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Vapour-liquid phase equilibria and thermodynamic properties of solutions of the ethylbenzene and n-alkylbenzenes binary systems

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Abstract

The methods of theoretical description of the patterns of changes in thermodynamic properties depending on the composition and structure of solution components are a priority direction in the development of the theory of solutions. This article is devoted to the establishment of relationships between the thermodynamic properties, composition of solutions, and the structure of their components. The study of the thermodynamic properties of binary solutions formed by a common solvent (ethylbenzene) and substances of the homologous series of n-alkylbenzenes contributes to the establishment of the aforementioned relationships. In the production of ethylbenzene and its homologues, solutions based on n-alkylbenzenes are quite common. Alkylbenzenes are widely used in various fields of science and chemical technology as solvents, extractants, and plasticisers.

Using the ebulliometric method, we measured the boiling points of solutions of four binary systems formed by ethylbenzene and n-alkylbenzenes under various pressure values. Compositions of equilibrium vapour phases of the binary systems were calculated using the obtained isotherms of saturated vapour pressure of the solutions. Using the Runge-Kutta method, the composition of the vapour phases of the solutions of the systems was calculated by the numerical integration of the Duhem–Margules equation on a computer. The obtained data on the vapour-liquid equilibrium became the basis for calculating the thermodynamic functions of the systems' solutions. The Gibbs and Helmholtz energy values, the enthalpies of vaporisation and mixing, the internal energy, and entropy of solutions were calculated. The thermodynamic properties of the solutions were calculated using a comparison of the values based on two standards: an ideal solution and an ideal gas.

It was found that the values of the Helmholtz energy linearly depend on the molar mass of the substance (the number of $-\text{CH}_2-$ groups in a molecule) in the homologous series of n-alkylbenzenes. An increase in the Helmholtz energy values for n-alkylbenzenes in the homologous series is associated with a linear increase in the molar volume of liquid substances and an exponential decrease in the saturated vapour pressure of substances. For binary solutions of constant molar concentrations formed by ethylbenzene and n-alkylbenzenes, the Helmholtz energy linearly depends on the molar mass (number of $-\text{CH}_2-$ groups in the molecule) of n-alkylbenzene in the homologous series. We obtained an equation that makes it possible to predict the thermodynamic properties of solutions of binary systems with high accuracy. The equation accelerates the process of studying vapour-liquid phase equilibria and thermodynamic properties of solutions of binary systems by 300 times. The determined patterns confirm the hypothesis of the additive contribution of functional groups to the thermodynamic properties of solutions. This hypothesis underlies the statistical theory of group models of solutions. The thermodynamic patterns determined by this study can also be used to solve a wide range of technological issues in the chemical industry.

Keywords: Solutions of binary systems, Vapour-liquid phase equilibria, Gibbs and Helmholtz energies, Enthalpies of vaporisation and mixing, Internal energy and entropy of solutions

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1. Introduction

To determine the relation between thermodynamic properties, molar characteristics, and the concentration of the components of solutions, the data on the properties of binary systems formed by substances of homologous series are the most valuable [1]. The existing methods for calculating the properties of multicomponent systems are also based on the properties of their binary components [2]. In the production of ethylbenzene and its homologues, solutions formed by *n*-alkylbenzenes are quite common [3,4]. The literature data on the properties of these solutions are fragmentary, since they have been mainly studied for technological purposes. At various temperatures, we studied vapour-liquid phase equilibria and bulk properties of solutions of the binary systems formed by ethylbenzene (common solvent) and: benzene, toluene, *n*-propylbenzene, *n*-butylbenzene (the second components of the solutions). The article attempts to establish the relationship between the Helmholtz energy values and the composition and molar mass of the components of solutions of the ethylbenzene and *n*-alkylbenzenes systems. Such relationships were previously established for solutions of 160 binary systems formed by substances of organic compounds of various classes.

2. Experimental

Benzene and ethylbenzene of kh. ch. (chemically pure) grade, toluene of os. ch. (special purity) grade, and *n*-propylbenzene and *n*-butylbenzene from Merk of “for synthesis” grade were purified as recommended in [5] and distilled without the access of air on a laboratory rectification column. Residual moisture was determined by potentiometric titration using

the Fischer reagent [6]. The content of water in the reagents did not exceed 0.01%. The physical constants of the purified substances, provided in Table 1, satisfactorily coincided with the literature data [7, 8, 9]. The saturated vapour pressure (*P*) was measured at the boiling point of liquid (*T*) using the Swietoslowski ebulliometers. The constant pressure in the system was maintained by an isodromic regulator with a precision of up to $\pm 6.6 \text{ N/m}^2$. The saturated vapour pressure of the solutions was measured with a mercury manometer using a V-630 cathetometer (GOST 15150-69) with a precision of $\pm 6.6 \text{ N/m}^2$; and atmospheric pressure was measured with a first-class mercury barometer with the same precision. The density of solutions was measured with the Ostwald pycnometers with a precision of $\pm 0.1 \text{ kg/m}^3$ [10].

3. Results and discussion

The isotherms of saturated vapour pressure $P = f(x)$ of the solutions constructed on the basis of experimental data $P = f(T)$ served as the basis for calculating the compositions of equilibrium vapour phases of the systems. Earlier it was established that at low pressure values the vapour phase of solutions of the systems is regulated by the ideal gas laws with the accuracy presented in our experiment [11]. The compositions of the equilibrium vapour phases of solutions of the systems were calculated by numerical computer integration of the Duhem–Margules equation, which at $T = \text{const}$ and under the condition of the ideal vapour phase takes the form [11]:

$$dy = y(1-y)dP / (y-x)P, \quad (1)$$

where *x*, *y* are the mole fractions of the high-boiling component in liquid and vapour forms; *P*

