Enthalpies of squalane dissolution in mixtures of acetone with isomeric butyl alcohols

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The enthalpies of dissolution of squalane in mixtures of acetone with isomeric butyl alcohols at 25 °C were measured. Different approaches were used for the description of experimental data and the calculation of transfer enthalpies. The factors responsible for deviation of the concentration dependence of the transfer enthalpies from additivity were revealed.

Key words: squalane, acetone, isomeric butyl alcohols, enthalpies of dissolution.

Isomers of butyl alcohol have close values of molar volumes, enthalpies of evaporation, and refractive indices. At the same time, their empirical parameters of solvent polarity differ substantially. For example, the Dimroth—Reichardt parameter E_T is equal to 50.2, 49.0, 47.1, and 43.9 for Bu^{n}OH, Bu^{i}OH, Bu^{s}OH, and Bu^{t}OH, respectively.[1] The empirical parameters of the acidity and basicity indicate that Bu^{n}OH is a stronger proton donor than Bu^{t}OH, whereas the latter is a stronger acceptor of protons.[2—4] In the series Bu^{n}OH, Bu^{i}OH, Bu^{s}OH, and Bu^{t}OH, the partition coefficient of the isomers between the aqueous and organic phases decreases by 2—3 times.[5]

Published data on the excess thermodynamic functions of mixtures of isomeric butyl alcohols with organic solvents are lacking. These measurements have recently been performed for mixtures of the alcohols with acetone.[6] Both alcohol—alcohol and alcohol—acetone interactions occur in these systems; however, the positive excess enthalpies (H^E) and excess volumes (V^E) indicate that interactions of the first type predominate. Isomerism slightly affects the H^E values, whereas V^E increase sharply on going from Bu^{n}OH to Bu^{t}OH solutions.

In this work, we determined the heats of dissolution of squalane in mixtures of acetone with isomeric butyl alcohols and compared different approaches for the description of experimental data and revealing of the solvation processes in acetone—butanol isomer—nonpolar non-electrolyte triple systems.

Experimental

Hydrocarbon squalane (2,6,10,15,19,23-hexamethyltetracosane) was chosen as a dissolved substance due to its low volatility, which provides some advantages in calorimetric experiments. Squalane ("for chromatography," Merck) was used as received. Solvents were purified by known procedures.[7] Acetone—butyl alcohol mixtures were prepared by the gravimetric method with an accuracy to 0.001 molar fractions. Heats of dissolution of squalane in mixtures of butyl alcohols with acetone were measured by a calorimeter with an isothermical shell. A glass tube containing 0.2—0.3 mL of squalane was broken in a calorimetric flask containing 60 mL of a solvent. The thermometric and thermal sensitivities of the installation were $5 \cdot 10^{-6}$ deg and $5 \cdot 10^{-3}$ J, respectively, per mm of the detector scale. The instrumental error of measurements was ≤0.5%.

The average values of two—three measurements of the thermal effect of dissolution were accepted as the standard enthalpies of dissolution (ΔH°_{sol}), because no noticeable dependences of the enthalpies of dissolution on the concentration of squalane were observed. For example, the enthalpies of dissolution of squalane in Bu^{n}OH at contents of the solvent m = 0.0109, 0.0187, and 0.0214 mol kg^{-1} were 8.21, 8.15, and 8.24 kJ mol^{-1}, respectively. The calorimeter was tested by measurements of the enthalpies of dissolution of squalane in $CHCl_3$ and CCl_4, which were found to be 11.10 and 4.84 kJ mol^{-1}. These are in agreement with the published data[8]: 11.12±0.05 and 4.67±0.08 kJ mol^{-1}.

Results and Discussion

The applicability of Eq. (1) for the description of the dependence of the enthalpy of dissolution on the composition of the binary solution has previously[8] been shown

$$\Delta H^\circ_{sol} = X_1 \Delta H^\circ_{sol,1} + X_2 \Delta H^\circ_{sol,2} - H^E_{12}, \qquad (1)$$

where ΔH°_{sol}, $\Delta H^\circ_{sol,1}$, and $\Delta H^\circ_{sol,2}$ are the enthalpies of dissolution of hydrocarbon in a mixture of the specified

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composition and in its components for the state of an infinitely dilute solution of the solute; H^E_{12} is the molar enthalpy of mixing for the binary system; and X is the molar fraction.

