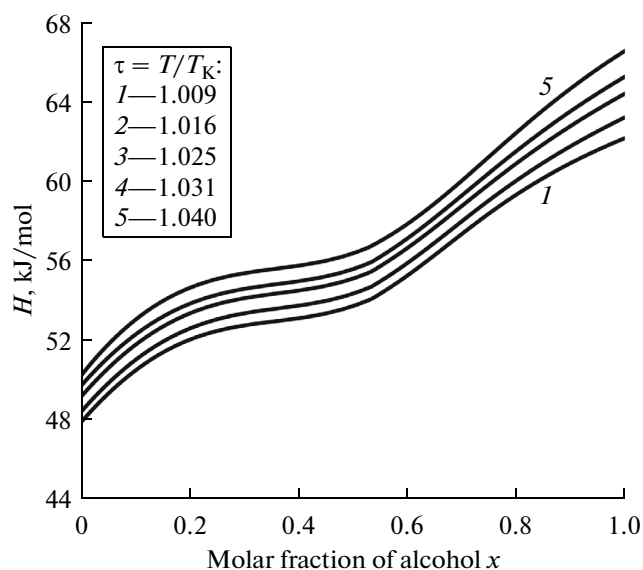
Fig. 23. Isotherms of water–ethanol system, which show dependence of H on concentration for reduced density $\omega = 0.4$.

while ethanol concentration rises up to $x = 0.8$, and then slightly decreases (Fig. 21).

The enthalpy. Figure 22 shows the dependence of the enthalpy of the equimolar water–ethanol ($x = 0.5$) system on density and temperature, calculated using expression [11]

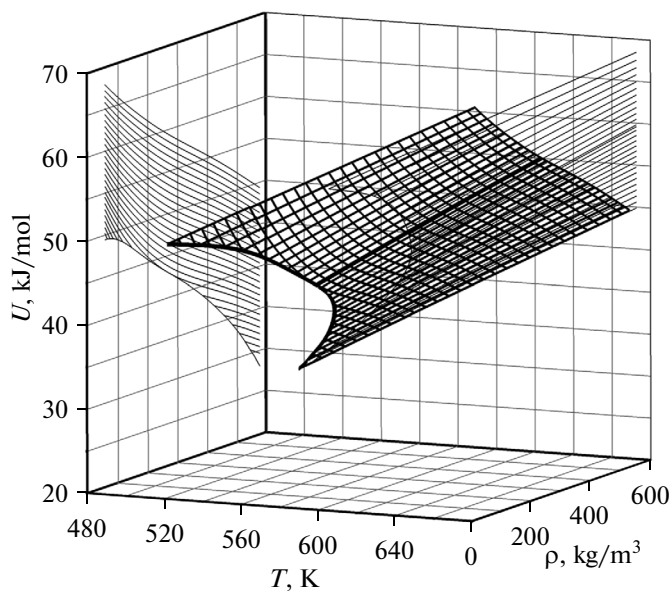$$H(\rho, T) = F(\rho, T) + TS(\rho, T) + RTZ(\rho, T). \quad (26)$$

As may be seen in Fig. 22, the value of the enthalpy decreases while density rises and increases while temperature rises. The dependence of the enthalpy on concentration is illustrated in Fig. 23. The retarded rise in enthalpy at molar fractions of alcohol from 0.2 to 0.5, apparently, is associated with a similar dependency for the isochoric heat capacity (Fig. 11).

The internal energy. The expression of the internal energy for the system of constant composition is the following:

$$U(\rho, T) = F(\rho, T) + TS(\rho, T). \quad (27)$$

One can calculate the values of the internal energy of the system by substitution of the Helmholtz free energy value (23) and the entropy value into expression (27). The dependencies of the U value on density, temperature and composition of the water–ethanol system are shown in Figs. 24 and 25.

The internal energy, as well as the entropy, decreases while the density rises and increases while temperature and concentration rise (Figs. 24 and 25).