Table 1. Properties of purified substances

| Substance | Experimental value | | | Literature value | | |
|-------------------------|--------------------|--------------|------------|------------------|--------------|------------------|
| | ρ_4^{20} | <i>T</i> , K | n_D^{20} | ρ_4^{20} | <i>T</i> , K | n_D^{20} |
| benzene | 0.8789 | 353.3 | 1.5008 | 0.8790 | 353.25 | 1.5011 |
| ethylbenzene | 0.8671 | 383.8 | 1.4965 | 0.8669 | 383.77 | 1.4969 1.4961 |
| этилбензол | 0.8672 | 409.4 | 1.4959 | 0.8671 | 409.3 | 1.4959 |
| <i>n</i> -propylbenzene | 0.8620 | 432.3 | 1.4916 | 0.8619 | 432.4 | 1.4920 |
| <i>n</i> -butylbenzene | 0.8613 | 456.4 | 1.4898 | 0.8609 | 456.4 | 1.4898 |

Designations: ρ_4^{20} - density, g/cm³, *T* – boiling point K under normal pressure, n_D – refractive index at *T* = 293 K.

is the saturated vapour pressure of a binary solution. Analysing the compositions of equilibrium vapour phases of solutions, we can see that solutions of the ethylbenzene and n-alkylbenzenes systems have negative deviations from the ideal state. The toluene concentration in the vapour phase of the systems increases with an increase in the molar mass of the second component of solution (Table 2). When rectifying solutions of the systems, the concentration of ethylbenzene in the vapour phase of the systems

is higher than the concentration of propyl- and butylbenzene, and less than the concentration of benzene and toluene molecules. An increase in temperature (pressure) increases the concentration of ethylbenzene in the vapour phase of solutions of the ethylbenzene-benzene and ethylbenzene – toluene systems. On the contrary, for ethylbenzene – propylbenzene and ethylbenzene – butylbenzene solutions, an increase in temperature decreases the concentration of ethylbenzene in the vapour phase, since

Table 2. Vapour-liquid phase equilibria and the thermodynamic properties of solutions of the ethylbenzene and n-alkylbenzene systems at $T = 353\text{ K}$

| Parameter | ethylbenzene – benzene | | | | | | | | | | |
|-----------|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | x | 1.0000 | 0.9000 | 0.8000 | 0.7000 | 0.6000 | 0.5000 | 0.4000 | 0.3000 | 0.2000 | 0.1000 |
| y | 1 | 0.6102 | 0.4064 | 0.2833 | 0.2011 | 0.1424 | 0.0986 | 0.0648 | 0.0381 | 0.0168 | 0 |
| P | 16.75 | 24.52 | 32.65 | 40.88 | 49.20 | 57.62 | 66.14 | 74.75 | 83.46 | 92.27 | 101.00 |
| V | 130.5 | 127.0 | 123.5 | 120.0 | 116.5 | 113.0 | 109.5 | 106.0 | 102.5 | 99.0 | 96.0 |
| G^e | 0.00 | -36.50 | -47.70 | -55.40 | -60.20 | -62.00 | -60.70 | -55.50 | -45.30 | -28.10 | 0.00 |
| H^e | 0.000 | -2.097 | -2.912 | -3.135 | -3.038 | -2.746 | -2.329 | -1.825 | -1.259 | -0.647 | 0.000 |
| S^e | 0.00 | -5.84 | -8.11 | -8.72 | -8.43 | -7.60 | -6.42 | -5.01 | -3.44 | -1.75 | 0.00 |
| H | 39.53 | 36.11 | 34.47 | 33.41 | 32.68 | 32.14 | 31.72 | 31.40 | 31.13 | 30.91 | 30.72 |
| U^r | 36.60 | 35.25 | 34.40 | 33.56 | 32.73 | 31.89 | 31.06 | 30.24 | 29.41 | 28.59 | 27.80 |
| A^r | 18.21 | 17.80 | 17.37 | 16.93 | 16.50 | 16.06 | 15.62 | 15.19 | 14.75 | 14.30 | 13.85 |
| S^r | 50.69 | 49.43 | 48.26 | 47.11 | 45.98 | 44.85 | 43.74 | 42.64 | 41.55 | 40.48 | 39.51 |
| | ethylbenzene – toluene | | | | | | | | | | |
| y | 1 | 0.7942 | 0.6305 | 0.4976 | 0.3878 | 0.2957 | 0.2175 | 0.1506 | 0.0929 | 0.0429 | 0 |
| P | 16.66 | 18.83 | 21.07 | 23.32 | 25.60 | 27.90 | 30.24 | 32.58 | 34.96 | 37.36 | 39.69 |
| V | 130.5 | 128.8 | 127.1 | 125.5 | 123.8 | 122.1 | 120.4 | 118.8 | 117.1 | 115.4 | 113.7 |
| G^e | 0.00 | -15.00 | -20.40 | -24.40 | -27.00 | -27.90 | -27.00 | -23.90 | -18.20 | -9.00 | 0.00 |
| H^e | 0.000 | -0.211 | -0.581 | -0.994 | -1.365 | -1.620 | -1.699 | -1.557 | -1.176 | -0.587 | 0.000 |
| S^e | 0.00 | -0.56 | -1.59 | -2.75 | -3.79 | -4.51 | -4.74 | -4.34 | -3.28 | -1.64 | 0.00 |
| H | 39.53 | 38.95 | 38.22 | 37.44 | 36.71 | 36.08 | 35.64 | 35.42 | 35.43 | 35.66 | 35.88 |
| U^r | 36.60 | 36.02 | 35.29 | 34.51 | 33.77 | 33.15 | 32.71 | 32.48 | 32.50 | 32.72 | 32.95 |
| A^r | 18.21 | 18.03 | 17.82 | 17.60 | 17.39 | 17.18 | 16.96 | 16.75 | 16.53 | 16.30 | 16.09 |
| S^r | 52.01 | 50.95 | 49.47 | 47.87 | 46.38 | 45.23 | 44.59 | 44.57 | 45.23 | 46.50 | 47.74 |
| | ethylbenzene – n-propylbenzene | | | | | | | | | | |
| y | 1.0000 | 0.9540 | 0.9003 | 0.8385 | 0.7673 | 0.6851 | 0.5898 | 0.4783 | 0.3468 | 0.1897 | 0.0000 |
| P | 16.66 | 15.67 | 14.72 | 13.77 | 12.85 | 11.93 | 11.04 | 10.16 | 9.293 | 8.426 | 7.621 |
| V | 130.5 | 132.3 | 134.1 | 135.8 | 137.6 | 139.4 | 141.1 | 142.9 | 144.6 | 146.4 | 148.2 |
| G^e | 0.00 | -35.30 | -50.60 | -59.30 | -62.80 | -62.20 | -57.80 | -50.30 | -39.70 | -26.40 | 0.00 |
| H^e | 0.000 | -0.703 | -0.834 | -0.887 | -0.960 | -1.033 | -1.054 | -0.972 | -0.758 | -0.411 | 0.000 |
| S^e | 0.00 | -1.89 | -2.22 | -2.34 | -2.54 | -2.75 | -2.82 | -2.61 | -2.04 | -1.09 | 0.00 |
| H | 39.53 | 39.85 | 40.22 | 40.69 | 41.04 | 41.10 | 41.18 | 41.19 | 41.28 | 42.06 | 44.02 |
| U^r | 36.60 | 36.92 | 37.29 | 37.76 | 38.11 | 38.17 | 38.25 | 38.26 | 38.34 | 39.13 | 41.08 |
| A^r | 18.21 | 18.44 | 18.64 | 18.84 | 19.04 | 19.23 | 19.42 | 19.61 | 19.79 | 19.98 | 20.15 |
| S^r | 52.04 | 52.32 | 52.79 | 53.56 | 54.17 | 54.11 | 53.34 | 52.38 | 52.26 | 54.22 | 59.26 |

