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Enthalpy of Solution of Squalane in Alcohols

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Abstract—Enthalpy of solution at 25°C of squalane in butyl alcohols and 1-octanol is determined calorimetrically. The endothermic effect of dissolution increases in the order 1-OctOH < BuOH < *i*-BuOH < *t*-BuOH. A linear correlation is found between the enthalpies of solution of squalane and hexadecane, from which the enthalpy of solution of squalane in methanol is determined. The contributions of the cavity formation and solute–solvent interaction to the enthalpy of solution are estimated by multiple regression analysis. The enthalpy of cavity formation is only slightly dependent on the length of the main chain of an alcohol and also on the branching type, varying in the order 1-OctOH ~ BuOH ~ *i*-BuOH < MeOH ~ *s*-BuOH < *t*-BuOH. Interaction of squalane with alcocols increases in the order MeOH < *t*-BuOH < BuOH < ~ *i*-BuOH ~*s*-BuOH < 1-OctOH.

It was demonstrated previously [1] that the enthalpy of solvation of a methylene group of alkanes in 19 individual solvents (18 organic solvents of various natures + water) are fitted well by a two-parameter equation with the polarizability $[(n^2 - 1)/(2n^2 + 1)]$ and polarity/polarizability π^* by Kamlet and Taft as parameters. In the cited work the authors themselves noted that they found no theoretical substantiation for this equation. It is worth noting that the parameter π^* is not an intrinsic characteristic of a solvent, but only its response to interaction with some probe. Furthermore, Kamlet *et al.* indicated in [2] that some difficulties arise in development of the π^* scale for H-bonded solvents, among them alcohols, since in this case the contribution of specific interaction between a solvent and a probe cannot be ignored.

Batov and Korolev [3] derived equations allowing estimation of the enthalpy of solution of an alkane in an individual solvent from the cohesion energy density of the solvent and the van der Waals molar volume of the solute. However, in this case the authors were forced to subdivide solvents into two groups: unassociated and H-bonded solvents.

It should be pointed out that the problem of dividing the integral enthalpy of solvation into particular contributions from various kinds of interaction in solution remains to be further sudied. For example, it is still not understood why the endo effect in dissolution of alkanes drastically increases in a series of alcohols 1-OctOH, BuOH, *t*-BuOH, MeOH and how the enthalpies of cavity formation and solvent–solute interaction change in this series. The thought of Solomonov and Konovalov [4] is that the interaction energy of an alkane with a solvent is independent of their nature. Then weakening solvation of *n*-alkanes in a series of alcohols on passing from 1-octanol to methanol [1] can be attributed only to increasing endo effect of cavity formation. However, calculations in terms of the scaled particle theory showed that the enthalpies of cavity formation in various alcohols differ insignificantly, only slightly decreasing in the series 1-OctOH, *t*-BuOH, *s*-BuOH, BuOH, MeOH, *i*-BuOH [5]. If so, the observed weakening of solvation of an alkane on passing from 1-octanol to methanol can be attributed only to a weaker interaction between the hydrocarbon and methanol, as compared to octanol.

Table 1. Enthalpy of solution (kJ mol^{-1})[a] of squalane in alcohols at 25°C

Alcohol	$m \times 10^4$	ΔH_m	Alcohol	$m \times 10^4$	ΔH_m
BuOH	85	8.29	*s*-BuOH	117	11.81
	96	8.16		129	11.91
	109	8.21		201	11.70
	120	8.25	*t*-BuOH	51	14.00
	180	8.12		104	13.90
	187	8.15		112	13.99
	214	8.24	1-OctOH	128	4.68
	262	8.18		158	4.76
i-BuOH	163	10.14		311	4.66
	179	10.10			
	346	9.88			

[a] m is the molal concentration of squalane and ΔH_m is the enthalpy of solution at a given concentration.

Table 2. Solvent characteristics at 25°C [12–14][a]

Alcohol	V_m, cm^3 mol^{-1}	$\alpha_e \times 10^3$, K^{-1}	$\beta_T \times 10^{10}$, Pa^{-1}	$\Delta_{vap}H^0$, kJ mol^{-1}	n_D
1-OctOH	158.4	0.827	7.778	71.0	1.4275
BuOH	92.0	0.932	9.445	52.4	1.3973
i-BuOH	92.9	0.953	9.970	50.8	1.3939
s-BuOH	92.3	1.072	9.760	49.7	1.3950
t-BuOH	94.9	1.408	10.820	46.8	1.3851
MeOH	40.7	1.196	12.616	37.8	1.3265

[a] (V_m) Molar volume, (α_e) thermal expansion coefficient, (β_T) isothermal compressibility factor, ($\Delta_{vap}H^0$) enthalpy of vaporization, and (n_D) refractive index.

