

New Method of Predicting the Thermodynamic Properties of Solutions

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Abstract: Thermodynamic functions solutions of a 25 binary systems formed *n*-alcohols and esters of aliphatic acids by were calculated using the standards ideal solution and ideal gas. The value change regularity of the thermodynamic functions of solutions depending on their molar mass and concentration of the solutions' components was determined by the thermodynamic analysis. The method of prediction of the thermodynamic properties of binary solutions was suggested on the basis of the determined regularities. The corresponding equations were obtained.

Key words: Vapor-liquid equilibrium, Helmholtz energy, enthalpy, entropy of solutions, equation of state.

1. Introduction

Thermodynamic properties of solutions are a basis for calculations of the technological parameters, defining a direction and speed of technological processes. In the USA, it is counted up, that the economy of energy on distillation processes conducts 10% to annual economy of 500 million dollars [1]. Calculation of thermodynamic properties of solutions in full volume is practically realizable only on the basis of experimental data about phase equilibriums of various However, research of phase types. equilibriums is connected with the big experimental difficulties. In connection with this, the authors the importance of prediction understand of thermodynamic properties of solutions, based on the minimum number of experimental data. The solution to this problem is connected with the establishment of relationships between thermodynamic properties of solutions and properties forming their components. Data on the properties of binary systems containing members of a homologous series are of great interest

in establishing relations between the molecular characteristics of components and the thermodynamic characteristics of solutions. The existing methods for calculating the properties of multi component systems are also based on the properties of their binary constituents [1]. Analysis of the scientific literature shows that the properties of these solutions are fragmented [2]. This required from us conducting additional research of large. The liquid-vapor equilibrium for 33 binary systems and also their volume and thermodynamic properties were studied previously, for example [3-5]. In this work, an attempt was made to determine the relation between the contributions of intermolecular interactions to the thermodynamic functions of binary solutions and the molecular weights (structure) and the concentration of solution components. The paper discusses the solutions of 25 binary systems formed: (1) Ethanol (a common solvent) and methyl ethanoate, ethyl ethanoate, n-propyl ethanoate, n-butyl ethanoate and *n*-pentyl ethanoate (the second solution components); (2) Ethanol (a common solvent) and methyl propanoate, ethyl propanoate, n-propyl propanoate, *n*-butyl propanoate and *n*-pentyl propanoate (the second solution components); (3) Ethanol (a common

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solvent) and methyl butanoate, ethyl butanoate, *n*-propyl butanoate, *n*-butyl butanoate and *n*-pentyl butanoate (the second solution components); (4) *n*-Propanol (a common solvent) and methyl ethanoate, ethyl ethanoate, *n*-propyl ethanoate, *n*-butyl ethanoate and *n*-pentyl ethanoate (the second solution components); (5) *n*-Butanol (a common solvent) and methyl ethanoate, ethyl ethanoate, *n*-propyl ethanoate, *n*-butyl ethanoate and *n*-pentyl ethanoate (the second solution components).

2. Results and Discussion

The *p*-*x*-*y*-*T* data obtained were used in the well known thermodynamic equations [1] to calculate the activity coefficients (γ_i), excess component chemical potentials in mixtures (μ_i), and excess Gibbs energies (G^e) of solutions at *p*, *T* = const. The excess entropies of solutions were calculated using Eq. (1).

$$S^{e} = -(\partial G^{e} / \partial T)_{p, x_{1}, \cdots x_{k-1}}$$
(1)

While the excess enthalpies of solutions were calculated using the Gibbs equation. Concentration and temperature dependences of the solution properties are indicative of a complex character of molecular interactions in the solutions, which manifests itself in deviations of binary systems from ideality (Fig. 1 and Table 1).

Lewis-Randal calculations do not allow us to directly relate the thermodynamic function values of solutions to the molecular weight (structure) of solution components. The chief disadvantage of calculations by the Lewis-Randal method is that thermodynamic functions of solutions are not related directly to molecular characteristics of components of mixtures [6, 7]. To achieve the assigned tasks the following algorithm of research was used: (1) Thermodynamic properties of liquid substances in homologous series were investigated; (2) Properties of solutions of the binary liquid systems formed by the common solvent and substances of these homologous series were investigated; (3) An ideal gas at the temperature (T), volume (V) and composition (x) of the real liquid, which obeyed the statistics of the real liquid, was used as a standard for calculating the contributions of intermolecular interactions to the thermodynamic functions of solutions; (4) For the solutions at a constants molar concentration (at T, V = const.), the functional relationship between the thermodynamic properties of solutions and the molar mass (structure) of the components forming solutions was attempted to be determined [8, 9].