End of Table 2

| | ethylbenzene – n-butylbenzene | | | | | | | | | | |
|----------------------|-------------------------------|--------|--------|--------|---------|--------|--------|--------|--------|--------|--------|
| <i>y</i> | 1.0000 | 0.9830 | 0.9618 | 0.9355 | 0.9022 | 0.8591 | 0.8015 | 0.7207 | 0.5996 | 0.3984 | 0.0000 |
| <i>P</i> | 16.66 | 15.24 | 13.76 | 12.32 | 10.91 | 9.53 | 8.19 | 6.87 | 5.59 | 4.33 | 3.18 |
| <i>V</i> | 130.5 | 134.0 | 137.5 | 140.9 | 144.4 | 147.9 | 151.4 | 154.9 | 158.4 | 161.8 | 165.3 |
| <i>G^e</i> | 0.00 | -57.10 | -83.90 | -97.00 | -100.60 | -96.70 | -86.70 | -71.50 | -51.60 | -27.60 | 0.00 |
| <i>H^e</i> | 0.000 | -0.810 | -1.259 | -1.510 | -1.609 | -1.584 | -1.451 | -1.225 | -0.917 | -0.533 | 0.000 |
| <i>S^e</i> | 0.00 | -2.13 | -3.33 | -4.00 | -4.27 | -4.21 | -3.87 | -3.27 | -2.45 | -1.43 | 0.00 |
| <i>H</i> | 39.53 | 39.05 | 39.41 | 39.97 | 40.69 | 41.53 | 42.48 | 43.52 | 44.64 | 45.84 | 47.18 |
| <i>U^r</i> | 36.60 | 36.95 | 37.23 | 37.59 | 38.07 | 38.73 | 39.61 | 40.77 | 42.28 | 44.22 | 46.68 |
| <i>A^r</i> | 18.21 | 18.69 | 19.13 | 19.57 | 19.99 | 20.41 | 20.83 | 21.24 | 21.65 | 22.06 | 22.40 |
| <i>S^r</i> | 52.05 | 51.71 | 51.23 | 51.03 | 51.19 | 51.87 | 53.19 | 55.30 | 58.42 | 62.74 | 68.74 |

Designations: *x* and *y* – mole fractions of ethylbenzene in liquid and vapour phases of the systems, respectively (*x* – refers to solutions of all systems); *P* – saturated vapour pressure of solutions (kPa); *V* – molar volume of solutions (cm³/mol); *G^e* – excess Gibbs energy J·mol⁻¹·K⁻¹; *H^e* – excess enthalpy of solutions (kJ·mol⁻¹); *S^e* – excess entropy of solutions (J·mol⁻¹·K⁻¹); *H* – enthalpy of vaporisation of solutions (kJ·mol⁻¹); *U^r* – internal energy (kJ·mol⁻¹); *A^r* – Helmholtz energy of solutions (kJ·mol⁻¹); *S^r* – entropy of solutions (J·mol⁻¹·K⁻¹)

ethylbenzene has a lower enthalpy of vaporisation. The noted deviations in the vapour phase equilibrium of the systems are consistent with Konovalov's and Vrevesky's laws [12]. Based on the obtained *P*-*X*-*Y*-*T* data, using the known thermodynamic relations, we calculated the values of the activity coefficients (γ_i) and the excess chemical potentials of the mixture components (μ_i^e), as well as the values of the excess Gibbs energy (*G^e*) for solutions of the systems [1, 12]:

$$\gamma_i = Py_i / P_i^0 x_i, \quad (2)$$

$$\mu_i^e = RT \ln \gamma_i, \quad (3)$$

$$G^e = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2), \quad (4)$$

where x_i , y_i are the concentration of the *i*-component in the liquid and vapour phase of the solution; *P*, *P_i⁰* are, respectively, the saturated vapour pressure of the solution and pure *i*-component; *R* is the universal gas constant; *T*, K. The results of calculations show that for the components of solutions $\gamma_i < 1$, $\mu_i^e < 0$ for the entire concentration range. An increase in the molecular mass of the second component of solutions is associated with an alternation of negative deviations in the systems' properties. The absolute values of the excess Gibbs energy ($G^e < 0$) decrease for the series of ethylbenzene-benzene, ethylbenzene-toluene solutions and again increase for the ethylbenzene and