The ΔH°_{sol} and H^E_{12} values[6] were approximated by polynomials (2) and (3) whose coefficients are given in Table 1. The approximated values of the enthalpies of dissolution are presented in Table 2.

$$\Delta H^\circ_{sol} = \Sigma\, a_i X_2^{\,i}, \qquad (2)$$

$$H^E_{12} = b_0 X_1 X_2. \qquad (3)$$

The accuracy of the description depends on the symmetry of the excess heats of mixing of the components of the mixture and excess heats of dissolution of squalane. As follows from Table 2, Eq. (1) describes the acetone—*n*-butyl alcohol and acetone—isobutyl alcohol systems sufficiently well; the description is satisfactory for the acetone—*sec*-butyl alcohol system but is much worse for acetone—*tert*-butyl alcohol. This is related to the fact that in the case of a system containing *tert*-butyl alcohol, H^E_{12} is symmetric, and the minimum of the excess enthalpy of squalane is shifted toward alcohol formation.

It was established[9—11] that the enthalpy of transfer (dissolution) of substances in binary mixtures can be expressed by Eq. (4), which describes different contributions to the overall effect of solvation:

$$\Delta H^\circ_{tr} = \frac{PX_2}{X_1 + PX_2}\Delta\Delta H^\circ_{int,21} - \frac{\alpha n + \beta N}{X_1 + PX_2}(x_1 L_1 + PX_2 L_2) + (\alpha n + \beta N)\frac{PX_2}{X_1 + PX_2}\Delta\Delta H^\circ_{vap}. \qquad (4)$$

Here L_1 and L_2 are the relative partial molar enthalpies of the components of the binary solvent; $\Delta\Delta H^\circ_{int,21} = \Delta H^\circ_{int,2} - \Delta H^\circ_{int,1}$ is the difference in the enthalpies of the interaction of the solute with the components of the mixture; P is the factor of correspondence of the composition of the solvate shell to the composition of the mixture (at $P = 1$ no selective solvation is observed, at $0 < P < 1$ the solute is predominantly solvated by molecules of the first component, and at $P > 1$ it is solvated by molecules of the second component); $\alpha n + \beta N$ is the parameter that reflects the influence of the solute on intermolecular interactions in the binary mixed solvent; and $\Delta\Delta H^\circ_{vap}$ is the difference in the enthalpies of evaporation of the second and first components.

In the general case, E . (4) is solved by iteration with respect to the $\alpha n + \beta$, P, and $\Delta\Delta H^\circ_{int,21}$ parameters, which suggests the character of the intermolecular interactions and solvation of the solute in the binary mixture. We performed th corresponding calculations for all systems under study The results of calculations are presented in Table 3. approximated values of the enthalpies of dissolution w re used (the coefficients of the polynomials are presen d in Table 1).

Table 1. Coefficients (kJ mol^{-1}) of polynomials (2) and (3) for the approximation of enthalpies of dissolution and their parameters (s and r)

Coefficient	Bu^{n}OH	Bu^{i}OH	Bu^{s}OH	Bu^{t}OH
a_0	27.0	27.1	27.0	27.0
$-a_1$	26.5	24.0	21.1	18.5
a_2	7.7	7.0	−3.1	−10.9
a_3	—	—	8.9	16.3
s_2	0.09	0.10	0.23	0.13
r_2^2	0.999	0.999	0.999	0.999
b_0	6.6	6.8	6.3	6.1
s_3	0.04	0.03	0.07	0.03
r_3^2	0.995	0.998	0.992	0.998

Table 2. Experimental (ΔH°_{sol} $_{,p}$) and calculated by Eqs. (1), (2), (4), and (7) enthalpic of dissolution of squalane (kJ mol^{-1}) in mixtures of aceto e with isomers of butyl alcohols at 25 °C

