Enthalpies of solution of *n*-alkanes in mixtures of MeCN with alkan-1-ols at 298.15 K. Relations between the thermodynamic properties of binary and ternary systems

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The solution enthalpies of *n*-hexane, *n*-nonane, and *n*-undecane in mixtures of MeCN with EtOH, PrOH, and BuOH were determined by calorimetric method at 298.15 K. Relations between the thermodynamic properties of ternary systems and the properties of the binary solvents and the solute are discussed. To predict the enthalpies of solution of hydrocarbons in mixed solvents whose components have strongly different molar volumes ($V_2/V_1 > 1.5$), it is proposed to use the values that are additive in the volume fraction scale. The solution enthalpies of hydrocarbons in mixtures characterized by close molar volumes of the components strongly depend on the excess properties of the binary solvent.

Key words: solution enthalpy, mixed solvents, *n*-alkanes, alkan-1-ols, acetonitrile, deviation from additivity.

Mixed solvents offer the advantage of preparing mixtures with desired properties in a targeted manner. At the same time, the variety of such mixtures requires considerable experimental efforts. This also holds for the enthalpies of solution and solvation of compounds in mixed solvents. Therefore, in studies of ternary systems of the "binary solvent—solute" type particular attention is given to search for interrelations between their thermodynamic properties and the properties of the mixed solvent, its components, and the solute. Interest in this problem is due to the fact that the properties of ternary systems are much less studied compared to the properties of binary mixtures.[1—4] The fundamental characteristics of binary mixtures are their thermal (H^E) and volume (V^E) properties. To solve the problem posed, it is appropriate to choose such ternary systems whose parameters can be varied in a targeted way. Mixtures of MeCN with MeOH, EtOH, PrOH, and BuOH meet this requirement. The enthalpies of mixing of MeCN with alkan-1-ols increase[5—7] as the hydrocarbon radicals of the alcohol molecules increase (Fig. 1), whereas the excess volumes calculated using the published data[8,9] decrease and even change their signs (Fig. 2). Interest in studies of the enthalpies of solution ($\Delta_{sol}H°$) of hydrocarbons in mixtures of MeCN with alkanols is also due to the fact that the thermal properties of these ternary systems (in particular, MeCN—MeOH—*n*-alkane[10]) cannot be described by a "simple mixing model."[11] The authors of the model[11] believe that the reason for deviation of the enthalpies of solution of *n*-alkanes in binary mixtures from the additive values is the change in the energy characteristics of the interactions between the solution components

$$\Delta\Delta H°_X = -H^E, \quad (1)$$

$$\Delta\Delta H°_\phi = -V_3H^E/(X_1V_1 + X_2V_2), \quad (2)$$

where $\Delta\Delta H°_X$ and $\Delta\Delta H°_\phi$ are the deviations of the enthalpies of solution of a compound in a mixed solvent from the additive values based on the mole fraction and volume fraction scales, respectively (hereafter, mole-fraction and volume-fraction additive values). They are calculated by the following equations:

$$\Delta\Delta H°_X = \Delta_{sol}H° - X_1\Delta_{sol}H°_1 + X_2\Delta_{sol}H°_2, \quad (3)$$

$$\Delta\Delta H°_\phi = \Delta_{sol}H° - \phi_1\Delta_{sol}H°_1 + \phi_2\Delta_{sol}H°_2. \quad (4)$$

In expressions (1)—(4) H^E is the enthalpy of mixing of components of the binary solvent, X and ϕ are their mole and volume fractions, respectively, V is the molar volume; the quantities with no subscripts refer to the solutions in the mixed solvent, the subscripts "1" and "2" characterize the properties of the components of the mixed solvent, and the subscript "3" characterizes the properties of solute.

We determined the enthalpies of solution of (i) *n*-hexane and *n*-undecane in the MeCN—EtOH mixture and (ii) *n*-octane in MeCN—PrOH and