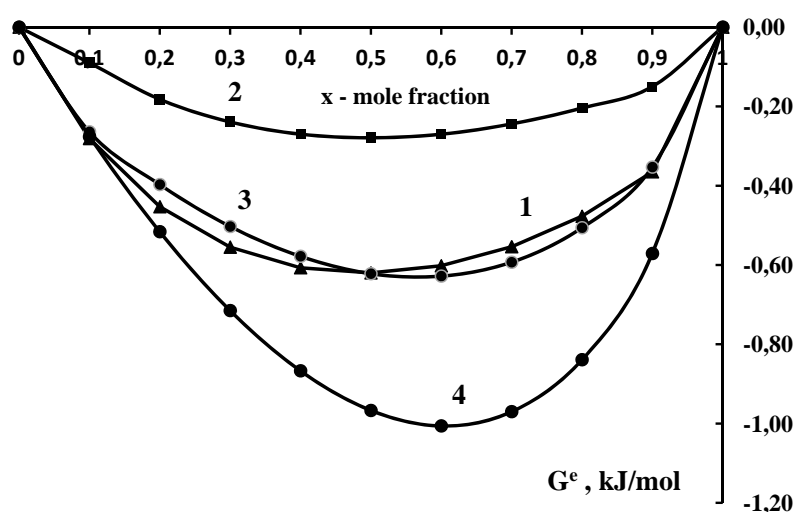


Fig. 1. Dependence of the excess Gibbs energy (*G^e*) on the composition of solutions of the systems at *T* = 353 K: 1 – ethylbenzene – benzene; 2 – ethylbenzene – ethylbenzene; 3 – ethylbenzene – n-propylbenzene; 4 – ethylbenzene – n-butylbenzene; *x* – ethylbenzene concentration

n-propylbenzene, ethylbenzene, and n-butylbenzene solutions (Fig. 1). The enthalpies of mixing (excess enthalpies) of solutions (H^e) were calculated by equation (5), using experimental and literature data [7, 9, 13]:

$$H^e = -RT^2 \left[x_1 \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{x_2} + (1-x_1) \left(\frac{\partial \ln \gamma_2}{\partial T} \right)_{x_1} \right], \quad (5)$$

where γ_1, γ_2 are the activity coefficients of ethylbenzene and n-alkylbenzene, x_1 is the mole fraction of ethylbenzene in the mixture, R is the gas constant. The enthalpy of vaporisation of solutions of the systems (H_x) was calculated using equation (6):

$$H_x = H_1^0 x_1 + H_2^0 (1-x_1) + H^e, \quad (6)$$

where H_1^0, H_2^0 are the enthalpies of vaporisation of the pure components H^e is the excess enthalpy of the solution, x_1 is the mole fraction of ethylbenzene in the mixture [13, 14]. When the components are mixed, in solutions of the systems, we can observe exothermic heat effects ($H^e < 0$). This value also alternates with an increase in the molar mass of the second component (Fig. 2). The values of the excess entropy of solutions of the systems (S^e) were calculated using the Gibbs equation. By analysing the obtained data, we determined that the concentration relation of the excess entropy $S^e = f(x)$ of solutions symbatically imitates the isotherm $H^e = f(x)$ (Table 2). This can be explained by the affinity of the mechanisms for structuring solutions of the systems characterised by correlation distribution functions [15, 16]. In the Gibbs equation, the predominance of the en-

thalpy component over its entropy component causes negative deviations in the properties ($G^e < 0$) of solutions of the systems (Table 2). We did not manage to formulate an equation representing the relation between the values of the Gibbs energy, enthalpy, and entropy of solutions (calculated using the standard of an ideal solution) and the molar mass and composition of the components of solutions. Calculating the properties of solutions based on the properties of ideal solutions makes it difficult to assess the intermolecular interaction (IMI) in solutions. It should be noted that in pure liquids IMI sometimes has a more complex nature than in solutions [15, 16]. The choice of the standard state proposed by Lewis makes the assessment of IMI in solutions insensitive. For example, for an individual liquid in equilibrium with vapour, the Gibbs energy change is: $\Delta G = G_{\text{vapour}} - G_{\text{liq}} = 0$. Back in 1935, Rakovskii wrote that "the path of the Lewis' school is practically useful, but it began to dominate researchers, obscuring the theoretical side of thermodynamics from them" [17]. A number of researchers (Bell and Gatty, Hirschfelder, Curtiss and Bird, Nikolskii, Rowlinson) noted the insufficiency of the formal description of the thermodynamic properties of solutions, for example, [18, 19, 20]. The studies of these and some other scientists contain interesting attempts to assess the contribution of the intermolecular interactions to changes in the thermodynamic functions of solutions. The possibility of developing a general approach to assessing the contribution of the IMI

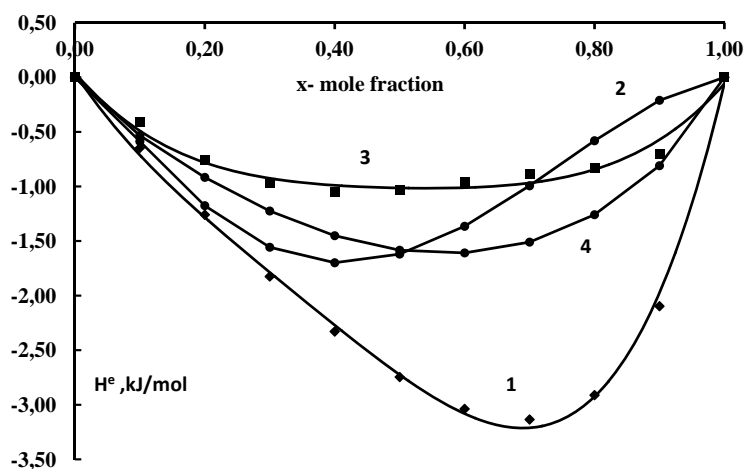


Fig. 2. Dependence of the excess enthalpy (H^e) on the composition of solutions of the systems at $T = 353$ K: 1 – ethylbenzene – benzene; 2 – ethylbenzene – ethylbenzene; 3 – ethylbenzene – n-propylbenzene; 4 – ethylbenzene – n-butylbenzene; x – ethylbenzene concentration