An ideal gas has two degrees of freedom; therefore, the authors shall impose two restrictions. First, it is necessary to exclude work against any forces, except for those of intermolecular interaction therefore V =const. Consider two possible cases: (1) the adiabatic case, S = const. (2) the isothermal case (T = const.) —when the entropy of the system varies due to the intermolecular interaction rather than temperature. These reasons explain the necessity of conducting the process under condition of V, T = const.. The intermolecular interaction to the thermodynamic function (F^r) is defined as:

$$F^r = F^* - F \tag{2}$$



x (mole fractions *n*-propanol)

Fig. 1 Dependences of excess Gibbs energy G^e on the composition of: 1—*n*-propanol-methyl ethanoate; 2—*n*-propanol-ethyl ethanoate; 3—*n*-propanol-n-propyl ethanoate; 4—*n*-propanol-n-butyl ethanoate; 5—*n*-propanol-*n*-pentyl ethanoate; T = 353.15 K.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		-	·								
n-batanol—methyl ethanoate T (K) = 353 K v 0.0000 0.0370 52,315 9.5868 17,337 47,295 44,361 0 0.0000 0.2326 79,232 9.4718 16,789 48,118 44,919 301 0.7000 0.1534 102,990 9.5599 16,663 48,026 45,099 383 0.6000 0.1125 123,988 9.2420 15,361 47,887 44,962 441 0.5000 0.0646 159,517 9.0121 14,042 47,164 44,243 475 0.3000 0.04480 174,903 8.8972 13,432 45,990 44,0667 360,066 243 0.2000 0.0033 189,261 8.782 12,865 45,354 40,627 360 0.1000 0.182 203,713 8.6673 12,349 39,015 36,096 243 0.0000 0.5618 34,530 9.8206 17,735 46,350 44,3417 133 0.3000 0.5618	X (mole fractions <i>n</i> -butanol)	Y (mole fractions <i>n</i> -butanol)	$P \times 10^{5}$ (N/m ² (Pa))	$V \times 10^{-5}$ (m ³ · mol ⁻¹)	$A^r \times 10^4 (\text{J} \cdot \text{mol}^{-1})$ Helmholtz energy	$H \times 10^4$ (J·mol ⁻¹)	$U^r \times 10^4$ (J·mol ⁻¹)	G^e (J·mol ⁻¹)			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>n</i> -butanol—methyl ethanoate $T(K) = 353 \text{ K}$										
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1.0000	1.0000	21,291	9.7129	18,378	47,295	44,361	0			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.9000	0.3770	52,315	9.5868	17,537	47,889	44,958	197			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.8000	0.2236	79,232	9.4718	16,789	48,118	45,190	301			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.7000	0.1534	102,990	9.3569	16,063	48,026	45,099	383			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.6000	0.1125	123,988	9.2420	15,361	47,887	44,962	441			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.5000	0.0850	142,692	9.1270	14,687	47,642	44,719	473			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.4000	0.0646	159,517	9.0121	14,042	47,164	44,243	475			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.3000	0.0480	174,903	8.8972	13,432	45,990	43,069	443			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.2000	0.0333	189,261	8.7822	12,865	43,547	40,627	369			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.1000	0.0182	203,713	8.6673	12,349	39,015	36,096	243			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.0000	0.0000	215,605	8.5438	11,973	29,849	26,931	0			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>n</i> -butanol—ethyl etha	noate $T(\mathbf{K}) = 353 \ \mathbf{K}$									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1.0000	1.0000	21.291	9.7129	18.378	47.295	44.361	0			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.9000	0.5618	34.530	9.8206	17.735	46.350	43.417	133			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.8000	0.3761	46.262	9.9151	17.141	45.240	42.309	223			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.7000	0.2713	56.928	10.010	16,566	44.044	41.114	295			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.6000	0.2067	65,993	10.104	16,011	42.660	39.731	346			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5000	0.1646	73,126	10.199	15,487	41.102	38,173	368			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.4000	