

A RELATION FOR THERMAL CHARACTERISTICS OF MIXTURES AS FUNCTIONS OF CONCENTRATIONS

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By using perturbation theory for an isothermic-isobaric ensemble, we have deduced a formula that allows one to predict the properties of mixtures on the basis of the known characteristics of pure components. We have calculated such properties of mixtures as the molar volume, coefficient of isothermal compressibility, coefficient of volumetric expansion, compressibility of the water–acetone mixture, and density of the acetonitrile–benzene mixture under various thermodynamic conditions. The results of calculations are in good agreement with the experimental data for the indicated mixtures.

Introduction

In many technological calculations, it is necessary to know the main thermal properties of mixtures at various concentrations. The theoretical determination of these properties is a rather complicated problem even for the mixtures with simple molecules. Almost the same difficulties are met upon the experimental determination of the physical parameters characterizing the equilibrium properties of mixtures. In this case, we need to deduce the formulas that would allow one to predict the main thermal properties of mixtures on the basis of the corresponding properties of components of a mixture. To this end, we will use perturbation theory for an isothermic-isobaric ensemble [1].

Procedure of Derivation of Computational Formulas

Consider a binary mixture composed from N_1 particles of the first kind and N_2 particles of the second one with potentials of intermolecular interaction $\varphi_{st}(r_{is} - r_{jt})$, where s and t mean kinds of particles. The statistical sum for such a system in an isothermic-isobaric ensemble has the form

$$Y(P, T, N_1, N_2) = AZ_1 Z_2 \int_0^\infty e^{-\beta PV} dV \times \int_Y e^{-P(U_1+U_2+U_{12})} d\Gamma_R, \quad (1)$$

where $A = (h^{3N} N_1! N_2!)^{-1}$; h is the Planck constant, $\beta = 1/k_B T$, k_B is the Boltzmann coefficient, P, V, T are, respectively, the pressure, volume, and temperature defining a state of the mixture; $Z_s = (2\pi m_s k_B T)^{\frac{3}{2} N_s}$; m_s is the mass of a molecule of the kind s ($s = 1, 2$), and

$$U_s = \sum_{1 \leq i < j \leq N_s} \varphi_{ss}(|r_i - r_j|),$$

$$U_{12} = \sum_{1 \leq i \leq N_1, 1 \leq j \leq N_2} \varphi_{12}(|r_{1i} - r_{2j}|),$$

$$d\Gamma_R = dr_1^1 dr_2^1 \dots dr_{N_1}^1 dr_1^2 dr_2^2 \dots dr_{N_2}^2,$$

where dr_i^s is the volume per the i -th particle of the kind s .

Prior to calculations within perturbation theory, we introduce the functions

$$\psi_{st}(|\vec{r}_{is} - \vec{r}_{jt}|) = \varphi_{st}(|\vec{r}_{is} - \vec{r}_{jt}|) - \varphi_{00}(|r_1 - r_2|)$$

that indicate the deviations of the intermolecular potentials of molecules of the kinds s and t of the binary mixture under consideration from the potentials of intermolecular interaction in the basic system. We note that, as a basic system, we can consider one of the mixture components. Then relation (1) can be represented in terms of the modified Mayer functions $\tilde{f}(r_{ij}) = \exp(-\beta\psi_{ts}(r_{ij})) - 1$ as

$$Y = AZ_1 Z_2 \int e^{-\beta PV} dV \int e^{-\beta U_{00}} \times \prod_{1 \leq i < j \leq N_1} (1 + \tilde{f}_{11}(r_{ij})) \prod_{1 \leq i < j \leq N_2} (1 + \tilde{f}_{22}(r_{ij})) \times \prod_{1 \leq i \leq N_1, 1 \leq j \leq N_2} (1 + \tilde{f}_{12}(r_{ij})) d\Gamma_R \quad (2)$$

where

$$U_{00} = \sum_{1 \leq i < j \leq N} \varphi_{00}(r_{ij}).$$

Table 1a. Molar volumes of the water-acetone mixture $V, 10^{-3} \text{ m}^3/\text{kmole}$ (V^* is the volume at the fixed concentration $x_1 = 0.925$; V_{e1}, V_{t1} are the experimental and theoretical values of the volume at $x_1 = 0.900$; V_{e2}, V_{t2} at $x_1 = 0.800$; V_{e3}, V_{t3} at $x_1 = 0.700$)