to thermodynamic functions based on these ideas was considered by Rudakov and the author of this study in works [13, 21–24]. It is known that the laws of thermodynamics do not contain the concepts of interaction. These concepts come from other areas. Using statistical methods, equations of state, mechanical analogies, we can get an idea of the interaction between molecules and assess its influence at thermodynamic parameters. Usually, the energy of intermolecular interaction is defined as the work of molecular separation over an infinite distance. However, the issue may be solved another way. Molecules may be isolated from interacting with each other by introducing an external energy field while maintaining the distance between them. If the energies of the “isolated” and “separated” molecules are equal, then the same work is required to block the intermolecular interaction in both cases. In a thermodynamic system, the calculation results also depend on the manner the process is carried out: whether intermolecular interaction is blocked by expanding the system to a volume of $V \rightarrow \infty$, or at $V = \text{const}$. The number of ways to carry out the process increases indefinitely if we take into account the intermediate cases (between $V \rightarrow \infty$ and $V = \text{const}$), as well as the cases of different heat exchange with the environment. It is not enough to say that a standard system without intermolecular interaction is an ideal gas; it is necessary to determine its state accurately. First of all, it is necessary to exclude work done against any forces, except for intermolecular interaction, which leads to the condition $V = \text{const}$. Then we have two options: 1) adiabatic option, $S = \text{const}$; 2) isothermal option ($T = \text{const}$) – when the system’s entropy changes due to intermolecular interaction, not temperature. These considerations explain the need to carry out the process under the condition $V, T = \text{const}$. We assumed two provisions: the first defines the standard state of the system; the second defines the contributions of intermolecular interaction to the change in the thermodynamic functions of a liquid system.

1. The standard state of a system without intermolecular interaction at any degree of compression is an ideal gas at temperature (T), volume (V), and with the composition of a real liquid.

2. The contributions of intermolecular interactions to the change in the thermodynamic

function are determined as the difference between the values of this function for standard and real liquid systems:

$$F^r = F^* - F, \quad (7)$$

where F^r is the contribution of intermolecular interaction to the change in the thermodynamic function, F – in the real state; F^* – in the state of an ideal gas, is considered to be the standard state for the system. By deduction of $F^* - F$, we obtain positive values of F^r . It should be noted that when intermolecular interaction in a liquid is blocked, the sign of F^r changes.

Let’s consider a binary liquid solution at temperature (T), in equilibrium with a saturated vapour at pressure (P). The molar Helmholtz energy of a binary solution (A) is defined as follows:

$$A = x_1\mu_1 + x_2\mu_2 - PV, \quad (8)$$

where x_1 and x_2 are mole fractions; μ_1 and μ_2 are the chemical potentials of the solution components P , V are the saturated vapour pressure and the molar volume of the solution. For the chemical potential of the solution component, we have:

$$\mu_i = \mu_i^0 + RT \ln \bar{p}_i, \quad (9)$$

where μ_i^0 is a function that depends only on the temperature; \bar{p}_i is the partial pressure of the i -component in the solution. Since we do not know the absolute values of the Helmholtz energy, we take as the standard state of the system a mixture of ideal gases of the same concentration as a liquid binary solution, at the same temperature (T), and with the same molar volume (V). The pressure in this standard state is defined as $P^* = RT/V$, when the molar Helmholtz energy is defined as (A^*):

$$A^* = x_1\mu_1^* + x_2\mu_2^* - RT, \quad (10)$$

where μ_1^* ; μ_2^* are the chemical potentials of 1 and 2 components in the standard state of the mixture; R is the universal gas constant. For the chemical potential of a component in the standard state of an ideal gas, we have:

$$\mu_i^* = \mu_i^0 + RT \ln(x_i P^*). \quad (11)$$

As $P^* = RT/V$, equation (11) rearranges to the following:

$$\mu_i^* = \mu_i^0 + RT \ln \frac{x_i RT}{V}. \quad (12)$$

We define the contribution of the intermolecular interaction to the change in the mole Helmholtz energy (A^r) as a difference of its values in the standard and real states of the system:

$$A^r = A^* - A = x_1(\mu_1^* - \mu_1) + x_2(\mu_2^* - \mu_2) - RT + PV. \quad (13)$$

Substituting expressions for chemical potentials (9, 12) into equation (13) and dividing by RT (which makes the equation dimensionless), we obtain:

$$\frac{A^r}{RT} = x_1 \ln \frac{x_1 RT}{p_1 V} + x_2 \ln \frac{x_2 RT}{p_2 V} - 1 + \frac{PV}{RT}, \quad (14)$$

where p_1, p_2 are the partial pressure values of 1 and 2 components of the solution. In the extreme cases for pure $x_1 = 1$ ($x_2 = 0$) and $x_2 = 1$ ($x_1 = 0$) components, we have:

$$\begin{aligned} \frac{A_1^r}{RT} &= \ln \frac{RT}{P_1 V_1} - 1 + \frac{P_1 V_1}{RT}, \\ \frac{A_2^r}{RT} &= \ln \frac{RT}{P_2 V_2} - 1 + \frac{P_2 V_2}{RT}, \end{aligned} \quad (15)$$

where P_1, P_2, V_1, V_2 are the pressure and molar volume of 1 and 2 pure components at T , respectively.

We define the excess dimensionless molar Helmholtz energy as:

$$\frac{A^e}{RT} \equiv \frac{A^r}{RT} - x_1 \frac{A_1^r}{RT} - x_2 \frac{A_2^r}{RT}. \quad (16)$$

We take into account that activity coefficient of a component of solution is defined as γ_i . When combined with equations (14, 15), equation (16) rearranges as follows:

$$\begin{aligned} \frac{A^e}{RT} &= x_1 \ln \frac{1}{\gamma_1} + x_2 \ln \frac{1}{\gamma_2} + x_1 \ln \frac{V_1}{V} + \\ &+ x_2 \ln \frac{V_2}{V} + \frac{PV - x_1 P_1 V_1 - x_2 P_2 V_2}{RT}. \end{aligned} \quad (17)$$