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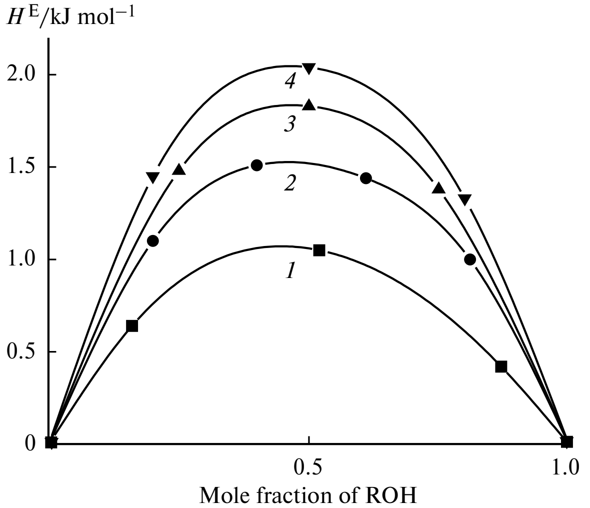

Fig. 1. The excess enthalpies of mixing (H^E) of MeCN with MeOH (*1*), EtOH (*2*), PrOH (*3*), and BuOH (*4*) at 298.15 K.

MeCN—BuOH mixtures. The experimentally determined thermal effects and the standard enthalpies of solution are listed in Tables 1 and 2, respectively. The results for the MeCN—MeOH mixture were taken from Ref. 10.

Experimental

Alcohols used in this work were prepared according to the known procedures;[12] EtOH was preliminarily dried over anhydrous K_2CO_3 and then distilled over metallic Ca; PrOH and BuOH ("analytically pure" grade) were twice distilled over anhydrous K_2CO_3; MeCN ("pure" grade) was dried over P_2O_5 and twice distilled (the second distillation was over anhydrous K_2CO_3 to remove traces of phosphoric acid). n-Alkanes ("chromatographically pure" grade) were used without further purification. The content of water in the organic solvents was controlled by titration using the Fischer reagent,[13] being at most 0.08 mass.% in the alcohols, 0.01 mass.% in MeCN, and 0.005 mass.% in alkanes. The enthalpies of solution were measured on an isothermic-shell ampule microcalorimeter (the volume of the reaction vessel was 50 cm^3) similar to that reported earlier.[14] To validate the experimental data, reproducibility of the results, and the absence of systematic errors in the operation of the calorimetric setup we measured the thermal effects of solution of anhydrous KCl in water. Statistical treatment of the data showed that the maximum relative (random) error of experi-

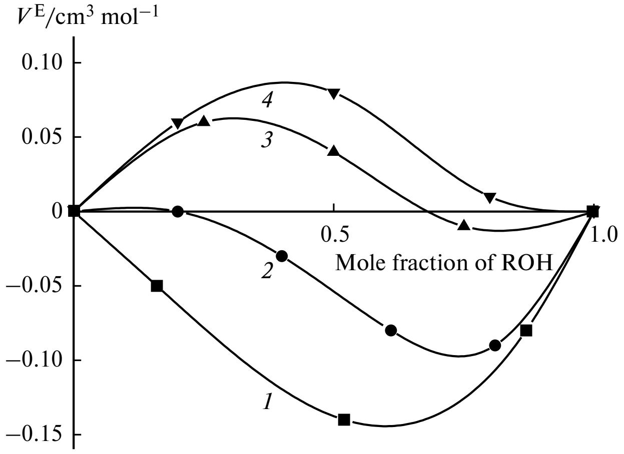

Fig. 2. The excess volumes (V^E) of MeCN—MeOH (*1*), MeCN—EtOH (*2*), MeCN—PrOH (*3*), and MeCN—BuOH (*4*) mixtures at 298.15 K.

Table 1. Enthalpies of solution ($\Delta_{sol}H^m$/kJ mol^{-1}) of n-alkanes in MeCN—EtOH, MeCN—PrOH, and MeCN—BuOH mixtures at 298.15 K

MeCN—EtOH					MeCN—PrOH			MeCN—BuOH		
X	C_6H_{14}		$C_{11}H_{24}$		X	C_8H_{18}		X	C_8H_{18}	
	m	$\Delta_{sol}H^m$	m	$\Delta_{sol}H^m$		m	$\Delta_{sol}H^m$		m	$\Delta_{sol}H^m$
0	0.0320	10.09	0.0102	17.60	0	0.0154	13.30	0	0.0154	13.30
0	0.0456	10.15	0.0185	17.67	0	0.0354	13.36	0	0.0354	13.36
0.20	0.0296	9.23	0.0111	16.33	0.25	0.0169	9.81	0.20	0.0179	6.80
0.20	0.0421	9.22	0.0202	16.43	0.25	0.0356	9.85	0.20	0.0413	6.77
0.40	0.0256	7.60	0.0141	13.84	0.50	0.0195	7.45	0.50	0.0161	6.44
0.40	0.0501	7.68	0.0205	13.88	0.50	0.0351	7.38	0.50	0.0324	6.31
0.61	0.0450	6.05	0.0119	11.14	0.75	0.0182	5.07	0.80	0.0220	3.63
0.61	0.0482	6.11	0.0198	11.15	0.75	0.0366	5.07	0.80	0.0409	3.64
0.81	0.0203	4.38	0.0099	8.36	1.00	0.0160	2.87	1.00	0.0208	2.31
0.81	0.0404	4.38	0.0187	8.32	1.00	0.0320	2.85	1.00	0.0405	2.30
1.00	0.0322	2.68	0.0141	5.69						
1.00	0.0401	2.72	0.0206	5.71						