0.1278	79.992	10.293	15,000	39.404	36.476	352			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3000	0.0948	86.658	10.388	14.543		,				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.2000	0.0634	93.324	10.482	14.117	35.805	32.878	231			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.1000	0.0316	100.323	10.577	13.719	34.158	31.232	127			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.0000	0.0000	107.523	10.661	13.359	32.845	29.920	0			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>n</i> -butanol— <i>n</i> -propyl	ethanoate $T(K) = 353$	K			,	_,,,				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 0000	1 0000	21 291	9 7129	18 378	47 295	44 361	0			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.9000	0.7563	26 797	10.002	17 812	47 398	44 464	235			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.8000	0.5846	30,930	10.274	17,012	46 852	43 919	305			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.7000	0.4613	34 663	10.546	17,122	46.078	43 145	364			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.7000	0.3597	38 396	10.819	16,677	45,078	42 545	415			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5000	0.2995	40 796	11.091	16,334	45 175	42,545	413			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4000	0.2355	42 796	11.363	16,031	45 151	42 220	432			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3000	0.1907	44 662	11.635	15,771	45 133	42,220	381			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2000	0.1291	46 529	11.000	15,771	44 648	41 718	303			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.1000	0.0684	48 129	12 180	15,337	43.032	40 101	197			
n-butanol—n-butyl ethanoate $T(K) = 353 K$ 1.0000 1.0000 21,291 9.7439 18,378 47,295 44,361 0 0.9000 0.8498 22,624 10.188 18,100 56,064 53,130 146 0.8000 0.7310 23,664 10.632 17,850 63,602 60,669 273 0.7000 0.6358 24,384 11.076 17,630 67,861 64,927 372 0.6000 0.5595 24,811 11.519 17,450 67,264 64,331 441 0.5000 0.4988 24,927 11.963 17,210 51,833 48,899 437 0.4000 0.4361 24,758 12.407 17,210 51,833 48,899 437 0.3000 0.3704 24,264 12.851 17,210 40,469 37,536 354 0.2000 0.2738 23,491 13.295 17,210 31,195 28,261 249 0.1000 0.1532 22,398 13.739 17,250 29,056 26,123 116	0.0000	0.0000	48,528	12.445	15,235	36,970	34,040	0			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<i>n</i> -butanol— <i>n</i> -butvl et	hanoate $T(\mathbf{K}) = 353 \mathbf{k}$,		,	,	,				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.0000	1.0000	21.291	9.7439	18.378	47.295	44.361	0			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.9000	0.8498	22.624	10.188	18,100	56.064	53,130	146			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.8000	0.7310	23.664	10.632	17.850	63.602	60.669	273			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.7000	0.6358	24.384	11.076	17.630	67.861	64.927	372			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.6000	0.5595	24,811	11.519	17,450	67,264	64,331	441			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5000	0.4988	24.927	11.963	17.210	61.564	58.630	465			
0.3000 0.3704 24,264 12.851 17,210 40,469 37,536 354 0.2000 0.2738 23,491 13.295 17,210 31,195 28,261 249 0.1000 0.1532 22,398 13.739 17,250 29,056 26,123 116 0.0000 0.0000 21,265 14,183 17,280 20,580 26,647 0	0.4000	0.4361	24,758	12.407	17,210	51,833	48,899	437			
0.2000 0.2738 23,491 13.295 17,210 31,195 28,261 249 0.1000 0.1532 22,398 13.739 17,250 29,056 26,123 116 0.0000 0.0000 21,265 14,183 17,280 30,580 26,647 0	0.3000	0.3704	24.264	12.851	17.210	40.469	37.536	354			
0.1000 0.1532 22,398 13.739 17,250 29,056 26,123 116 0.0000 0.0000 21,265 14,182 17,280 20,580 26,647 0	0.2000	0.2738	23,491	13.295	17.210	31.195	28,261	249			
	0.1000	0.1532	22,398	13.739	17.250	29.056	26.123	116			
0.0000 0.0000 21,203 14.163 17,260 39,360 30,047 0	0.0000	0.0000	21,265	14.183	17,280	39,580	36,647	0			

 Table 1
 Vapor-liquid equilibrium and thermodynamic properties of the binary system.