Let's provide two relations of the excess Gibbs energy (G^e) and molar volume (V^e) for a binary solution:

$$G^e = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2), \quad (18)$$

$$V^e = V - x_1 V_1 + x_2 V_2. \quad (19)$$

Taking into account relations (18, 19), equation (17) rearranges to the following:

$$\begin{aligned} \frac{A^e}{RT} &= \frac{G^e}{RT} - \ln(V^e + x_1 V_1 + x_2 V_2) + x_1 \ln V_1 + \\ &+ x_2 \ln V_2 + \frac{PV^e + x_1 V_1(P - P_1) + x_2 V_2(P - P_2)}{RT}. \end{aligned} \quad (20)$$

Equation (20) establishes the relation between the values of the excess Gibbs energy (G^e – calculated using the standard of an ideal solution) and the Helmholtz energy (A^e – calculated using the standard state of an ideal gas). Using the known thermodynamic relations for internal energy (U^r) and entropy (S^r), we have [1, 12]:

$$S^r = - \left(\frac{\partial A^r}{\partial T} \right)_{v,x}, \quad (21)$$

$$U^r = -T^2 \left(\frac{\partial (A^r / T)}{\partial T} \right)_{v,x}. \quad (22)$$

After differentiation and transformations, we got the following for a binary solution:

$$S^r = \frac{H}{T} - R \left(x_1 \ln \frac{x_1 RT}{p_1 V} + x_2 \ln \frac{x_2 RT}{p_2 V} \right), \quad (23)$$

$$U^r = H - RT + PV, \quad (24)$$

where p_1, p_2 are the partial pressure values of 1 and 2 components of the solution; H, V, P are the molar enthalpy of vaporisation, molar volume, and saturated vapour pressure of the solution with x_i mole fractions in it. The values of the functions are interrelated by the Gibbs-Helmholtz equation: $A^r = U^r - TS^r$.

The correlation analysis determined that the values of A^r for n-alkylbenzenes linearly depend on the molar mass of the substance in the homologous series:

$$A^r = 151.5M + 2065, R = 0.9993, \quad (25)$$

where M is the molar mass of n-alkylbenzene. R is the correlation coefficient. Equation (25) describes the Helmholtz energy A^r of n-alkylbenzenes at $T = 353.15$ K with a precision of ± 50 J/mol. We can explain the linear dependence of the Helmholtz energy values on the molecular mass of n-alkylbenzene in the homologous series by the “similarity” of the molecular-statistical structure of liquid n-alkylbenzenes, characterised by the correlation distribution functions [16]. If such “similarity of structures” exists, then an increase in the size of molecules of n-alkyl benzenes

should lead to a decrease in the density of the liquid, which is consistent with an increase in the molar volume (V) of n -alkylbenzenes (Table 2). An increase in the Helmholtz energy values A^r [J/mol] complicates the transition of molecules from the liquid to vapour phase of systems and decreases exponentially the saturated vapour pressure of n -alkylbenzenes (P , N/m²):

$$A^r = -2468.4 \ln P + 42255, R = 0.9998. \quad (26)$$

The analysis showed that the molar volumes of n -alkylbenzenes (V , m³/mol) linearly depend on the values of A^r [J/m] of n -alkylbenzenes in the homologous series:

$$A^r = 121.8 \cdot 10^6 V + 2229, R = 0.9992. \quad (27).$$

Equations (25–27) can be used to predict the properties of substances in the homologous series of n -alkylbenzenes. Using equations (14, 23, 24), we calculated the values of A^r, U^r, S^r of solutions of the systems (Table 2). The internal energy values U^r , characterising the entire scope of energy spent to block the intermolecular interaction in solutions, raise with the increase in the molecular mass of n -alkylbenzene in the homologous series of n -alkylbenzenes. This can be explained by the increase in the role of the molecules of the second component in the intermolecular interaction in solutions of the systems (Fig. 3). The values of the solution entropy S^r , calculated using the Helmholtz equation, also raise when the molecular mass of n -alkylbenzene increases

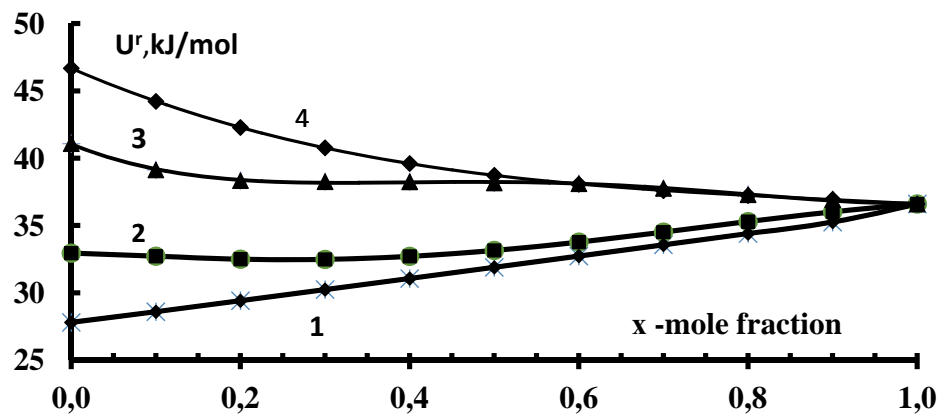


Fig. 3. Dependence of the internal energy of solutions (U^r) on the composition of the systems at $T = 353$ K: 1 – ethylbenzene - benzene; 2 – ethylbenzene - ethylbenzene; 3 – ethylbenzene - n -propylbenzene; 4 – ethylbenzene - n -butylbenzene; x – ethylbenzene concentration