Table 3. Solvent parameters including the enthalpies of solution of squalane (kJ mol^{-1}) at 25°C, both experimental (ΔH^0_{exp}) and calculated by Eqs. (2)–(4) (ΔH^0_{calc})

Parameter[a]	1-OctOH	BuOH	*i*-BuOH	*s*-BuOH	*t*-BuOH	MeOH
p	0.499	0.625	0.599	0.589	0.538	1.000
P_R	1.000	0.902	0.891	0.894	0.862	0.676
π	0.817	0.758	0.735	0.844	1.000	0.729
α_e	0.587	0.662	0.677	0.761	1.000	0.849
ΔH^0_{exp}	4.70	8.20	10.0	11.8	14.0	20.5
ΔH^0_{calc} (2)	4.87	9.22	9.50	10.7	14.5	20.6
ΔH^0_{calc} (3)	4.56	9.31	9.91	10.6	14.4	20.5
ΔH^0_{calc} (av.)	4.72	9.26	9.70	10.7	14.4	20.5
ΔH^0_{calc} (4)	5.22	9.28	9.07	10.6	14.5	20.6

[a] [$p = (\Delta_{vap}H^0 - RT)/V_m$] Cohesion energy density, {$P_R = [(n^2 - 1)/(2n^2 + 1)]^2$} Rummens' function, and ($\pi = \alpha_e T/\beta_T$) internal pressure. Each parameter is normalized to one of the alcohol.

It should be pointed out that it is a rather difficult problem to study alkane solutions by the thermochemical method. High volatility of many alkanes causes some side effects which are difficult to take into account in a calorimetric experiment. Therefore, in this work we used the low-volatile branched alkane, squalane (2,6,10,15,19,23-hexamethyltetracosane) as a solute. Squalane is liquid over a wide temperature range, which also can be regarded as an advantage. Data on the enthalpies of solution of squalane in alcohols are given in Table 1.

Unfortunately, we were unable to determine the enthalpy of solution of squalane in methanol, because of its extremely low solubility in this solvent. This value was then determined theoretically (20.5 kJ mol^{-1}) from a linear correlation (1) between the enthalpies of solution of squalane and hexadecane [5, 6] in 5 alcohols studied.

$$\Delta H^0(C_{30}H_{62}) = 0.19 + 1.506\Delta H^0(C_{16}H_{34}); \quad (1)$$

$$s\ 0.23,\ r\ 0.9990.$$

Here s is the standard deviation (kJ mol^{-1}) and r is the correlation factor.

The fact of a perfect direct correlation between the enthalpies of solution of squalane and haxadecane confirms the conclusion that the enthalpy of solution is practically totally controlled by the size of an alkane molecule, but not by its structure [3, 7].

Presently there are no sufficiently rigorous methods for determination of various particular contributions to the integral enthalpy of solvation. In terms of formal modeling multiple regression analysis is widely used. Physicochemical characteristics of the solvents and parameters used by various authors in analysis of solvation effects [3, 8–11] are presented in Tables 2 and 3. The corresponding comments regarding selection of these parameters will be offered in the discussion below.

Our analysis showed that single-parameter equations cannot provide acceptable results in treating the enthalpy of solution of squalane in six alcohols studied. Among two-parameter equations, Eqs. (2)–(4) gave the best quality of approximation.

$$\Delta H^0 = 46.57 - 51.869P_R + 12.449\pi; \quad (2)$$
$$s\ 0.93,\ r\ 0.985;$$

$$\Delta H^0 = 39.43 - 40.797P_R + 10.093\alpha_e; \quad (3)$$
$$s\ 0.96,\ r\ 0.984;$$

$$\Delta H^0 = -16.77 + 19.986p + 20.480\alpha_e; \quad (4)$$
$$s\ 1.16,\ r\ 0.977.$$

In multiple regression analysis the equation parameters should not be in linear correlation to each other. In our case this requirement is met. The correlation factors for the corresponding pairs of parameters are low: 0.42 (P_R and π), 0.40 (p and α_e), and 0.42 (P_R and α_e). Under these conditions the second and third terms in Eqs. (2)–(4) should correspond to various particular contributions to the enthalpy of solution.

Let us first consider the Rummens' function. It was used earlier by Stengle *et al*. [10] in analysis of the chemical shift of xenon in aliphatic alcohols. The thought of the authors of the cited work is that P_R is a parameter characterizing the solvent–solute dispersion interaction, and we are apt to agree with them. Note that Eqs. (2) and (3) including the parameter P_R best reproduce the enthalpy of solution. Negative values of the factors at P_R mean that the solvent–solute interaction increases with increasing P_R, which appears quite logical.