Note. In Tables 1—3 X is the mole fraction of the corresponding alcohol and m is the molal concentration of n-alkane in solution (mol (1000 g of solvent)$^{-1}$). For the superscript "m" in the expression $\Delta_{sol}H^m$, see a note in the text.

Table 2. Standard enthalpies of solution (kJ mol^{-1}) of *n*-alkanes in mixtures of MeCN with alkan-1-ols at 298.15 K

MeCN—MeOH				MeCN—EtOH			MeCN—PrOH		MeCN—BuOH	
X	C_5H_{12}	C_6H_{14}	C_7H_{16}	X	C_6H_{14}	$C_{11}H_{24}$	X	C_8H_{18}	X	C_8H_{18}
0	8.45	10.00	11.63	0	10.12	17.64	0	13.33	0	13.33
0.16	8.62	10.29	12.13	0.20	9.23	16.38	0.25	9.83	0.20	6.79
0.52	7.36	8.62	10.13	0.40	7.64	13.86	0.50	7.42	0.50	6.38
0.87	4.81	5.90	7.32	0.61	6.08	11.15	0.75	5.07	0.80	3.64
1.00	3.81	4.69	5.52	0.81	4.38	8.34	1.00	2.86	1.00	2.31
				1.00	2.70	5.70				

Table 3. Deviation of the enthalpies of solution of *n*-alkanes ($\Delta\Delta H$/kJ mol^{-1}) in mixtures of MeCN with alkan-1-ols from the additive values at 298.15 K

MeCN—MeOH							MeCN—EtOH			
X	C_5H_{12}			C_7H_{16}			X	$C_{11}H_{24}$		
	$\Delta\Delta H^\circ_X$	$\Delta\Delta H^\circ$	$\Delta\Delta H^\circ_\phi$	$\Delta\Delta H^\circ_X$	$\Delta\Delta H^\circ$	$\Delta\Delta H^\circ_\phi$		$\Delta\Delta H^\circ_X$	$\Delta\Delta H^\circ$	$\Delta\Delta H^\circ_\phi$
0.16	0.91	0.15	0.76	1.48	0.2	1.28	0.2	1.14	−0.2	1.34
0.52	1.32	0.3	1.02	1.68	0.4	1.28	0.4	0.94	−0.3	1.24
0.87	0.4	0.15	0.25	1.01	0.2	0.81	0.61	0.74	−0.29	1.03
							0.81	0.33	−0.19	0.52

mental values, $\Delta_{sol}H^m$ *, was at most 0.6%. All measurements were carried out at 298.15 K. The solute concentration varied between 0.01 and 0.05 mol (kg of solvent)$^{-1}$. In this concentration range the thermal effect of solution is independent of concentration.[15] Taking into account this fact, the arithmetic means of the thermal effects of solution (see Table 1) served as the standard values of the enthalpies of solution (see Table 2). A comparison of the $\Delta_{sol}H^\circ$ values obtained in this work (see Table 2) with the known data ($\Delta_{sol}H^\circ$ for C_6H_{14} in EtOH and MeCN is 2.51 and 10.00 kJ mol^{-1}, respectively[16]) demonstrated a good correspondence between them.

Results and Discussion

Equations (1) and (2) were experimentally confirmed for those ternary systems that are characterized by universal character of all interactions between the solution components and by opposite signs of the parameters $\Delta\Delta H^\circ_X$ ($\Delta\Delta H^\circ_\phi$) and H^E.[11] The solutions studied in this work do not belong to such systems. Here, the solute and solvent molecules are involved in dispersion and induction interactions while universal and specific (donor-acceptor) interactions occur in mixed solvent. The systems under study are characterized by positive $\Delta\Delta H^\circ_X$ ($\Delta\Delta H^\circ_\phi$), and H^E values (see Table 2). This indicates a significant effect of the volume effects observed upon the formation of a binary solvent on the dissolution of the third component.