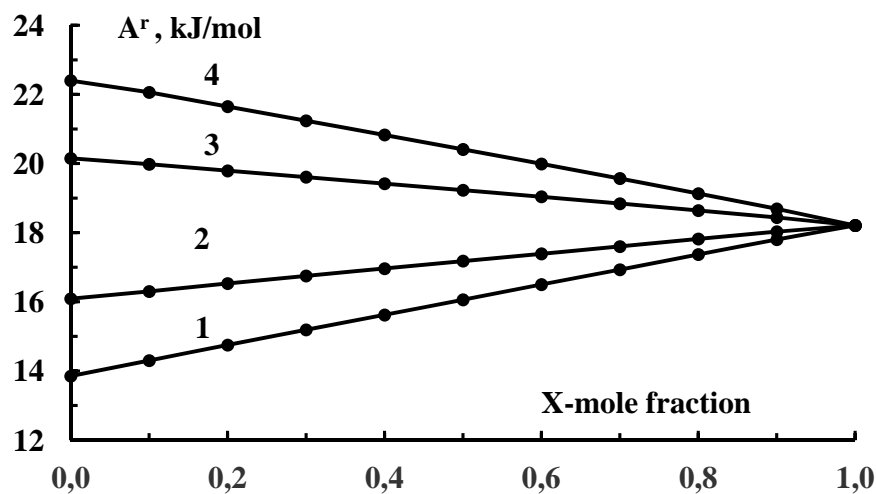


Fig. 4. Dependence of the Helmholtz energy (A^r) on the composition of the systems at $T = 353$ K: 1 – ethylbenzene - benzene; 2 – ethylbenzene - ethylbenzene; 3 – ethylbenzene - n -propylbenzene; 4 – ethylbenzene - n -butylbenzene; x – ethylbenzene concentration

(Table 2). Note that solutions of ethylbenzene and n-alkylbenzene systems demonstrate the sybatic pattern of the isotherms $U^r = f(X)$ and $S^r = f(X)$ [21–26]. It is consistent with the previously studied solutions of systems: benzene – n-alkylbenzenes, toluene – n-alkylbenzenes, n-butylbenzene – n-alkylbenzenes, ethanol – n-alkylethanoates, ethanol – n-alkylpropanoates, ethanol – n-alkylbutanoates, n-propanol – n-alkylethanoates, n-propanol, n-butanol, and substances of the homologous series of aliphatic ketones; isopropanol, isobutanol and substances of the homologous series of aliphatic ketones. The values of the Helmholtz energy (A^r) for solutions of the systems also increase with an increase in the molecular mass of n-alkylbenzene (Fig. 4). An increase in the values of the Helmholtz energy characterising the intermolecular interactions, decreases the saturated vapour pressure of solutions of the binary systems (Table 2). An analysis of the obtained data showed that for solutions with constant molar concentration ($x_1 = \text{const}$), the Helmholtz energy (A^r) linearly depends on the molecular mass (M) of n-alkylbenzene: $A^r = k_i M + b_i$ (Fig. 5). The values of the coefficients k_i and b_i of the isotherms $A^r = k_i M + b_i$ in turn, are linearly dependent on the composition of the systems. The established patterns allowed us to propose the following equation:

$$A^r = (-0.1500x + 0.1513)M + 16.06x + 2.070, \quad (28)$$

where: x is the mole fraction of ethylbenzene (common solvent) in a binary solution; M is the

molar mass of n-alkylbenzene. Equation (28) describes the Helmholtz energy (A^r , kJ/mol) of solutions of the systems at $T = 353$ K with a precision of ± 50 J/mol. The established regularity of the change in the Helmholtz energy for solutions of systems of constant molar composition (in the case of pure components, the condition is $x = 0$) can be explained by the “affinity” of the molecular-statistical structure of such solutions [16].

Above, we considered thermodynamic functions that characterise the intermolecular interaction of all molecules in a solution simultaneously. Let’s consider a function that characterises the interaction of one molecule with the rest of the molecules. At $T, P = \text{const}$, the following derivative is the partial molar Helmholtz energy:

$$\bar{A}_i^r = \left(\frac{\partial A^r}{\partial x_i} \right)_{T,P}. \quad (29)$$

Taking into account the Gibbs equation:

$$x_1 RT d \ln \bar{p}_1 + x_2 RT d \ln \bar{p}_2 - V dP = 0, \quad (30)$$

where \bar{p}_1, \bar{p}_2 are the partial pressure values of 1 and 2 components in a solution with x_1 mole fractions of 1 component. After transformations, for a binary solution with x_1 mole fractions we have:

$$\bar{A}_i^r = RT \ln \frac{x_i RT}{\bar{p}_i V} - RT \frac{\bar{V}_i}{V} + P \bar{V}_i, \quad (31)$$

where \bar{V}_i, \bar{p}_i are the partial molar volume and partial pressure, respectfully, of i -th component

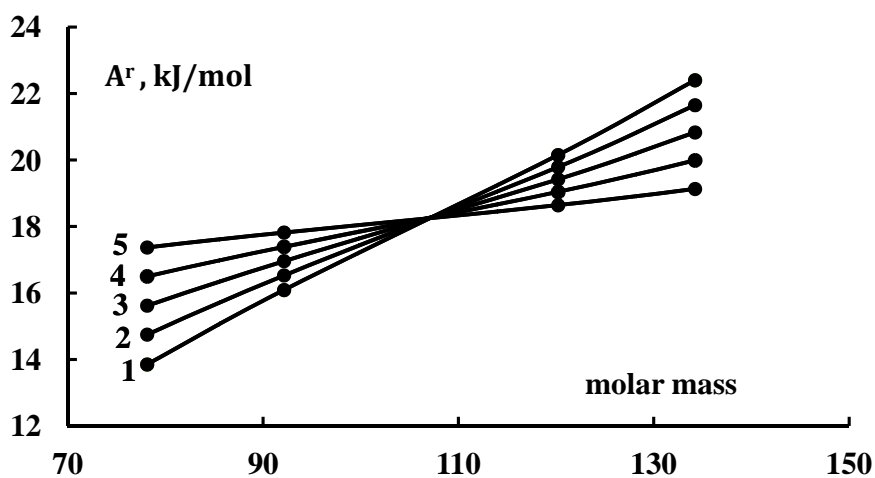


Fig. 5. Dependence of the Helmholtz energy (A^r) on the molar mass of n-alkylbenzene the in solutions with a constant molar concentration of the ethylbenzene and n-alkylbenzene systems at $T = 353$ K: 1 – $x = 0$; 2 – $x = 0.2$; 3 – $x = 0.4$; 4 – $x = 0.6$; 5 – $x = 0.8$, which are mole fractions of ethylbenzene