X_2	$\Delta H^\circ_{sol,exp}$	ΔH°_{sol} (1)	Δ $^\circ_{sol}$ (2)	ΔH°_{sol} (4)	ΔH°_{sol} (7)
		Acetone—*n*-	utyl alcohol		
0.000	27.0	27.0	27.0	27.0	27.0
0.241	21.0	21.3	21.1	21.2	20.9
0.496	15.9	16.0	15.8	15.8	15.8
0.755	11.3	11.5	11.4	11.4	11.5
1.000	8.2	8.2	8.2	8.2	8.2
		Acetone—is	utyl alcohol		
0.250	21.6	21.6	21.5	21.5	21.4
0.500	16.8	16.9	16.8	16.9	16.8
0.750	12.9	13.0	13.0	13.1	13.1
1.000	10.0	10.0	10.0	10.0	10.0
		Acetone—*se*	butyl alcohol		
0.250	21.6	22.0	21.7	21.5	21.2
0.501	17.0	17.8	16.8	16.8	16.9
0.752	13.1	14.3	13.2	13.3	13.5
1.000	11.8	11.8	11.8	11.8	11.8
		Acetone—*ter*	butyl alcohol		
0.248	22.0	22.7	22.0	21.7	20.7
0.500	17.1	19.0	17.1	17.2	17.3
0.646	15.0	17.2	14.9	15.1	16.0
0.752	13.8	16.1	13.9	14.3	15.3
1.000	14.0	13.9	13.9	13.9	13.9

Table 3. Parameters of solva on of squalane in mixtures of acetone with isomeric butyl cohols calculated by Eqs. (4) and (7)

Alcohol	$\alpha n + \beta N$	$\Delta\Delta H$ $_{nt,21}$ /kJ r ol^{-1}	P (4)	P (7)
Bu^{n}OH	1.14	−4[illegible].2	1.00	1.51
Bu^{i}OH	1.04	−3[illegible].6	1.01	1.50
Bu^{s}OH	2.34	−[illegible].7	0.74	1.65
Bu^{t}OH	3.29	−[illegible].7	0.60	2.86

Let us consider the possibility of an unprejudiced reflection of the solvation effects in the systems under study by the data obtained. According to the model,[9–11] the positive value of the $\alpha n + \beta N$ parameter indicates that the solute weakens the solvent—solvent interaction in the solvate shell. However, this is not entirely adequate in our case. In fact, the third term in Eq. (4) is positive and, hence, the additive contribution to the solvent—solvent interaction is also positive, *i.e.*, squalane weakens the interaction. However, the second term is negative for all systems, because the enthalpies of mixing of acetone with all isomeric butyl alcohols are positive. Thus, the excess enthalpy of mixing in the solvate shell of squalane becomes negative, *i.e.*, the solvent—solvent interaction is enhanced.

The value of the P parameter calculated by Eq. (4) indicates the absence of preferential solvation of squalane in the mixtures of acetone with $\mathrm{Bu^nOH}$ and $\mathrm{Bu^iOH}$ and the enrichment of the solvate shell of squalane in acetone in the acetone—*sec*-butyl alcohol and acetone—*tert*-butyl alcohol systems. The $\Delta\Delta H^\circ_{\mathrm{int},21}$ parameter in all systems is much less than zero. This indicates that in individual solvents squalane interacts with the alcohol much more strongly than with acetone. If squalane, which interacts poorly with the solvent, interacts more strongly with the alcohol (see Table 3), the question arises as to why in the binary systems the preferential solvation is either absent or is present but manifested from acetone? This contradiction cannot be explained in the framework of the model described.[9]

Let us consider the $\Delta\Delta H^\circ_{\mathrm{int},21}$ values. If we know the difference in the enthalpies of interaction of the solute with pure components of the mixture, the difference in the enthalpies of interaction of squalane with isomers of butyl alcohol can be calculated from the data in Table 3. Based on the general concepts, it must not be too high. At the same time, the difference in the enthalpies of interaction obtained from Eq. (4), especially in the case of $\mathrm{Bu^tOH}$ and $\mathrm{Bu^nOH}$, is so substantial that the results presented in Table 3 seem doubtful. Note that "unreal" enthalpies of interaction were also obtained, in several cases by the authors of the model described.[9–12] For example, the difference in the enthalpies of interaction of $\mathrm{Bu^tOH}$ with dioxane and water[12] is equal to 213±35 kJ $\mathrm{mol^{-1}}$, and that for tetrabutylammonium bromide with dioxane and water[11] is 2500±2400 kJ $\mathrm{mol^{-1}}$. This is due to the fact that the enthalpy of evaporation in the majority of solvents cannot adequately reflect the formation of a cavity. In addition, another reason can lead to the uncertainty in the values obtained. If preferential solvation is not observed ($P = 1$), Eq. (4) can be written as follows:

$$\Delta H^\circ_{\mathrm{tr}}/X_2 = \Delta\Delta H^\circ_{\mathrm{int},21} + (\alpha n + \beta N)H^{\mathrm{E}}/X_2 - \\ - (\alpha n + \beta N)\Delta\Delta H^\circ_{\mathrm{vap}}. \qquad (5)$$

It can easily be noticed that the excess enthalpy of transfer of the dissolved substance is determined by the second term. Therefore, the $\alpha n + \beta N$ parameter can unambiguously be calculated from the excess enthalpy of transfer and enthalpy of mixing. Then Eq. (5) can be solved at any values of the enthalpies of evaporation and the $\alpha n + \beta N$ parameter, which can result in doubtful $\Delta\Delta H^\circ_{\mathrm{int},21}$ values. In this case, the $\Delta\Delta H^\circ_{\mathrm{int},21}$ parameter should be excluded from Eq. (4), combining in the latter the first and third terms:

$$\Delta H^\circ_{\mathrm{tr}} = \frac{PX_2}{X_1 + PX_2}\Delta\Delta H^\circ_{\mathrm{sol},21} - \\ - \frac{\alpha n + \beta N}{X_1 + PX_2}(x_1L_1 + PX_2L_2). \qquad (6)$$

Here the first term takes into account the contribution from the preferential solvation $\Delta H^\circ_{\mathrm{tr}} = f(P)$, and the second term corresponds to the excess enthalpy of mixing in the solvate shell $(H^{\mathrm{E}})'$. Thus, the deviation of the transfer enthalpy from additivity in the framework of the accepted model can be due to two reasons: preferential solvation and the "non-ideal" character of mixing of the solvent in the solvate shell ($(H^{\mathrm{E}})' \neq 0$). It is easy to obtain the one-parameter equation (7) from Eq. (6) under the assumption that $\alpha n = -\beta N$, *i.e.*, if the enthalpy of mixing of the components in the solvate shell is accepted to be equal to zero.

$$\Delta H^\circ_{\mathrm{tr}} = \frac{PX_2}{X_1 + PX_2}(\Delta H^\circ_{\mathrm{sol},2} - \Delta H^\circ_{\mathrm{sol},1}). \qquad (7)$$

In the framework of the model,[9] the composition of the solvate shell of a particle of the solute X_2' is determined from the correlation

$$X_2' = PX_2/(X_1 + PX_2). \qquad (8)$$

The correlation proposed earlier[13] follows from Eqs. (7) and (8)

$$\Delta H^\circ_{\mathrm{tr}} = X_2'(\Delta H^\circ_{\mathrm{sol},2} - \Delta H^\circ_{\mathrm{sol},1}). \qquad (9)$$

Based on Eq. (7), we calculated P for all systems, which results are presented in Table 3. It turned out that the experimental data are mainly described with an error close to the experimental one; however, it is higher in the acetone—*tert*-butyl alcohol system. Since $P > 1$, this indicates the preferential solvation of squalane by alcohol.

Thus, two variants of calculation, which appropriately, as a whole, describe the experimental data, are available. The accuracy of the description is a necessary but insufficient condition for the adequacy of the model. In all alcohols, the dissolution of squalane occurs by 15—20 kJ $\mathrm{mol^{-1}}$ more exothermically than in acetone. This difference is probably due to a stronger interaction of squalane with alcohol. Thus, based on the presented considerations, we may state that the P values obtained from Eq. (7) are more realistic than those calculated from Eq. (4).