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Table 1 continued

X (mole fractions	Y (mole fractions	$P \times 10^5$	$V \times 10^{-5}$	$A^r \times 10^4 (\text{J} \cdot \text{mol}^{-1})$	$H \times 10^4$	$U^r \times 10^4$	G^e			
<i>n</i> -butanol)	<i>n</i> -butanol)	$(N/m^2 (Pa))$	$(m^3 \cdot mol^{-1})$	Helmholtz energy	$(J \cdot mol^{-1})$	$(J \cdot mol^{-1})$	$(J \cdot mol^{-1})$			
<i>n</i> -butanol— <i>n</i> -pentyl ethanoate $T(K) = 353 K$										
1.0000	1.0000	21,291	9.7439	18,378	47,295	44,365	0			
0.9000	0.9363	20,998	10.325	18,265	47,991	44,134	274			
0.8000	0.8637	20,131	10.942	18,235	48,354	43,830	443			
0.7000	0.7972	19,331	11.558	18,226	48,128	43,455	529			
0.6000	0.7315	18,531	12.175	18,239	47,369	43,008	546			
0.5000	0.6693	17,732	12.791	18,283	46,282	42,488	511			
0.4000	0.6396	16,932	13.408	18,449	45,083	41,896	438			
0.3000	0.6126	15,998	14.024	18,723	43,935	41,233	338			
0.2000	0.4842	14,799	14.640	18,751	42,986	40,497	222			
0.1000	0.3662	12,932	15.257	19,059	42,481	39,689	101			
0.0000	0.0000	8,866	15.873	19,507	43,020	38,809	0			

where, F is a thermodynamic function for the real liquid and F^* is the corresponding thermodynamic function for the ideal gas. Subtraction $(F^* - F)$ provides positive values of F^r . Note that the activation of the intermolecular interaction in the liquid will change the sign of F^r . Consider a binary liquid solution at temperature (T) in equilibrium with vapor at pressure of the saturated vapor p. Its molar Helmholtz energy (A) is given by:

$$A = x_1 \mu_1 + x_2 \mu_2 - pV \tag{3}$$

where, x_1 and x_2 are the mole fractions and μ_1 and μ_2 are the chemical potentials of the species in solution; p—pressure of the saturated vapor; V—is the molar volume of the solution. Because absolute values of the Helmholtz energy are unknown, take as a reference state an ideal-gas mixture of the same composition as the liquid solution at the same temperature and with the same molar volume. This is a liquid-like state with the properties of an ideal gas [8]. The pressure in this reference state is then $P^* = RT/V$ and the molar Helmholtz energy is:

$$A^* = x_1 \mu_1^* + x_2 \mu_2^* - RT \tag{4}$$

where, μ_1^* , μ_2^* —chemical potentials of 1 and 2 components in the reference state of the mixture; *R*—the universal gas constant. Define a residual molar Helmholtz energy A^r as the difference between the reference value and the real value:

$$A^{r} = A^{*} - A = x_{1}(\mu_{1}^{*} - \mu_{1}) + x_{2}(\mu_{2}^{*} - \mu_{2}) - RT + PV$$
(5)

For the real saturated-liquid solution, the chemical potential may be expressed as:

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i \tag{6}$$

where, specific to species *i*, is a function of *T* only, originating as an integration constant, and is the fugacity (not the fugacity coefficient) of species *i* in solution. Note that the value in the liquid solutions is the same as in the equilibrium vapor phase. If the vapor phase is considered an ideal gas, then its value is the partial pressure ($y_i P$). For ideal gas, we have:

$$\mu_i^* = \Gamma_i(T) + RT \ln\left(x_i P^*\right) \tag{7}$$

The product is the partial pressure of species *i* in the ideal gas, where *i* is that of the liquid solution. Because $P^* = RT/V$, Eq. (7) becomes:

$$\mu_i^* = \Gamma_i(T) + RT \ln \frac{x_i RT}{V} \tag{8}$$

Combination Eqs. (5), (6) and (8), after division by RT (making the equation dimensionless):

$$\frac{A^{r}}{RT} = x_{1} \ln \frac{x_{1}RT}{\hat{f}_{1}V} + x_{2} \ln \frac{x_{2}RT}{\hat{f}_{2}V} - 1 + \frac{pV}{RT}$$
(9)

where, \hat{f}_1, \hat{f}_2 —is the fugacity 1 and 2 component in solution. For pure species *i* ($x_2 = 0$) as limited cases:

$$\frac{A_i^r}{RT} = \ln \frac{RT}{\hat{f}_i V_i} - 1 + \frac{p_i^0 V_i}{RT}$$
(10)