The Gibbs energy. Based on known dependencies of enthalpy and entropy on density and temperature for the system of constant composition, one can calculate the Gibbs energy:

$$G(\rho, T) = H(\rho, T) - TS(\rho, T). \quad (28)$$

The dependencies of the Gibbs energy on density, temperature and concentration (Figs. 26 and 27) are similar to one for the Helmholtz free energy (Figs. 18 and 19).

The differential isothermal throttling effect represents a decrease in enthalpy of the system when it is
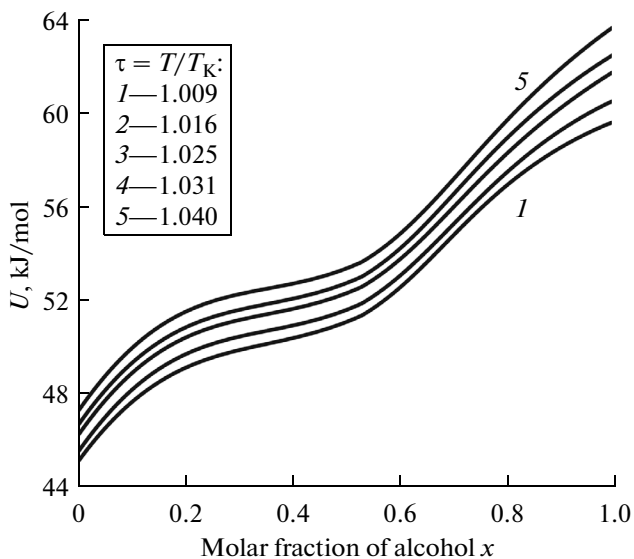

Fig. 24. U, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

Fig. 25. Isotherms of water–ethanol system, which show dependence of U on concentration for reduced density $\omega = 0.4$.

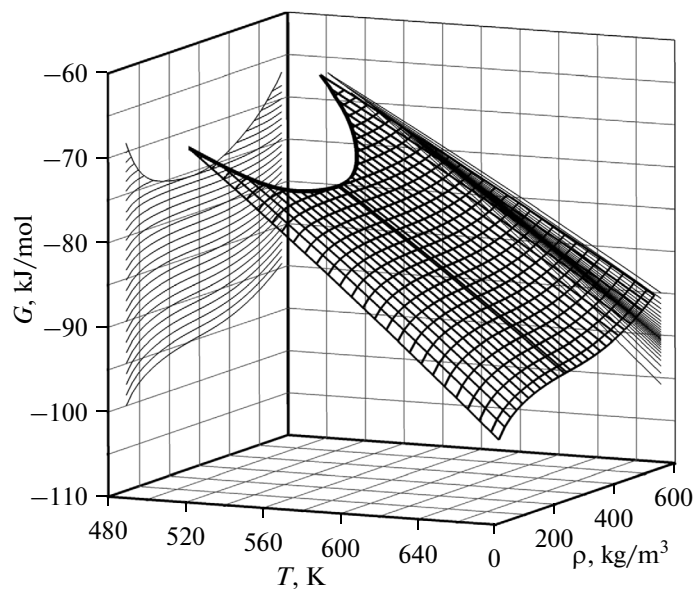**Fig. 26.** G, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.

forced through a porous plug under constant difference in pressure and constant temperature:

$$d^{\text{is}} = \left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{\rho} - \frac{T}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}. \quad (29)$$

Taking into account (1) and (29), we have the following expression:

$$d^{\text{is}}(\rho, T) = \frac{1}{\rho} - \frac{T}{\rho^2}\left(R\rho\left(1 + \sum_{i=1}^{n}\sum_{j=0}^{S_i} a_{ij}\frac{T_k^j \rho^i (i-j)}{\rho_k^i T^j}\right)\right)$$
$$\times \left(RT\left(1 + \sum_{i=1}^{m}\sum_{j=0}^{n_i} a_{ij}\frac{T_{\text{cr}}^j \rho^i (i+1)}{\rho_{\text{cr}}^i T^j}\right)\right)^{-1}. \quad (30)$$