$P, \text{ bar}$	1	200	400	600	1000
$T, \text{ K}$	298.15				
Water	18.07	17.93	17.79	17.67	17.42
Acetone	66.77	66.07	65.44	64.85	63.90
V^*	21.72	21.54	21.36	21.21	20.90
V_{e1}	22.94	22.56	22.75	22.38	22.07
V_{t1}	22.94	22.55	22.74	22.39	22.06
V_{e2}	28.04	27.49	27.75	27.26	26.84
V_{t2}	27.80	27.31	27.56	27.11	26.70
V_{e3}	33.21	32.45	32.81	32.14	31.60
V_{t3}	32.67	32.07	32.37	31.83	31.35
$T, \text{ K}$	308.15				
Water	18.05	17.91	17.78	17.64	17.40
Acetone	68.45	67.65	66.94	66.36	65.22
V^*	21.83	21.65	21.47	21.29	20.99
V_{e1}	23.10	22.90	22.71	22.52	22.19
V_{t1}	23.09	22.90	22.70	22.51	22.19
V_{e2}	28.30	27.99	27.72	27.47	27.03
V_{t2}	28.13	27.88	27.62	27.37	26.97
V_{e3}	33.80	33.37	33.00	32.68	32.06
V_{t3}	33.17	32.86	32.54	32.24	31.76
$T, \text{ K}$	323.15				
Water	18.15	18.01	17.87	17.74	17.50
Acetone	70.27	69.30	68.47	67.75	66.50
V^*	22.06	21.86	21.67	21.49	21.18
V_{e1}	23.37	23.15	22.97	22.75	22.41
V_{t1}	23.36	23.14	22.94	22.74	22.41
V_{e2}	28.76	28.43	28.13	27.85	27.39
V_{t2}	28.58	28.28	28.00	27.74	27.31
V_{e3}	34.40	33.92	33.50	33.14	32.48
V_{t3}	33.79	33.41	33.07	32.74	32.22

Table 1b. Molar volumes of the water-acetone mixture $V, 10^{-3} \text{ m}^3/\text{kmole}$ (V^* is the volume at the fixed concentration $x_1 = 0.300$; V_{e1}, V_{t1} are the experimental and theoretical values of the volume at $x_1 = 0.600$; V_{e2}, V_{t2} at $x_1 = 0.500$; V_{e3}, V_{t3} at $x_1 = 0.100$)

$P, \text{ bar}$	1	200	400	600	1000
$T, \text{ K}$	298.15				
Water	14.85	15.17	15.35	15.53	15.67
Acetone	73.87	72.24	70.90	69.76	67.97
V^*	56.16	55.12	54.24	53.49	52.28
V_{e1}	38.87	38.28	37.81	37.43	36.73
V_{t1}	37.54	37.18	36.84	36.55	35.99
V_{e2}	44.60	43.92	43.32	42.81	41.96
V_{t2}	44.36	43.71	43.13	42.64	41.82
V_{e3}	68.02	66.55	65.34	64.31	62.66
V_{t3}	67.97	66.53	65.35	64.34	62.74
$T, \text{ K}$	308.15				
Water	15.15	15.44	15.67	15.59	15.87
Acetone	74.85	73.14	71.69	70.58	68.55
V^*	56.94	55.83	54.88	54.11	52.75
V_{e1}	39.40	38.83	38.33	37.91	37.13
V_{t1}	38.21	38.21	37.45	37.11	36.54
V_{e2}	45.17	44.42	43.80	43.26	42.30
V_{t2}	45.00	44.29	43.68	43.12	42.21
V_{e3}	69.01	67.45	66.16	65.18	63.30
V_{t3}	68.88	67.37	66.09	65.09	63.28
$T, \text{ K}$	323.15				
Water	15.22	15.65	15.92	16.07	16.11
Acetone	76.66	74.63	73.00	71.63	69.60
V^*	58.23	56.94	55.88	54.96	53.55
V_{e1}	40.20	39.54	39.00	38.52	37.69
V_{t1}	39.00	38.54	38.13	37.74	37.12
V_{e2}	46.10	45.24	44.54	43.94	42.88
V_{t2}	45.94	45.14	44.46	43.85	42.85
V_{e3}	70.66	68.81	67.34	66.18	64.26
V_{t3}	70.52	68.73	67.29	66.07	64.25