Transformation of Eqs (3) and (4) gives relationships (5) and (6), which demonstrate an interrelation between the parameters $\Delta\Delta H^\circ_X$ and $\Delta\Delta H^\circ_\phi$.

$$\Delta\Delta H^\circ_X = \Delta\Delta H^\circ + \Delta\Delta H^\circ_\phi \qquad (5)$$

$$\Delta\Delta H^\circ = (\phi_2 - X_2)(\Delta_{sol}H^\circ_2 - \Delta_{sol}H^\circ_1) \qquad (6)$$

Therefore, the deviation of the enthalpies of solution of an alkane from the mole-fraction additive value is the sum of two contributions, namely, $\Delta\Delta H^\circ$, which is due to the packing effects associated with the difference between the molar volumes of the components of a binary solvent, and $\Delta\Delta H^\circ_\phi$, which is determined by intermolecular interactions. Using Eqs (3)—(6), we calculated the deviations of the enthalpies of solution of *n*-alkanes in the binary solvents studied from the additive values. The results of calculations are shown in Fig. 3 and listed in Table 3.

The sign and magnitude of $\Delta\Delta H^\circ$ depend on the ratio of the molar volumes of the components of the mixed solvent. The addition of the component 2 with a smaller molar volume to component 1 with a larger molar volume (MeCN—MeOH) causes the formation of a more close-packed mixture. Dissolution of the third component in this binary system is accompanied by an increase in the energy expenditure ($\Delta\Delta H^\circ > 0$). As should be expected, the $\Delta\Delta H^\circ$ increase with the size of the dissolved hydrocar-

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* The subscript "*m*" means that this value of the enthalpy of solution refers to the concentration of solute equal to *m*, in contrast to the standard value ($\Delta_{sol}H^\circ$), which characterizes an infinitely dilute solution.