The third term in Eqs. (2) and (3) includes different parameters, namely, the internal pressure of a fluid and thermal expansion coefficient. The former was previously used in [11] for estimating the contribution of cavity formation, and the latter is used for the same purpose in the scaled particle theory (as $\alpha_e RT^2$). Note that the factors at π and α_e are positive, i.e., the endo effect of cavity formation increases with increasing the internal pressure and thermal expansion coefficient.

Since Eq. (4), similar to Eq. (3), also includes α_e in the third term, it is natural to suppose that this term corresponds to the contribution of cavity formation. Then the second term in Eq. (4) should correspond to the contribution of solvent–solute interaction. This result appears to be important in view of the fact that the cohesion energy density is often used to take into account the effect of cavity formation, regardless of the solvent nature. Our analysis suggests that in H-bonded solvents this parameter reflects the contribution of solvent–solute interaction rather than of cavity formation [Eq. (4)]. In this case the higher the cohesion energy density, the weaker the solvent–solute interaction. This conclusion is also supported by the fact that we found a correlation between P_R and p (r 0.93) for six alcohols studied. Therefore, to estimate the contribution of cavity formation in protic solvents, one may recommend the equation $\Delta_{cav}H^0 = \pi V_m$, where V_m is the solute molar volume [11].

The enthalpies of solution of squalane in alcohols, experimental and calculated by Eqs. (2)–(4), are given in Table 3. Although the standard deviation estimated for Eq. (4) is only slightly higher than that for Eqs. (2) and (3), the enthalpies estimated for four alcohols by Eq. (4) differ from the experimental values by 10% and more. For this reason we excluded Eq. (4) from further analysis. The enthalpies estimated by Eqs. (2) and (3) and then averaged differ from the experimental value for four alcohols by no more than 3% and for only two alcohols (BuOH and *s*-BuOH) of six the difference was about 1 kJ mol^{-1} (10%).

To estimate the particular contributions to the enthalpy of solution by Eqs. (2) and (3), it is necessary to pass from the dissolution parameters to parameters characterizing transfer from the solvent S_1 to the solvent S_2, thus eliminating the constants in the equations.

$$\Delta_{tr}H^0(S_1 \rightarrow S_2) = -51.869[P_R(S_2) - P_R(S_1)]$$
$$+ 12.449[\pi(S_2) - \pi(S_1)] = H_{int}(P_R) + H_{cav}(\pi), \quad (5)$$

$$\Delta_{tr}H^0(S_1 \rightarrow S_2) = -40.797[P_R(S_2) - P_R(S_1)]$$
$$+ 10.093[\alpha_e(S_2) - \alpha_e(S_1)] = H_{int}(P_R) + H_{cav}(\alpha_e). \quad (6)$$

The enthalpy terms assigned as $H_{int}(P_R)$, $H_{cav}(\pi)$, and $H_{cav}(\alpha_e)$ are given in Table 4. Since the particular contributions estimated by Eqs. (5) and (6) are reasonably consistent, in discussion we will use the averaged values (H^{av}).

Interaction of squalane with alcohols increases noticeably in the series of *n*-alcohols (MeOH, BuOH, 1-OctOH), being insignificantly dependent of the isomer nature, only slightly decreasing for *t*-BuOH (*t*-BuOH < BuOH ~ *i*-BuOH ~ *s*-BuOH). The difference in the enthalpies of cavity formation in the alcohols studied is within 3 kJ mol^{-1}, i.e., it is considerably lower than the difference in the interaction enthalpies (up to 15 kJ mol^{-1}). The highest endo effect of cavity formation is found in *t*-BuOH. For the rest five alcohols the difference in H_{cav} is no more than 1 kJ mol^{-1}. Therefore, the solvent tends to preserve such orientation of its molecules that provides the most favorable conditions for intermolecular interaction.

Table 4. Enthalpies (kJ mol^{-1}) of interaction of squalane with alcohols (H_{int}) and of cavity formation (H_{cav}), estimated by Eqs. (5) and (6), and the entropy of cavity formation [S_{cav} (J mol^{-1} K^{-1})][a]

Alcohol	H_{int} (P_R)	H_{int} (P_R)	H_{int}^{av}	H_{cav} (π)	H_{cav} (α_e)	H_{cav}^{av}	H_{cav}^{SPT}	S_{cav}
1-OctOH	–16.80	–13.22	–15.0	–2.28	–4.17	–3.2	0.6	–10.7
BuOH	–11.72	–9.22	–10.5	–3.01	–3.41	–3.2	–2.4	–10.7
i-BuOH	–11.15	–8.77	–10.0	–3.30	–3.26	–3.3	–3.8	–11.1
s-BuOH	–11.31	–8.89	–10.1	–1.94	–2.41	–2.2	–2.1	–7.4
t-BuOH	–9.65	–7.59	–8.6	0	0	0	0	0
MeOH	0	0	0	–3.37	–1.52	–2.4	–3.2	–8.1

[a] H_{cav}^{SPT} is estimated from data of [5] for heptane in alcohols, and S_{cav}, by Eq. (7) from data on H_{cav}^{av}.