Using (2), we define the thermodynamic potential of a mixture as

$$G(P, T, N_i) = -k_B T [\ln(AZ_1Z_2) + \ln \sum (1, 1, 1, P, T, N_1, N_2)], \quad (3)$$

where

$$\begin{aligned} \sum &= \int_0^\infty e^{-\beta PV} Q_0(N, V, T) \times \\ &\times \langle \left[\prod_{t=1}^2 \prod_{1 \leq i < j \leq N} (1 + \varepsilon_{tt} \tilde{f}_{tt}(r_{ij})) \right] \rangle \times \\ &\times \prod_{1 \leq i \leq N_1, 1 \leq j \leq N_2} (1 + \varepsilon_{12} \tilde{f}_{12}(r_{ij})) dV, \end{aligned} \quad (4)$$

$Q_0(N, V, T)$ is the configurational part of the statistical sum of an isothermic-isobaric ensemble, and the

parameters $\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{12}$ are introduced in order to employ the method of generalized cumulative expansions [2] by means of formula (4) in calculations of the thermodynamic potential $G(P, T, N_i)$ (3). In the approximation taking into account only the first degrees of ε_{st} , the thermodynamic potential G is reduced to the form

$$G = G_0 + \frac{k_B T}{2N} (N_1^2 \Phi_{11} + N_2^2 \Phi_{22} + 2N_1 N_2 \Phi_{12}), \quad (5)$$

where

$$\begin{aligned} \Phi_{ts} &= \int_{\langle V(P, T, N) \rangle_0} d\tilde{r}_{ij} g_0(r_{ij}, T, \langle V(P, T, N) \rangle_0) \times \\ &\times \tilde{f}_{ts}(r_{ij}) \vartheta_0^{-1}(P, T), \end{aligned}$$

ϑ_0^{-1} is the volume per one particle, $g_0(r_{ij}, T, \langle V(P, T, N) \rangle_0)$ is the radial distribution function. By

T a b l e 2a. Coefficients of isothermal compressibility of the water-acetone mixture $\beta_T, 10^5 \text{ bar}^{-1}$ (β_T^* is the coefficient of isothermal compressibility at the fixed concentration $x_1 = 0.925$; β_{e1}, β_{t1} are the experimental and theoretical values of the coefficient of isothermal compressibility at $x_1 = 0.900$; β_{e2}, β_{t2} at $x_1 = 0.800$; β_{e3}, β_{t3} at $x_1 = 0.700$)

P, bar	1	200	400	600	100
T, K	298.15				
Water	4.51	4.30	4.10	3.91	3.57
Acetone	12.57	10.56	8.90	7.65	6.54
β_T^*	4.42	4.18	3.95	3.73	3.33
β_{e1}	4.44	4.29	4.09	3.84	3.22
β_{t1}	4.42	4.16	3.92	3.69	3.27
β_{e2}	5.38	4.95	4.55	4.19	3.59
β_{t2}	5.42	4.89	3.88	4.20	3.40
β_{e3}	6.39	5.75	5.17	4.66	3.86
β_{t3}	6.43	5.69	5.10	4.64	3.86
T, K	308.15				
Water	4.47	4.23	4.02	3.83	3.53
Acetone	14.23	11.18	8.94	7.61	8.02
β_T^*	4.44	4.21	3.99	3.79	3.46
β_{e1}	4.67	4.40	4.13	3.88	3.43
β_{t1}	4.46	4.22	3.99	3.79	3.45
β_{e2}	5.79	5.22	4.73	4.33	3.80
β_{t2}	5.66	5.27	4.78	4.40	3.69
β_{e3}	7.08	6.02	5.25	4.80	4.92
β_{t3}	7.09	6.08	5.29	4.98	5.05
T, K	323.15				
Water	4.41	4.19	3.99	3.80	3.49
Acetone	16.08	12.58	9.88	8.12	7.82
β_T^*	4.60	4.48	4.28	4.02	3.26
β_{e1}	4.90	4.64	4.35	4.06	3.43
β_{t1}	4.69	4.59	4.38	4.10	3.20
β_{e2}	6.12	5.59	5.09	4.63	3.88
β_{t2}	6.16	5.49	4.92	4.42	3.88
β_{e3}	7.80	6.60	5.72	5.16	5.12
β_{t3}	7.84	6.68	5.60	5.18	5.11