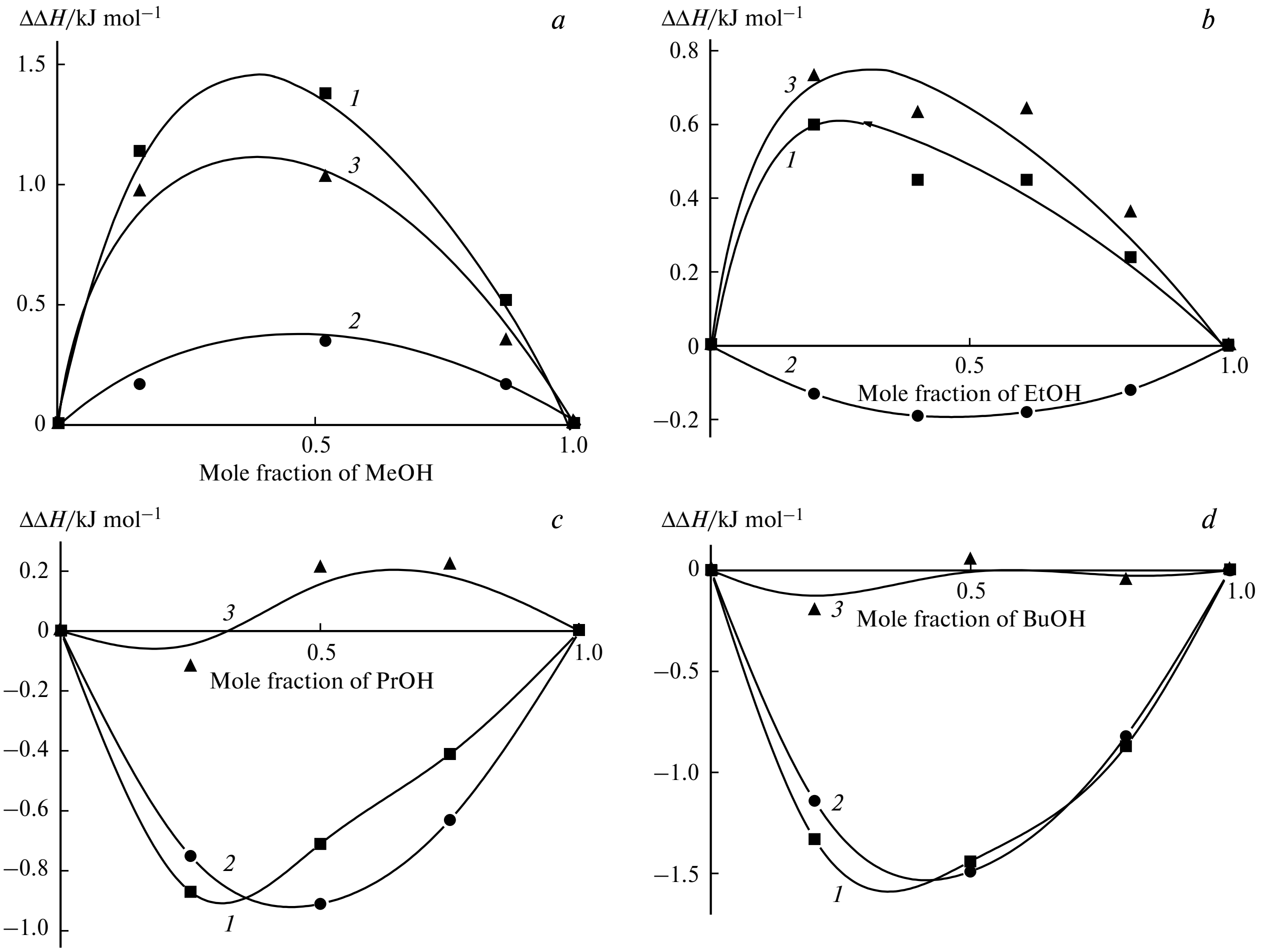

Fig. 3. Deviations of the enthalpies of solution ($\Delta\Delta H$) *n*-hexane (*a*, *b*) and *n*-octane (*c*, *d*) in MeCN—MeOH (*a*), EtOH (*b*), PrOH (*c*) and BuOH (*d*) mixtures at 298.15 K from additive values: $\Delta\Delta H^\circ_X$ (*1*), $\Delta\Delta H^\circ$ (*2*) and $\Delta\Delta H^\circ_\phi$ (*3*) (see text).

bon molecules (see Table 3). If $V_2 > V_1$, the opposite is observed (systems MeCN—EtOH, MeCN—PrOH, and MeCN—BuOH). Analysis of the contributions to $\Delta\Delta H^\circ_X$ shows that for the mixtures whose components have strongly different molar volumes ($V_2/V_1 > 1.5$), this corresponds to $\phi_2 - X_2 > 0.1$, the contribution $\Delta\Delta H^\circ$ is predominant. Some examples of this type of systems are provided by the MeCN—BuOH mixtures (see Fig. 3) and by the MeOH—CCl_4 and MeOH—DMF mixtures studied earlier.[17] The deviation of the enthalpies of solution of *n*-nonane from the mole-fraction additive value and its component, $\Delta\Delta H^\circ$, in the equimolar mixture MeOH—CCl_4 are −1.00 and −1.02 kJ mol^{-1}, respectively, and in the equimolar mixture MeOH—DMF they are 0.60 and 0.66 kJ mol^{-1}, respectively. The properties of the MeCN—PrOH mixed solvent are similar to those of the systems in question. In this case the enthalpies of solution of a hydrocarbon in a mixed solvent can be calculated using the volume-fraction additive values. Clearly, the larger the differences between the molar volumes of the components of the mixed solvent, the more accurate the predictions. However, it should be noted that certain systems do not follow this trend. For instance, the $\Delta\Delta H^\circ_X$ and $\Delta\Delta H^\circ$ parameters of nonane in equimolar mixtures MeOH—toluene[17] (−1.50 and −0.89 kJ mol^{-1}) and MeOH—C_6H_6 [17] (−0.70 and −0.16 kJ mol^{-1}) differ appreciably. A possible reason for these differences is provided by selective solvation of *n*-alkanes by aromatic hydrocarbons.