The value of the isothermal throttling effect decreases while the density rises, achieves its minimum at the critical point and then increases (Fig. 28).
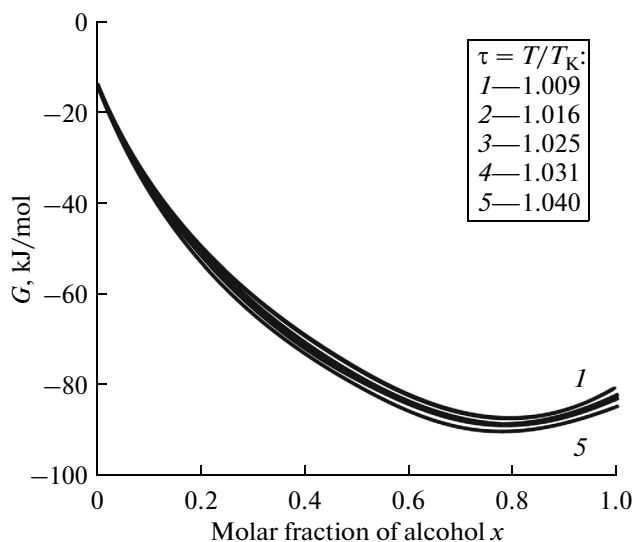

Fig. 27. Isotherms of water–ethanol system, which show dependence of G on concentration for reduced density $\omega = 0.4$.
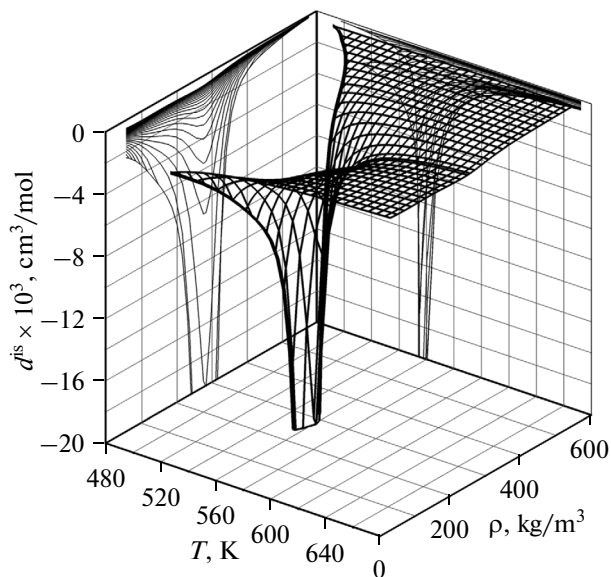

Fig. 28. d^{is}, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.
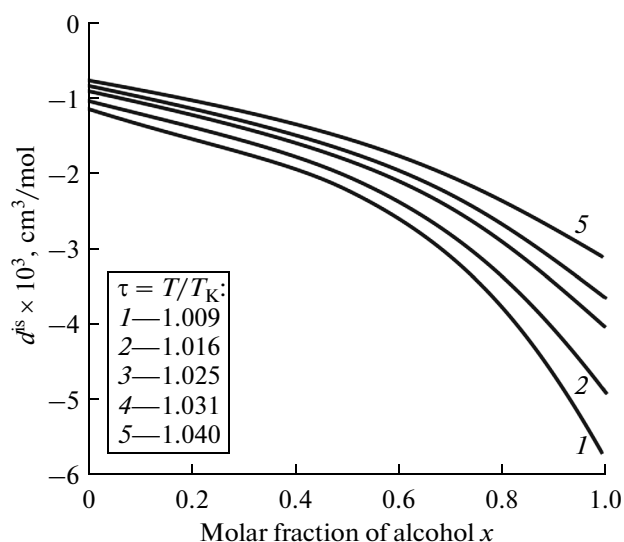
Fig. 29. Isotherms of water–ethanol system, which show dependence of d^{is} on concentration for reduced density $\omega = 0.4$.

d^{is} increases while the temperature rises and gradually decreases while the concentration of alcohol rises (Fig. 29).