T a b l e 2b. Coefficients of isothermal compressibility of the water-acetone mixture $\beta_T, 10^5 \text{ bar}^{-1}$ (β_T^* is the coefficient of isothermal compressibility at the fixed concentration $x_1 = 0.300$; β_{e1}, β_{t1} are the experimental and theoretical values of the coefficient of isothermal compressibility at $x_1 = 0.600$; β_{e2}, β_{t2} at $x_1 = 0.500$; β_{e3}, β_{t3} at $x_1 = 0.100$)

P, bar	1	200	400	600	1000
T, K	298.15				
Water	4.51	4.30	4.10	3.91	3.57
Acetone	12.57	10.56	8.90	7.65	6.54
β_T^*	10.24	8.76	7.49	6.45	5.19
β_{e1}	7.34	6.48	5.74	5.12	4.28
β_{t1}	7.33	6.46	5.66	5.01	4.16
β_{e2}	8.27	7.30	6.42	5.65	4.47
β_{t2}	8.24	7.32	6.54	5.69	4.51
β_{e3}	11.79	10.06	8.56	7.34	5.86
β_{t3}	11.80	9.97	8.43	7.24	6.05
T, K	308.15				
Water	4.47	4.23	4.02	3.83	3.53
Acetone	14.23	11.18	8.94	7.61	8.02
β_T^*	10.91	9.12	7.72	6.77	6.33
β_{e1}	8.11	6.87	5.94	5.36	5.31
β_{t1}	7.94	6.74	5.61	5.22	5.12
β_{e2}	9.11	7.68	6.59	5.87	5.64
β_{t2}	8.88	7.73	6.78	6.07	5.37
β_{e3}	13.11	10.41	8.44	7.30	7.77
β_{t3}	13.09	10.50	8.56	7.36	7.42
T, K	323.15				
Water	4.41	4.19	3.99	3.80	3.49
Acetone	16.08	12.58	9.88	8.12	7.82
β_T^*	12.08	10.33	8.79	7.49	5.77
β_{e1}	9.08	7.63	6.50	5.75	5.42
β_{t1}	8.91	7.37	6.52	5.70	5.36
β_{e2}	10.39	8.60	7.24	6.36	6.18
β_{t2}	9.65	8.70	7.74	6.75	5.96
β_{e3}	14.91	11.96	9.62	8.00	7.24
β_{t3}	14.70	11.86	9.58	7.97	7.07

introducing the concentration $x_i = N_i/N$, relation (5) can be rewritten as

$$G = G_0 + \frac{k_B T N}{2} (x_1^2 \Phi_{11} + x_2^2 \Phi_{22} + 2x_1 x_2 \Phi_{12}). \tag{6}$$

By differentiating the thermodynamic potential (6) with respect to various variables or taking the derivatives of the second and higher order with respect to the collection of thermodynamic quantities, we obtain the following formula for the calculation of various thermal characteristics M of a binary mixture:

$$M = M_0 + (x_1^2 \Lambda_{11} + x_2^2 \Lambda_{22} + x_1 x_2 \Lambda_{12}). \tag{7}$$

In particular, if relation(6) is differentiated with respect to pressure, we get a formula of the form (7) for the specific volume of a binary mixture. The quantities Λ_{st} are defined by derivatives Φ_{st} with respect to the corresponding variables. In the general case in a wide

interval of thermodynamic variables, the calculation of Λ_{st} is an unsolvable task.

To calculate Λ_{st} , we employ a method, according to which we first find Λ_{11} , by using relation (7) at $x_t = 1$. Then $\Lambda_{tt} = M_t(P, T) - M_0(P, T)$, where $M_t(P, T)$ is the considered property of a component which is assumed to be known, and $M_0(P, T)$ is the corresponding property of the basic (standard) system. To determine Λ_{12} , it is necessary to know the value of the considered parameter $M_y(P, T, y_1, y_2)$ of the binary mixture at some fixed value of a single concentration ($x_1 = y_1, x_2 = y_2, y_1 + y_2 = 1$). Then

$$\Lambda_{12} = \frac{M_y(y_1, y_2) - M_0 - (M_1 - M_0)y_1^2}{2y_1 y_2} - \frac{(M_2 - M_0)y_2^2}{2y_1 y_2}. \tag{8}$$

T a b l e 3a. Coefficients of compressibility of the water-acetone mixture k (k^* is the coefficient of compressibility at the fixed concentration $x_1 = 0.925$; k_{e1} , k_{t1} are the experimental and theoretical values of the coefficient of compressibility at $x_1 = 0.900$; k_{e2} , k_{t2} at $x_1 = 0.800$; k_{e3} , k_{t3} at $x_1 = 0.700$)