Mixtures with close molar volumes of their components (*e.g.*, MeCN—MeOH and MeCN—EtOH) are characterized by a large contribution $\Delta\Delta H^\circ_\phi$ (see Fig. 3). Analysis of the properties of binary and ternary systems shown in Figs 1—3 revealed no correlations between the $\Delta\Delta H^\circ_\phi$ values and the excess enthalpies and the volumes. Earlier,[18] a correlation was found between the $\Delta\Delta H^\circ_\phi$ values of *n*-alkanes in a number of binary non-aqueous mixtures and the excess cohesive energy density (p^E) of these systems. The parameter p^E characterizes all kinds of intermolecular interactions in a volume unit of a fluid.[19] The

Table 4. Coefficients and parameters of Eq. (8) for the systems MeCN—alkan-1-ol—*n*-alkane at 298.15 K

Solvent	*n*-Alkane	a_0/cm^3 mol^{-1}	se/kJ mol^{-1}	*R*	a_0/V_w
MeCN—MeOH	C_5H_{12}	−50.52	0.12	0.9671	−0.8706
	C_6H_{14}	−56.20	0.17	0.9418	−0.8232
	C_7H_{16}	−75.97	0.24	0.9229	−0.9679 [−0.8873±0.06]
MeCN—EtOH	C_6H_{14}	−26.49	0.09	0.9530	−0.3881
	$C_{11}H_{24}$	−46.94	0.21	0.9351	−0.3931 [−0.3906±0.00]
MeCN—PrOH	C_8H_{18}	−8.36	0.04	0.9522	−0.0942
MeCN—BuOH	C_8H_{18}	−0.44	0.04	0.2490	−0.0050

Note: se is the standard error and *R* is the correlation coefficient. The a_0/V_w ratios are given in brackets.

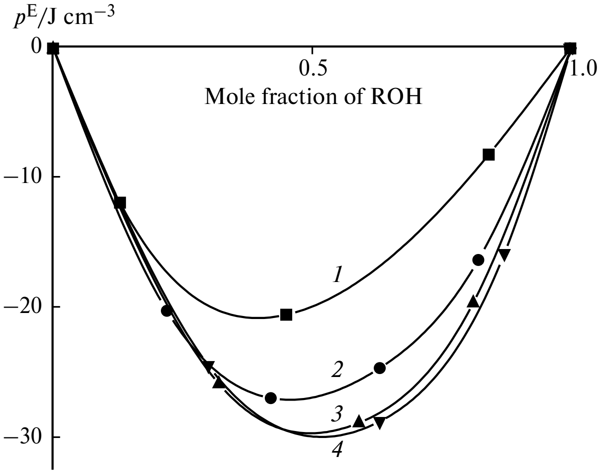

Fig. 4. The excess cohesive energy densities (p^E) of MeCN—MeOH (*1*), MeCN—EtOH (*2*), MeCN—PrOH (*3*), and MeCN—BuOH (*4*) mixtures plotted *vs*. mixture composition at 298.15 K.

parameter p^E was determined as the difference between the *p* values of the real and ideal solutions[18]

$$p^E = p - p_{id} =$$
$$= -[H^E - (\phi_1 p_1 + \phi_2 p_2)V^E]/(X_1V_1 + X_2V_2 + V^E). \quad (7)$$

The concentration dependences of p^E of the mixtures under study are shown in Fig. 4. All the mixtures studied are characterized by negative p^E values. This indicates weakening of intermolecular interactions in a volume unit of real mixtures compared to the corresponding ideal hypothetical mixtures. A comparison of the plots shown in Figs 3 and 4 shows that negative p^E parameters of mixed solvents (MeCN—MeOH, MeCN—EtOH, MeCN—PrOH) correspond to positive $\Delta\Delta H°_\phi$ values of *n*-alkanes. Correlations between the $\Delta\Delta H°_\phi$ and p^E values are described by linear dependences

$$\Delta\Delta H°_\phi = a_0 p^E, \quad (8)$$

where a_0 is a fitting parameter. The a_0 values and the regression parameters of Eq. (8) are listed in Table 4.

It seems to be quite reasonable that the absolute values of the coefficients a_0 increase in proportion to the van der Waals molar volumes of *n*-alkanes (V_w), which for C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, and $C_{11}H_{24}$ are[20] 58.03, 68.26, 78.49, 88.72, and 119.41 cm^3 mol^{-1}, respectively. This means that the a_0/V_w ratio is a dimensionless constant of a given mixed solvent and can serve as a parameter characterising structural changes in the solvation shell of the nonpolar solute molecules.

Thus, the results obtained in this study show that not only the energy characteristics of a binary mixture (as was assumed earlier) but also its volume properties are responsible for the energy characteristics of alkane solvation in binary non-aqueous mixtures. The relationships established make it possible to predict the enthalpies of solution of hydrocarbons in mixed solvents.

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