Using the known thermodynamic relation, for entropy (S^r) and internal energy (U^r) , it can be expressed:

$S^{r} = S^{*} - S = -\left(\frac{\partial F^{r}}{\partial T}\right)_{r,x} =$ $= \frac{H}{T} - R\left(x_{1}\ln\frac{x_{1}RT}{\hat{f}_{1}V} + x_{2}\ln\frac{x_{2}RT}{\hat{f}_{2}V}\right)^{(11)}$ $U^{r} = U^{*} - U = -T^{2}\left(\frac{\partial(F^{r}/T)}{\partial T}\right)_{r,x} = H - RT + PV$ (12)

where, *H*, *V*, *P*—molar enthalpy of vaporization, molar volume and pressure of the saturated vapor for a solution of composition x_1 of molar fractions; \hat{f}_1, \hat{f}_2 —is the fugacity of species 1 and 2 in solution.

3. Homologous Series of Substances

The values of A^r , U^r and TS^r were calculated by Eqs. (9)-(12) for liquid *n*-alkyl acetates, *n*-alkyl propionates, *n*-alkyl butyrate's, *n*-alcohols, *n*-alkanes, *n*-bromoalkanes, *n*-chloroalkanes, *n*-organic acids, *n*-alkyl amines, *n*-alkylarenes. An analysis of the calculation results suggests that, in homologous series, the functions A^r , U^r and TS^r depend linearly on the molecular mass:

$$U'' = k_1 M + b_1$$
 (13)

$$A^r = k_2 M + b_2 \tag{14}$$

$$TS^r = k_3 M + b_3 \tag{15}$$

The coefficients of Eqs. (13)-(15) were fit by the least-squares method using the Curve Expert 1.3 software (Table 2). Eqs. (13)-(15) make it possible to

calculate A^r , U^r , and TS^r values for the other members of the homologous series. For example, for *n*-heptyl propionate we obtained (kJ/mol): $J/_{calc.} = 47,777, (U_{expt})$ = 47,709), F_{calc} = 24,719, (F_{expt} = 24,681), and TS_{calc}^{r} = 23,051, $(TS^{r}_{expt} = 22,887)$. The observed regularities in the behavior of the A^r , U^r and TS^r functions associated with the M is in liquid compounds of homologous series can be used for further refinements of group models of solutions (UNTPAC, ASOG) [1]. The fact that A^r , U^r and TS^r depend linearly on the molecular mass of the compound in a homologous series suggests that the structures of the liquids are similar. Since A^r , a function most accurately determined in experiments, characterizes the intermolecular interaction in liquids, it is interesting to establish how this function is related to the molar volume V and saturation vapor pressure p of liquid compounds in homologous series. A correlation analysis reveals that, within a homologous series, $\ln p$ and V depend linearly on A^r :

$$\ln p = k_4 A^r + b_4 \tag{16}$$

$$V = k_5 A^r + b_5$$
 (17)

The coefficients of Eqs. (13)-(17) are listed in the Table 2. These equations describe A^r within a homologous series with an accuracy of ±50 J/mol. Eqs. (16) and (17) yield p and V values for the other members of the homologous series. For example, for *n*-heptyl acetate at T = 323.15 K, we obtained: $p_{calc} =$

 Table 2
 Coefficients of Eqs. (13)-(17) for compounds in homologous series.