P , bar	200	400	600	1000
T , K	298.15			
Water	0.0087	0.0170	0.0249	0.0393
Acetone	0.0226	0.0414	0.0569	0.0828
k^*	0.0084	0.0166	0.0239	0.0021
k_{e1}	0.0086	0.0169	0.0247	0.0384
k_{t1}	0.0083	0.0166	0.0237	0.0373
k_{e2}	0.0101	0.0195	0.0279	0.0429
k_{t2}	0.0093	0.0187	0.0265	0.0396
k_{e3}	0.0119	0.0226	0.0320	0.0483
k_{t3}	0.0107	0.0215	0.0323	0.0474
T , K	308.15			
Water	0.0086	0.0168	0.0244	0.0387
Acetone	0.0247	0.0441	0.0594	0.0872
k^*	0.0087	0.0164	0.0244	0.0383
k_{e1}	0.0091	0.0172	0.0253	0.0393
k_{t1}	0.0088	0.0164	0.0245	0.0383
k_{e2}	0.0108	0.0205	0.0293	0.0449
k_{t2}	0.0099	0.0207	0.0283	0.0439
k_{e3}	0.0127	0.0238	0.0333	0.0535
k_{t3}	0.0121	0.0217	0.0329	0.0511
T , K	323.15			
Water	0.0085	0.0166	0.0242	0.0383
Acetone	0.0282	0.0494	0.0665	0.0943
k^*	0.0090	0.0177	0.0258	0.0400
k_{e1}	0.0094	0.0184	0.0265	0.0410
k_{t1}	0.0092	0.0181	0.0264	0.0406
k_{e2}	0.0116	0.0218	0.0314	0.0477
k_{t2}	0.0111	0.0199	0.0299	0.0475
k_{e3}	0.0140	0.0262	0.0364	0.0557
k_{t3}	0.0134	0.0262	0.0350	0.0557

T a b l e 3b. Coefficients of compressibility of the water-acetone mixture k (k^* is the coefficient of compressibility at the fixed concentration $x_1 = 0.300$; k_{e1} , k_{t1} are the experimental and theoretical values of the coefficient of compressibility at $x_1 = 0.600$; k_{e2} , k_{t2} at $x_1 = 0.500$; k_{e3} , k_{t3} at $x_1 = 0.100$)

P , bar	200	400	600	1000
T , K	298.15			
Water	0.0087	0.0170	0.0249	0.0393
Acetone	0.0226	0.0414	0.0569	0.0828
k^*	0.0186	0.0344	0.0476	0.0692
k_{e1}	0.0136	0.0256	0.0361	0.0538
k_{t1}	0.0129	0.0250	0.0361	0.0536
k_{e2}	0.0153	0.0287	0.0403	0.0606
k_{t2}	0.0159	0.0296	0.0413	0.0605
k_{e3}	0.0215	0.0392	0.0545	0.0787
k_{t3}	0.0213	0.0391	0.0538	0.0782
T , K	308.15			
Water	0.0086	0.0168	0.0244	0.0387
Acetone	0.0247	0.0441	0.0594	0.0872
k^*	0.0196	0.0361	0.0497	0.0737
k_{e1}	0.0146	0.0271	0.0378	0.0578
k_{t1}	0.0137	0.0269	0.0380	0.0564
k_{e2}	0.0165	0.0303	0.0422	0.0635
k_{t2}	0.0163	0.0307	0.0428	0.0642
k_{e3}	0.0226	0.0414	0.0556	0.0827
k_{t3}	0.0230	0.0414	0.0562	0.0828
T , K	323.15			
Water	0.0085	0.0166	0.0242	0.0383
Acetone	0.0282	0.0494	0.0665	0.0943
k^*	0.0221	0.0404	0.0560	0.0803
k_{e1}	0.0163	0.0301	0.0417	0.0624
k_{t1}	0.0159	0.0308	0.0405	0.0618
k_{e2}	0.0186	0.0340	0.0468	0.0688
k_{t2}	0.0182	0.0340	0.0480	0.0696
k_{e3}	0.0263	0.0470	0.0635	0.0906
k_{t3}	0.0261	0.0464	0.0632	0.0899

Substituting (8) in (7), we get a value of the thermodynamic quantity M characterizing the binary mixture at the given values P and T and any concentrations x_1 and x_2 ($x_1 + x_2 = 1$):

$$\begin{aligned}
 M(P, T, N) &= M_0(P, T, N) + \sum_{i=1}^2 x_i^2 (M_i(P, T, N) - \\
 &- M_0(P, T, N)) + \frac{x_1 x_2}{y_1 y_2} [M_y(P, T, y_1, y_2) - \\
 &- M_0(P, T, N)(1 - y_1^2 - y_2^2) - M_1(P, T, N)y_1^2 - \\
 &- M_2(P, T, N)y_2^2]. \tag{9}
 \end{aligned}$$

Thus, to calculate some thermodynamic characteristic of a binary mixture at various concentrations, it is necessary to know the value of this characteristic for pure components of the mixture and its value at some single fixed concentration.