The differential adiabatic throttling effect is a change in system temperature when the system is forced through a porous plug under constant difference in pressure without heat transfer with the environment:

$$d^{ad}(\rho, T) = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{d^{is}(\rho, T)}{C_p(\rho, T)}. \qquad (31)$$

The adiabatic throttling effect has a complicated dependence on temperature and density; there is a crease on the d^{ad}, ρ, T-surface along the critical isochore (Fig. 30). d^{ad} decreases while density and temperature rise, increases while concentration rises up to $x = 0.8$ and then decreases (Fig. 31).

For comparison, we determined the coefficients of equation (1) using p, ρ, T-data for water presented in the paper [6] and calculated the values of its thermodynamic properties (Table 5).
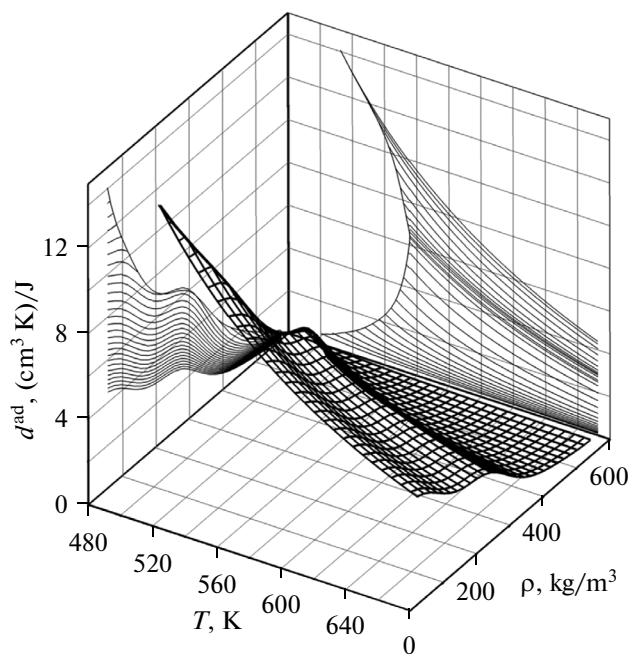

Fig. 30. d^{ad}, ρ, T-surface of equimolar water–ethanol ($x = 0.5$) system and its projections on p, T-plane and p, ρ-plane.
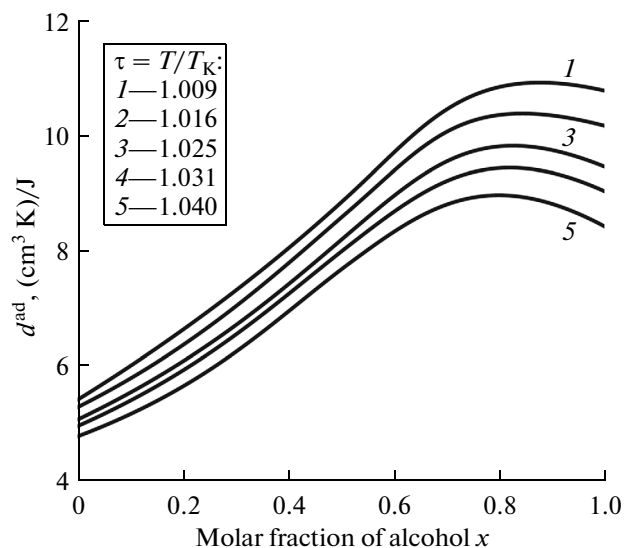

Fig. 31. Isotherms of water–ethanol system, which show dependence of d^{ad} on concentration for reduced density $\omega = 0.4$.

Table 5. The average relative deviation of the difference between the values of thermodynamic functions calculated using equation (1) and the values calculated according to IAPWS-IF97 for water [6]

Phase	δp, %	δH, %	δS, %	δC_p, %
VP, LP	0.8	1.7	4.0	5.7
SCF	0.4	4.0	4.6	7.6

Thus, equation (1) can be used for approximation of experimental p,ρ,T,x-dependencies and calculation of thermodynamic properties for polar component systems in a wide range of parameters, particularly, for water–aliphatic alcohol systems within the investigated parameter range.

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