Only in the case of *t*-BuOH, whose molecules are nearly spherical, having the highest symmetry, the structure-breaking effect of the solute is more clearly pronounced.

In Table 4 the results obtained are compared with the enthalpy of cavity formation estimated in [4] for heptane (molecular size 0.613 nm) in the framework of the scaled particle theory (H_{cav}^{SPT}). The difference in the size of squalane and heptane [by a factor of about 1.5, if the molecular diameters are estimated from the molar volumes as $(525/147)^{1/3}$] may be regarded as insignificant, if we want to follow the trends in variation of H_{cav}^{av} and H_{cav}^{SPT}. The both parameters equally demonstrate that the energy of cavity formation decreases on passing from *t*-BuOH to the other butyl alcohols. However, comparison of the H_{cav}^{SPT} values suggests that octanol is a more structured solvent than methanol, which casts a strong doubt. It follows from our analysis that methanol is a somewhat more structured solvent.

To conclude the discussion on the enthalpy characteristics, on the basis of our analysis we may firmly state, for example, that weakening of solvation of squalane in *t*-BuOH by 4 kJ mol^{-1} as compared to *i*-BuOH is caused for about one third by a weaker interaction and for the rest two thirds by a higher energy of cavity formation in *t*-BuOH. A stronger endo effect of dissolution of squalane in methanol as compared to 1-octanol (by 16 kJ mol^{-1}) is caused for 95% by a weaker interaction of the alkane with MeOH. The results obtained in this work do not confirm the hypothesis that the enthalpy of interaction of an alkane with solvents is independent of their nature [4]. In our case this is true only for butyl alcohol isomers. More likely, one can say that the enthalpy of cavity formation is a nearly constant value, at least in the series of normal aliphatic alcohols.

Finally, let us consider the question of the state of a solvent in the solvation sphere of a solute. Table 4 shows that H_{cav}^{av} takes the minimal and the maximal values in *i*-BuOH and *t*-BuOH, respectively. The rest alcohols take an intermediate position. To answer the question as to what is the difference between the states of an alcohol in the solvation sphere of an alkane and in the bulk, let us attract the results obtained by Grunwald and Steel [15]. They have demonstrated for a general case that the Gibbs energy of solvation (and, therefore, of transfer) of a particle includes only the contribution of its interaction with a solvent ($G_{solv} = G_{int}$). In solvation, cavity formation in a solvent (authors of [15] use the term solvent reorganization) provides no contribution to the Gibbs energy of solvation as a result of the enthalpy–entropy compensation [Eq. (7)].

$$H_{cav} = TS_{cav}. \qquad (7)$$

The entropy of cavity formation (solvent reorganization), estimated by Eq. (7), is also given in Table 4. This parameter allows judging the evolution in the solvent structuring on its transfer from the bulk to the solvation shell. Since cavity formation is an endothermic process, according to Eq. (7) the entropy of cavity formation should be positive, i.e., a solvent in the solvation shell is less structured as compared to its state in the bulk of solution. Data on S_{cav} (Table 4) show that the structure-breaking effect of the alkane on an alcohol increases in the order *i*-BuOH < 1-OctOH < BuOH, MeOH < *s*-BuOH, *t*-BuOH.

Note as a conclusion that the results of [15] seem to us basically important. The reason is as follows. It is almost commonly accepted to interpret changes in the enthalpies of solution of compounds in mixed, for example, aqueous-organic solvents in terms of structure making or structure breaking of water by organic nonelectrolyte additions. Results obtained in [15] theoretically substantiate for this concept.

EXPERIMENTAL

The solvents used were purified by the standard procedures [16]. Squalane (chromatographically pure grade, Merck) was used without further purification. The enthalpy of solution of squalane in 1-octanol and butyl alcohols was measured with a isothermal-shell variable-temperature ampule calorimeter. The thermometrical and thermal sensitivities of the experimental setup were 5×10^{-6} deg mm^{-1} and 5×10^{-3} J mm^{-1} measuring scale, respectively. As the standard enthalpies of solution (ΔH^0) we accepted the mean thermal effects of dissolution (ΔH_m), since it was demonstrated that the enthalpy of solution is practically independent of the squalane concentration. To test the calorimetric system efficiency and the quality of squalane, we initially measured its enthalpy of solution in chloroform and CCl_4. The results obtained are as follows (given in the parentheses are the reference data from [17]) (kJ mol^{-1}): 11.10 (11.12 ± 0.05) and 4.84 (4.67 ± 0.08), respectively.

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