One of the important problems in the calculation of the thermodynamic properties of a binary mixture at various concentrations by formula (9) is the choice of its basic value $M_0(P, T, N)$. As basic, we can take values of the corresponding quantities for one of the pure components of the mixture. This question can be considered in another way. Relation (7) for a binary mixture with fixed concentrations of the components y_1 and y_2 can be written as

$$\begin{aligned}
 M_y(P, T, y_1, y_2) &= M_0(P, T) + y_1^2 (M_1(P, T) - \\
 &- M_0(P, T)) + y_2^2 (M_2(P, T) - M_0(P, T)) + 2y_1 y_2 \lambda_{12}.
 \end{aligned}$$

We set $\lambda_{12} = 0$, then the basic value $M'_0(P, T)$ is defined by the expression

$$M'_0(P, T) = \frac{M_y(P, T, y_1, y_2) - y_1^2 M_1(P, T)}{1 - y_1^2 - y_2^2} -$$

Table 4a. Coefficients of volumetric expansion of the water-acetone mixture $\alpha, 10^3 \text{ K}^{-1}$ (α^* is the coefficient of volumetric expansion at the fixed concentration $x_1 = 0.925$; α_{e1}, α_{t1} are the experimental and theoretical values of the coefficient of volumetric expansion at $x_1 = 0.900$; α_{e2}, α_{t2} at $x_1 = 0.800$; α_{e3}, α_{t3} at $x_1 = 0.700$)

$P, \text{ bar}$	1	200	400	600	100
$T, \text{ K}$	298.15				
Water	0.26	0.27	0.30	0.32	0.35
Acetone	1.40	1.18	1.16	1.22	0.93
α^*	0.37	0.33	0.43	0.33	0.32
α_{e1}	0.64	0.59	0.63	0.59	0.55
α_{t1}	0.61	0.55	0.57	0.54	0.51
α_{e2}	0.85	0.77	0.74	0.70	0.64
α_{t2}	0.84	0.73	0.72	0.67	0.60
α_{e3}	2.03	1.95	1.93	1.94	1.67
α_{t3}	2.08	2.00	1.96	1.92	1.70
$T, \text{ K}$	308.15				
Water	0.34	0.35	0.36	0.38	0.39
Acetone	1.52	1.29	1.20	1.15	1.02
α^*	0.56	0.54	0.54	0.50	0.48
α_{e1}	0.71	0.67	0.66	0.63	0.60
α_{t1}	0.73	0.61	0.60	0.64	0.59
α_{e2}	0.98	0.92	0.87	0.84	0.78
α_{t2}	0.95	0.88	0.83	0.78	0.68
α_{e3}	1.52	1.43	1.38	1.35	1.20
α_{t3}	1.49	1.39	1.37	1.38	1.19
$T, \text{ K}$	323.15				
Water	0.46	0.46	0.46	0.46	0.45
Acetone	1.68	1.44	1.26	1.06	1.13
α^*	0.84	0.82	0.70	0.72	0.70
α_{e1}	0.80	0.78	0.69	0.70	0.67
α_{t1}	0.76	0.73	0.67	0.70	0.68
α_{e2}	1.17	1.13	1.08	1.02	0.98
α_{t2}	1.37	1.32	1.04	1.08	1.04
α_{e3}	0.84	0.75	0.65	0.57	0.57
α_{t3}	0.70	0.62	0.64	0.59	0.56

Table 4b. Coefficients of volumetric expansion of the water-acetone mixture $\alpha, 10^3 \text{ K}^{-1}$ (α^* is the coefficient of volumetric expansion at the fixed concentration $x_1 = 0.300$; α_{e1}, α_{t1} are the experimental and theoretical values of the coefficient of volumetric expansion at $x_1 = 0.600$; α_{e2}, α_{t2} at $x_1 = 0.500$; α_{e3}, α_{t3} at $x_1 = 0.100$)