It should specially be mentioned that the P values calculated from Eq. (7) and presented in Table 3 are average for the whole interval of compositions, *i.e.*, $P =$ const, as in the case of Eq. (4). If this restriction is removed, in the case of the extreme character of the dependence $\Delta H^\circ_{sol} = f(X)$, the value of the P parameter and the corresponding X_2' value in the region of an extreme have no physical sense. For example, in the Me_2CO-Bu^tOH system at $X_2 = 0.75$, we have $P = -21.2$ and $X_2' = 1.02$. Thus, in this case, the deviation of the enthalpy from additivity is due to at least two properties: preferential solvation and the "non-ideal" character of the binary solvent in the solvate shell of squalane. Now let us quantitatively estimate these contributions to the excess enthalpy of solvation and reveal which of the solvents, alcohol or acetone, preferentially solvates squalane?

Accept that the P parameter is a linear function of the composition of the mixture (*i.e.*, is additive with respect to the composition). The simplest form of the non-additive dependence $\Delta H^\circ_{sol} = f(X)$ is a square parabola.

Let us introduce the constant

$$C = -a_2/(a_1 + a_2). \qquad (10)$$

Then we obtain the equation with one constant

$$P = (1 + CX_1)/(1 - CX_2). \qquad (11)$$

The additive function is specified by the equation:

$$P_{ad} = (1 - C^2X_1)/(1 - C). \qquad (12)$$

After simplifications we obtain the equation for $\Delta P/P$:

$$\Delta P/P = C^3X_1X_2/[(1 + CX_1)(C - 1)]. \qquad (13)$$

The $|\Delta P/P|$ value takes the highest value in the medium region of compositions of the binary mixture. The $|\Delta P/P|$ values at $X_2 = 0.5$ are presented below. It can be seen that the $|\Delta P/P|$ ratio increases sharply as C increases, and at low C values, the nonlinear character of $P(X)$ can be neglected, whereas at $C > 0.5$, $|\Delta P/P| > 5\%$.

C	0.40	0.45	0.50	0.55	0.60
$\lvert\Delta P/P\rvert$ (%)	2.2	3.4	5.0	14.5	41.5

It can be accepted that at C lower or equal to 0.5, the P value is additive by composition. For mixtures of acetone with Bu^nOH and Bu^iOH, the C value is equal to 0.41.

The cubical polynomial $\Delta H^\circ_{sol} = f(X)$ for the Me_2CO-Bu^sOH and Me_2CO-Bu^tOH systems with the a_i coefficients (see Table 1) contains the C parameter:

$$C = -(a_2 + a_3)/(a_1 + a_2 + a_3). \qquad (14)$$

The C values calculated from Eq. (14) amount to 0.39 and 0.42 for the Me_2CO-Bu^sOH and Me_2CO-Bu^tOH systems, respectively.

Thus, for the four systems studied, the C constant has virtually the same value: $C_{av} = 0.40$ and, according to Eq. (12), $P_{add} = 1.40 + 0.27X_2$. It is clear that in all systems, the composition of the solvate shell of squalane similarly differs from the composition of the mixture, which confirms the previously drawn conclusion that the squalane—butyl alcohol interaction is almost independent of the type of isomer.

In the Me_2CO-Bu^sOH and Me_2CO-Bu^tOH systems, only a portion of the excess enthalpy of squalane is due to preferential solvation of the alkane by the alcohol. Calculation of the contributions $\Delta\Delta H^\circ_{sol}(P)$ and $(H^E)'$ for these systems ($X_2 = 0.75$) showed that in the Me_2CO-Bu^sOH system the excess enthalpy of mixing of the solvent in the solvate shell of squalane is ~50% of $\Delta\Delta H^\circ_{sol}$, whereas it is ~70% in the Me_2CO-Bu^tOH system. The mixing of the solvent in the solvate shell of squalane is more exothermic in the second of the systems under consideration.

Thus, the proposed approach to the analysis of the enthalpy parameters in triple systems has the advantage that it does not require knowledge of the enthalpy of the binary system, as is needed with the earlier described method.[13] At the same time, it has no limitations in the case of the extreme form of the $\Delta H^\circ_{sol}(X)$ function and allows one to distinguish contributions from preferential solvation and also those from the non-ideal character of the binary solvent in the solvate shell of the solute.

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