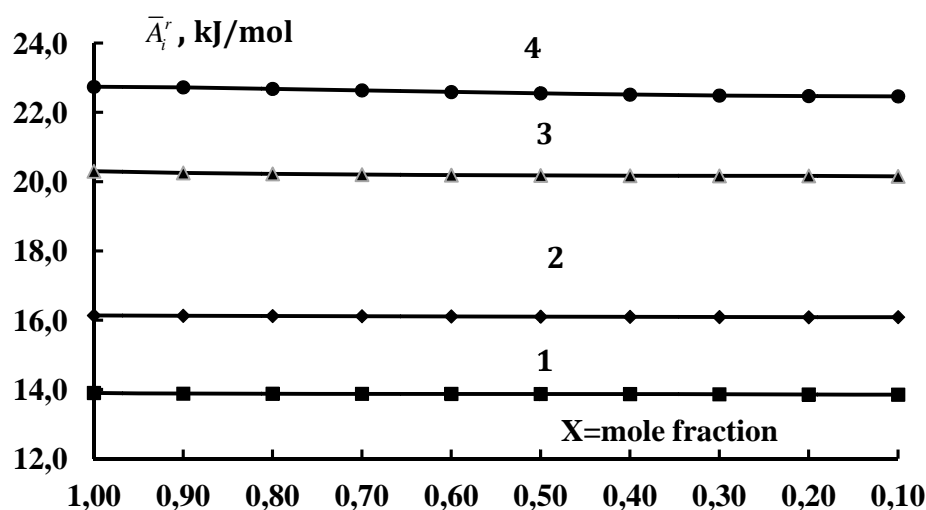


Fig. 6. Dependence of values of the partial Helmholtz energy (\bar{A}_i^r) of the second component of solution on the composition of the ethylbenzene and n-alkylbenzene systems at $T = 353$ K: 1 – ethylbenzene - benzene; 2 – ethylbenzene - toluene; 3 – ethylbenzene - n-propylbenzene; 4 – ethylbenzene - n-butylbenzene; x – ethylbenzene concentration

in a solution with x_i mole fractions; V, P are the molar volume and saturated vapour pressure of the solution. Note that at $x_i = 1$, equation (31) coincides with the equation for a pure component (15). Using equation (31), we calculated the values of partial molar Helmholtz energy \bar{A}_i^r . It appeared that the change in the \bar{A}_i^r value for the molecules of the common solvent (ethylbenzene) was insignificant, and the value of \bar{A}_i^r for n-alkylbenzene discretely increases with an increase in its molecular mass (the number of $-\text{CH}_2-$ groups) in the homologous series (Fig. 6). This regularity confirms the validity of the hypothesis underlying the statistical models of solutions, known as “group” models [1, 12]. At $P, T = \text{const}$, for the excess partial Helmholtz energy of the i -th component in a solution consisting of x_i mass fractions, we obtain:

$$\begin{aligned} \bar{A}_i^e &= A_i^r - \bar{A}_i^r = \\ &= RT \ln \gamma_i - RT \left(\ln \frac{V_i^0}{V} - \frac{\bar{V}_i}{V} + 1 \right) + P_i^0 V_i^0 - P \bar{V}_i, \end{aligned} \quad (32)$$

where γ_i, V_i^0, P_i^0 are the activity coefficient, molar volume, and saturated vapour pressure, respectively, of pure i component; V, \bar{V}_i are the molar volume of the solution and partial molar volume of the i -th component in the solution consisting of x_i mole fractions. There is significant difference between the values of \bar{A}_i^e and $RT \ln \gamma_i$ (the values of $RT \ln \gamma_i$ are often used to assess

the intermolecular interaction in solutions). This difference is associated with a change in the volumes of solutions when mixing components. It is taken into account by the last three terms of equation (32). From the data presented in Table 2, it can be seen that the role of volumetric effects increases with an increase in the molecule size of the solution components. It should be noted that equation (32) can be used to calculate the values of the activity coefficients (γ_i) of the solution components, often used in chemical technologies.

Then, using the known thermodynamic relations, we can calculate the values of chemical potentials, Gibbs energy, and other thermodynamic functions. It should be noted that equation (28) was earlier obtained for solutions of 160 binary systems, formed by various solvents and substances of various homologous series (for instance, studies [10, 13, 14, 21–26]). The form of equation (28) is the same for a wide temperature range for solutions of all studied binary systems. To derive equation (28) we need the P, X, Y, T – values and the data on the molar volume (V) of pure components (*reference data*) and only two solutions of the same molar composition. The accuracy of calculating the Helmholtz energy for solutions of binary systems according to equation (28) depends only on the accuracy of these experimental data. We believe that the established pattern is of a general nature

and can be used to predict the thermodynamic properties of solutions of binary systems formed by a common solvent and representatives of homologous series of organic substances.

4. Conclusions

1. The values of the Helmholtz energy (A') linearly depend on the molar mass of the substance (the number of $-\text{CH}_2-$ groups in a molecule) in the homologous series of n-alkylbenzenes.

2. An increase in the Helmholtz energy values (A') for substances in the homologous series of n-alkylbenzenes is associated with a linear increase in the molar volumes of liquid substances and an exponential decrease in the saturated vapour pressure of substances.

3. The Helmholtz energy (A') for binary solutions with constant molar concentration formed by ethylbenzene and substances of the homologous series of n-alkylbenzenes linearly depends on the molar mass of n-alkylbenzene (the number of $-\text{CH}_2-$ groups) in the homologous series. Equation (28) obtained on the basis of this pattern describes the Helmholtz energy for solutions of the systems with deviations of ± 50 J/mol from its values calculated from experimental data. The determined pattern confirms the validity of the hypothesis about the additive contribution of functional groups to the thermodynamic properties of solutions, which underlies the statistical models of solutions, known as “group” models.

4. The determined pattern (equation 28) makes it possible to predict the thermodynamic properties of solutions of unexamined binary systems using the properties of pure components and only two solutions with the same molar concentration. It accelerates the process of studying vapour-liquid phase equilibria and thermodynamic properties of binary systems approximately by 340 times. The accuracy of predicting the thermodynamic properties of solutions using equation (28) depends on the accuracy of the experimental data on the properties of pure components and their two solutions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal

relationships that could have influenced the work reported in this paper.

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