		-		-							
Homologous series	$T(\mathbf{K})$	k_l	b_I	<i>k</i> ₂	b_2	<i>k</i> ₃	b_3	$k_4(\times10^{-4})$	b_4	<i>k</i> ₅	b_5
<i>n</i> -Alkanes	293	318.9	2,411	188.9	-1,514	129.9	3,926	-4.446	16.17	$6.171\times 10^{\text{-9}}$	$3.919\times10^{\text{-5}}$
<i>n</i> -Bromalkanes	293	267.4	3,383	180.6	6,312	86.82	2,929	-4.941	17.46	$6.644\times 10^{\text{-9}}$	$\textbf{-1.485}\times10^{\textbf{-5}}$
n-Chlor alkanes	293	300.0	3,613	185.6	880.4	114.4	4,493	-4.932	17.29	$6.313\times 10^{\text{-9}}$	$1.670\times 10^{\text{-}6}$
n-Alkylarenes	353	317.3	3,468	150.4	2,187	166.9	1,281	-4.051	17.12	$8.203\times 10^{\text{-9}}$	$\textbf{-1.818}\times10^{\textbf{-5}}$
n-Organic acids	293	-	-	142.0	$1{,}429 \times 10^4$	-	-	-5.365	19.51	$8.617\times 10^{\text{-9}}$	$\textbf{-1.398}\times10^{\textbf{-4}}$
n-Alkylamines	293	207.6	16.69×10^4	139.6	5,692	-	-	-5.484	18.12	$8.752\times10^{\text{-9}}$	$\textbf{-3.980}\times10^{\textbf{-5}}$
n-Haloarenes	343	91.69	$\textbf{2,513}\times \textbf{10}^4$	59.17	$1{,}208\times10^4$	32.52	13,054	-3.668	16.41	$1.732\times 10^{\text{-9}}$	$7.417\times10^{\text{-5}}$
n-Alkyl ethanoates	323	272.6	7,690	125.5	4,105	146.5	3,632	-4.577	17.40	$9.935\times 10^{\text{-3}}$	-48.85
n-Alkyl propanoates	353	136.1	1,264	195.1	$1{,}417\times10^4$	58.75	12,931	-3.893	16.68	$9.143\times10^{\text{-3}}$	-14.37
n-Alkyl butanoates	353	1,756	16,040	134.7	1,307	40.88	14,720	-4.009	-16.88	$9.473 \times 10^{\text{-}9}$	-1.901
n-Alcohols	353	229.2	27.90×10^4	107.8	$1{,}825\times10^4$	121.5	9,282	-	-	-	-

547 Pa, $(p_{expt} = 580 \text{ Pa})$ and $V_{calc} = 190.0 \text{ cm}^3/\text{mol} (V_{expt})$ = 187.5 cm³/mol). For *n*-heptyl propionate at *T* = 353.15 K, $p_{calc} = 1,177.11 \text{ Pa} (p_{expt} = 1,144.6 \text{ Pa})$ and $V_{calc} = 211.2 \text{ cm}^3/\text{mol} (V_{expt} = 210.97 \text{ cm}^3/\text{mol})$. As the *A'* function associated with intermolecular interaction increases, it becomes more difficult for molecules to pass into the gas phase; as a result, the saturation vapor pressure decreases exponentially. Since the entropy of a liquid is smaller than that of the corresponding ideal

20000

0.00

0.20

 A^r function associated with intermolecular interaction increases, it becomes more difficult for molecules to pass into the gas phase; as a result, the saturation vapor pressure decreases exponentially. Since the entropy of a liquid is smaller than that of the corresponding ideal gas (T, V = const.), the switching off of the intermolecular interaction should increase entropy, or at least leave it unchanged. An analysis of the available data demonstrates that the linear increase of A^r is accompanied by the linear growth of TS for the intermolecular interaction in liquid compounds of homologous series. In accordance with universally accepted principles, an increase in the function $S = S^* - S^*$ S_{liq} is indicative of an increase in the molecular ordering of the liquid. If the structures of the liquids comprising a homologous series are similar, then an increase in the molecular size should cause a decrease in the density of the packing of the molecules in the liquid, in agreement with the linear increase of the molar volume of the liquids in homologous series [10].