$P, \text{ bar}$	1	200	400	600	100
$T, \text{ K}$	298.15				
Water	0.26	0.27	0.30	0.32	0.35
Acetone	1.40	1.18	1.16	1.22	0.93
α^*	1.33	1.26	1.20	1.21	0.85
α_{e1}	1.55	1.46	1.41	1.40	1.10
α_{t1}	1.58	1.46	1.37	1.41	1.13
α_{e2}	1.20	1.09	1.07	1.04	0.76
α_{t2}	1.19	1.05	1.08	1.08	0.75
α_{e3}	1.41	1.35	1.24	1.48	1.02
α_{t3}	1.40	1.34	1.20	1.40	0.99
$T, \text{ K}$	308.15				
Water	0.34	0.35	0.36	0.38	0.39
Acetone	1.52	1.29	1.20	1.15	1.02
α^*	1.42	1.29	1.19	1.11	0.94
α_{e1}	1.43	1.32	1.25	1.21	1.05
α_{t1}	1.43	1.31	1.21	1.19	1.09
α_{e2}	1.30	1.17	1.10	1.05	0.85
α_{t2}	1.28	1.16	1.07	0.99	0.83
α_{e3}	1.51	1.34	1.21	1.20	1.01
α_{t3}	1.51	1.32	1.22	1.15	1.00
$T, \text{ K}$	323.15				
Water	0.46	0.46	0.46	0.46	0.45
Acetone	1.68	1.44	1.26	1.06	1.13
α^*	1.54	1.33	1.18	0.97	1.07
α_{e1}	1.26	1.14	1.03	0.94	0.97
α_{t1}	1.25	1.14	1.09	1.00	0.99
α_{e2}	1.43	1.27	1.13	1.05	0.98
α_{t2}	1.44	1.27	1.15	1.07	0.96
α_{e3}	1.64	1.31	1.17	0.84	1.00
α_{t3}	1.65	1.32	1.20	1.04	1.02

$$\frac{y_2^2 M_2(P, T)}{1 - y_1^2 - y_2^2} \tag{10}$$

For such a choice of the basic system, the properties of a binary mixture of interest to us can be determined by the formula

$$M_y(P, T, x_1, x_2) = M_0'(P, T) + x_1^2(M_1(P, T) - M_0'(P, T)) + x_2^2(M_2(P, T) - M_0'(P, T)). \tag{11}$$

Results of Calculations and Their Discussion

With the purpose to verify formulas (9) and (11) deduced within the methods of statistical physics, we calculated such characteristics of a binary mixture as the coefficient of compressibility $k = \frac{V_{p_0} - V_p}{V_{p_0}}$, where V_{p_0}, V_p are the specific volumes of the mixture,

respectively, at atmospheric pressure and a pressure of p_0 , coefficient of isothermal compressibility $\beta_T = -\frac{1}{V_m}(\frac{\partial V_m}{\partial p})_{T,x}$, molar volume V_m , and coefficient of volumetric expansion $\alpha = \frac{1}{V}(\frac{\partial V_m}{\partial T})_{p,x}$ for the water-acetone mixture. The choice of an object for the study is related to the publication of the results of experimental studies of the $P - V_m - T - x$ properties of the water-acetone mixture in the intervals of temperature 298–323 K and pressure 1–1000 bar in works [3–5].

By using formula (9), we first took water as a basic system. Then the calculations were repeated in the case where acetone was taken as a basic system. The analogous properties of the water-acetone mixture were calculated by formula (11). In this case, the properties of the basic system were determined by formula (10).

Table 5. Densities of the acetonitrile-benzene mixture ρ , kg/m³ (ρ^* is the density at the fixed concentration $x_1 = 0.22439$; ρ_{e1} , ρ_{t1} are the experimental and theoretical values of density at $x_1 = 0.30296$; ρ_{e2} , ρ_{t2} at $x_1 = 0.48345$; ρ_{e3} , ρ_{t3} at $x_1 = 0.81607$)