4. Solutions of the Binary Systems

Eqs. (9)-(12) were used to calculate the Helmholtz energies A^r , internal energies U^r , and entropies S^r of the systems (as an example, the values of the functions for systems Table 1). For the *n*-propanol-*n*-alkyl ethanoate solutions (as for the ethanol-*n*-alkyl ethanoate, ethanol-*n*-alkyl propanoates, ethanol-*n*-alkyl butanoate, and *n*-butanol-*n*-alkyl ethanoate solutions), the isotherms the $U^r = f(x)$ and S^r = f(x) behave similarly (Figs. 2 and 3).

For all systems solutions, A^r of Helmholtz energies increases with the molar weight of ester correspondingly, the vapor pressure of the solutions decreases (Table 1, Fig. 4). The presence of a minimum in the isotherm $A^r = f(x)$ for the *n*-butanol-ethyl ethanoate system is indicative of the



x (mole fractions *n*-propanol)

0.40

0.60



Fig. 3 Dependences of the entropy TS^r of solutions on their composition at 353 K (Fig. 1 for notation).

most weak molecular interactions at this solution composition, which agrees with the existence of a positive azeotrope in this system (Table 1).

For solutions of constant molar concentrations, the Helmholtz energy was found to depend linearly on the molecular weight of substance in a homologous series, $A^r = k_i M + b_i$ (Fig. 5). The k_i and b_i coefficients of these isotherms in turn linearly depended on the composition of solutions. The results obtained allowed

1.00

0.80



Fig. 4 Dependences of the Helmholtz energy A^r of solutions on their composition at 343 K (Fig. 1 for notation).



Fig. 5 Dependences of the Helmholtz energy A^r of solutions of constant molar concentrations on the molecular weight of *n*-alkyl ethanoate in solutions for systems propanol-1-*n*-alkyl ethanoates; T = 353.15 K: 0.1; 0.3; 0.5; 0.7; 0.9—constant mole fraction *n*-propanol in solutions of systems.

us to suggest Eq. (16).

$$A^{r} = (k_{6}X + b_{6})M + k_{7}X + b_{7}$$
(16)

where, X is the mole fraction of common solvent in the system and M is the molecular weight of the second solution component Table 3.

Eq. (16) describes A^r accurate to ~ 40 J/mol and can be used for calculating properties of binary systems formed by *n*-alcohol and esters of aliphatic acids. The form of Eq. (16) is retained also at other temperatures. The following experimental data are necessary to find the factors in the Eq. (16) (at T = const.) for two solutions of identical mole concentration, formed by the common solvent and two substances of homologous series: pressure of the saturated vapor (P)composition of an equilibrium vapor phase (Y), molar volume of a solution (V). An accuracy prediction thermodynamic property of solutions depends only on the accuracy of the experimental data. The linear dependence of the Helmholtz energy for solutions of a constant molar composition on the molecular weight of the component in the homologous series (as with pure components, the boundary condition is $x_1 = 0$) can also be explained by the "similarity of the molecular-statistical structure of solutions" [10]. These results are in agreement with the hypothesis of additive contributions of chemical groups to the thermodynamic properties of solutions, which is basic for statistical models of solutions known as "group models" [1]. An equation similar to Eq. (16) was obtained for solutions of 33 binary systems formed by *n*-alcohols and compounds of the homologous series of esters of organic acids; formed by benzene (a common solvent) and methylbenzene, ethylbenzene, ethylbenzene, n-propylbenzene and n-butylbenzene (second solution components); formed by fluoroarene (a common solvent) and chloro-, bromo-, and iodoarenes (the second components) over the whole concentration range at various temperatures [11, 12].

The authors believe that this law is general in character and can be used to predict the thermodynamic properties of binary system solutions formed by a common solvent and representatives of homologous series of organic substances. Considering the widespread use in thermodynamic calculations by Lewis-Randall (standard ideal solution), it seemed appropriate to link this standard with the standard ideal gas. Define an excess dimensionless molar Helmholtz energy as:

1						
The name of systems	<i>T</i> (K)	k_6	b_6	<i>k</i> ₇	b_7	Accuracy (J·mol ⁻¹)
Ethanol— <i>n</i> -alkyl ethanoates	323	-117.54	119.38	11,045	4,566.9	50
Ethanol— <i>n</i> -alkyl propanoates	353	-136.37	132.91	12,766	1,520.5	50
Ethanol— <i>n</i> -alkyl butanoates	353	-152.56	141.93	14,925	-132.03	20
Propanol-1— <i>n</i> -alkyl ethanoates	353	-139.99	132.89	14,752	16,914	50
Butanol-1— <i>n</i> -alkyl ethanoates	353	-136.39	133.92	166,666	1,552.4	20
Methyl ethanoate- <i>n</i> -alkyl ethanoates	323	-130.12	129.41	9,677.3	3,578.1	50
Methyl propanoate- <i>n</i> -alkyl propanoates	353	-149.59	149.7	1,386.9	-432.77	50
Methyl butanoate— <i>n</i> -alkyl butanoates	353	-152.7	141.9	14,925	-132.0	20

Table 3Constants of the Eq. (16).

Table 4 The values of the excess Gibbs energy, calculated from the two standards: ideal solution and an ideal gas.

X (mole	G^e (J/mol)									
fractions	Ideal standard of solution	Standard of an ideal gas	Ideal standard of solution	Standard of an ideal gas						
n-butanol)	<i>n</i> -butanol—methyl ethanoa	te $T(K) = 353 K$	<i>n</i> -butanol—n-pentyl ethanoate $T(K) = 353 \text{ K}$							
1.00	0.0	0.0	0.0	0.0						
0.80	301	301	443	443						
0.60	441	441	546	546						
0.40	475	475	438	438						
0.20	369	369	222	222						
0.00	0.0	0.0	0.0	0.0						

$$\frac{A^e}{RT} \equiv \frac{A^r}{RT} - x_1 \frac{A_1^r}{RT} - x_2 \frac{A_2^r}{RT}$$
(17)

This equation, when combined with Eqs. (9) and (10) and after reduction yields:

$$\frac{A^{e}}{RT} = x_{1} \ln \frac{1}{\gamma_{1}} + x_{2} \ln \frac{1}{\gamma_{2}} + x_{1} \ln \frac{V_{1}}{V} + x_{2} \ln \frac{V_{2}}{V} + \frac{pV - x_{1}p_{1}V_{1} - x_{2}p_{2}V_{2}}{RT}$$
(18)

where, γ_1,γ_2 —activity coefficients 1 and 2 component in solution; V, p-molar volume and pressure of the saturated vapor for a solution of composition X_l of molar fractions; p_l , p_2 —pressure of the saturated vapor (N/m^2) and V_1 , V_2 —molar volume $(m^3 \cdot mol^{-1})$ of pure species 1 and 2, respectively. Eq. (18) connects the values of the excess energy of the Helmholtz solution and activity coefficients 1 and 2 component in solution. Next, using the well-known thermodynamic relations we can calculate the values of the chemical potentials, Gibbs energy, and all other thermodynamic functions. Values of the thermodynamics functions expected on the standard of ideal gas and ideal solution identical (for example Table 4).

5. Conclusions

(1) Values of the Helmholtz energy (A^r) , internal energy (U^r) and entropy (TS^r) are linearly dependent on the molar mass of substance in homologous series;

(2) Increase of values of the Helmholtz energy (A') for substances in homologous series is due to the linear magnification of molar volumes of fluid substances and reduction of pressure of the saturated vapor of substances under the exponential law;

(3) It is shown that the intermolecular interaction of components in solutions is expedient for estimating using the values of thermodynamic functions calculated under the standard of the ideal gas taken at the same temperatures and volume as the tested liquid and submitting to the same statistics. The correlation of thermodynamic properties of solutions with molecular characteristics of components forming them is determined provided that the solutions have constant mole concentration;

(4) It was determined by the analysis of thermodynamic properties of solutions of binary

mixtures that Helmholtz energy (A') of the binary solutions of the constant mole concentration formed by the common solvent and terms of homologous series of organic matters, are linearly dependent on molar mass of substance in homologous series. The equations describing thermodynamic properties of studied solutions with accuracy adequate for the technological purposes are obtained;

(5) The technique of predicting the thermodynamic properties of solutions of binary mixtures using properties of two pure components and two solutions of identical mole concentration is proposed. An accuracy prediction thermodynamic property of solutions depends only on the accuracy of the experimental data. Proposed a method speeds up the process of researching the thermodynamic properties of binary systems ~ 340 times.

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