T, K		298.15			
P, MPa	1.347	10.73	20.65	35.78	
Acetonitrile	779.0	786.3	793.7	804.3	
Benzene	874.8	882.2	889.9	899.8	
ρ^*	862.1	869.5	876.7	875.2	
ρ_{e1}	856.6	863.7	871.0	881.2	
ρ_{t1}	856.4	863.9	870.9	880.6	
ρ_{e2}	841.4	848.8	855.8	865.4	
ρ_{t2}	841.1	848.5	855.3	865.2	
ρ_{e3}	804.7	812.2	819.2	829.3	
ρ_{t3}	804.2	811.5	818.6	828.8	
T, K		318.15			
P, MPa	1.603	10.08	20.04	30.82	
Acetonitrile	757.4	764.9	773.5	781.9	
Benzene	853.8	861.4	869.7	877.8	
ρ^*	841.3	848.8	856.9	865.1	
ρ_{e1}	835.4	842.9	850.8	859.4	
ρ_{t1}	835.7	843.2	851.3	859.4	
ρ_{e2}	820.3	827.8	835.9	844.0	
ρ_{t2}	820.4	827.8	835.9	844.1	
ρ_{e3}	783.2	791.3	799.5	807.9	
ρ_{t3}	783.1	790.5	798.8	807.2	
T, K		328.15			
P, MPa	1.139	10.14	25.92	38.23	
Acetonitrile	746.3	755.1	768.7	778.4	
Benzene	843.1	851.4	864.7	873.9	
ρ^*	830.1	838.6	851.7	861.0	
ρ_{e1}	825.1	833.5	846.6	855.9	
ρ_{t1}	824.4	832.9	846.0	855.3	
ρ_{e2}	809.8	818.0	831.4	840.7	
ρ_{t2}	808.9	817.5	830.6	840.0	
ρ_{e3}	772.6	781.2	794.7	804.0	
ρ_{t3}	771.7	780.4	793.8	803.3	

The results of theoretical calculations of the dependence of the molar volume, coefficient of isothermal compressibility, coefficient of compressibility, coefficient of volumetric expansion of the water-acetone mixture by formula (9) under various thermodynamic conditions as functions of the concentration are given in Tables 1–4. For the sake of comparison, Tables 1–4 give also the experimental values of these parameters taken from works [3–5]. The calculations were carried out for different basic systems. As the last ones, we took water, acetone, and a basic system, whose properties were determined by formula (10). We showed that, to within the fourth decimal place, the results of calculations of various thermodynamic characteristics of mixtures as functions of the concentration by formula (9) are practically independent of the choice

of a basic system. In Tables 1a–4a, we give the thermodynamic parameters of the mixture at small concentrations of acetone. In this case, as a mixture with fixed concentration, we also took a mixture with small concentration of acetone. The relative error of the theoretical results of these tables is in the limits 0.01–0.6%. However, the error increases with the concentration of acetone and reaches 2.5–8%. In this case, as a mixture with fixed concentration and known properties, a mixture with the high concentration of acetone should be taken. In Tables 1b–4b, we give the results of calculations of the properties of mixtures at high values of the concentration of acetone, where a mixture with the high concentration of acetone is taken as a mixture with fixed concentration. In this case, the relative error is significantly decreased and is in the limits of 0.01–3%.

For the further verification of relation (9), we calculated the densities of the acetonitrile–benzene mixture at various concentrations. The results of these calculations and experimental values of the density of the acetonitrile–benzene mixture determined in [6] are given in Table 5. It follows from the analysis of the data given in Table 5 that relation (9) allows one to predict the dependence of the density of such a complicated mixture as acetonitrile–benzene which is a mixture of polar and nonpolar molecules on the concentration to within 0.01–0.2%.

Relation (9) can be easily generalized to the case of three-component mixtures, which allows one to calculate various characteristics of a three-component mixture if the properties of the pure components and binary mixtures composed from the components of this mixture at three fixed concentrations are known.

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РІВНЯННЯ КОНЦЕНТРАЦІЙНОЇ ЗАЛЕЖНОСТІ
ТЕПЛОФІЗИЧНИХ ВЛАСТИВОСТЕЙ СУМІШЕЙ*I. A. Фахретдінов, Е. Р. Жданов*

Резюме

За допомогою теорії збурень в ізотермічно-адіабатичному ансамблі отримано вираз, який дозволяє передбача-

ти властивості сумішей, знаючи властивості їхніх чистих компонентів. За одержаною формулою було розраховано такі характеристики сумішей, як молярний об'єм, коефіцієнт ізотермічної стисливості, коефіцієнт об'ємного розширення, стисливість суміші вода—ацетон і густину суміші ацетонітрил—бензол для різних термодинамічних умов. Результати розрахунків добре узгоджуються з експериментальними даними для вказаних сумішей.