

Thermochemical study of the solvation of alkanes in mixtures of methanol with butyl alcohol isomers

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A calorimetric method was applied at 25 °C to measure the enthalpies of dissolution of cyclohexane, heptane, and decane in the methanol–*n*-butanol mixed solvent and hexadecane in mixtures of methanol with *n*-, *iso*-, and *tert*-butyl alcohols. The standard enthalpies of dissolution of alkanes were determined. It was shown that the equation proposed in the literature for calculation of the enthalpies of dissolution of alkanes in mixtures with nonspecific intermolecular solvent–solvent interactions describes satisfactorily the enthalpies of dissolution of alkanes in mixtures of methanol with *n*- and *iso*-butyl alcohols. It was suggested that there is no preferential solvation of alkanes by one of the mixed solvent components in the MeOH–BuⁿOH and MeOH–BuⁱOH mixtures; in the MeOH–Bu^tOH system, the composition of alkane solvation shell differs slightly from the solvent composition in the bulk.

Key words: enthalpy of dissolution, enthalpy of transfer, excess enthalpy of mixing; alkanes, methanol, butyl alcohol isomers, mixed solvent.

Isomeric butyl alcohols have virtually equal molar volumes, enthalpies of vaporization, and refraction indices. Since the degrees of association of butyl alcohols differ by no more than 10%, it can be assumed that the bond energies in the isomeric self-associates are also similar.¹ However, the empirical parameters characterizing the solvent polarity of the isomers differ appreciably.^{2,3} Thus BuⁿOH is a stronger proton donor but a weaker proton acceptor than Bu^tOH.³ Thus, isomerization has a substantial influence on intermolecular interactions in solutions in these alcohols. Previously,⁴ various excess properties of MeOH mixtures with BuⁿOH, BuⁱOH, and Bu^tOH have been measured. Among the series of excess properties, excess enthalpy of mixing of alcohols (H^E) is of interest. Since the dispersion forces in these systems are virtually identical, the differences between their excess properties are related⁴ mostly to different strengths and numbers of the H-bonds formed between the alcohol molecules. Since the proton-acceptor capacity of alcohols increases in the sequence BuⁿOH–BuⁱOH << Bu^tOH, it can be assumed that the formation of a mixed associate of MeOH with Bu^tOH is energetically more favorable than that of MeOH with BuⁿOH. This is confirmed by the magnitudes of the excess enthalpies of mixing of these systems. In the MeOH–BuⁿOH and MeOH–BuⁱOH systems, the crucial role is played by the de-

struction of hydrogen bonds between the molecules, as indicated by positive H^E values. The negative H^E values found for the MeOH–Bu^tOH system are apparently⁴ due to the fact that in this system, the formation of H-bonds predominates.

Table 1. Coefficients of the polynomials describing the enthalpies of dissolution ($\Delta_{\text{sol}}H^\circ$) of alkanes in mixtures of MeOH with BuⁿOH, BuⁱOH, and Bu^tOH and excess enthalpies of mixing (H^E) for these systems at 25 °C

Mixture, alkane (enthalpy)	a_0	a_1	a_2	a_3	R^2	S
MeOH–Bu ⁿ OH (H^E)	0.06	0.81	–0.52	—	0.999	0.005
cyclo-C ₆ H ₁₂ ($\Delta_{\text{sol}}H^\circ$)	4.91	–9.90	11.90	–5.20	0.999	0.030
C ₇ H ₁₆ ($\Delta_{\text{sol}}H^\circ$)	5.77	–11.90	12.40	–4.57	0.999	0.020
C ₁₀ H ₂₂ ($\Delta_{\text{sol}}H^\circ$)	8.15	–16.80	19.60	–8.12	0.998	0.240
C ₁₆ H ₃₄ ($\Delta_{\text{sol}}H^\circ$)	13.30	–34.90	26.90	–10.05	0.999	0.210
MeOH–Bu ⁱ OH (H^E)	0.02	0.76	–0.51	—	0.999	0.006
C ₁₆ H ₃₄ ($\Delta_{\text{sol}}H^\circ$)	13.30	–21.20	22.40	–7.80	0.999	0.300
MeOH–Bu ^t OH (H^E)	–0.01	–1.46	–0.87	2.28	0.999	0.006
C ₁₆ H ₃₄ ($\Delta_{\text{sol}}H^\circ$)	13.6	–19.90	24.40	–8.75	0.998	0.160

Note. R is the correlation coefficient; S is the error of approximation. The ΔH and H values are expressed in kJ mol^{–1}.

Table 2. Enthalpies of dissolution of alkanes in mixtures of methanol with isomeric butyl alcohols at 25 °C

Mixture, alkane	X_2	Φ_2	$\Delta_{\text{sol}}H^\circ/\text{kJ mol}^{-1}$		
			exp ^a	app ^b	calc ^c
MeOH—Bu ⁿ OH, cyclo-C ₆ H ₁₂	0.00	0.00	4.93	4.91	4.91
	0.10	0.20	4.00	4.03	4.02
	0.30	0.49	2.89	2.87	3.00
	0.57	0.75	2.06	2.16	2.27
	1.00	1.00	1.66	1.66	1.66
MeOH—Bu ⁿ OH, C ₇ H ₁₆	0.00	0.00	5.75	5.77	5.77
	0.10	0.20	4.74	4.71	4.60
	0.30	0.49	3.20	3.21	3.47
	0.80	0.90	1.88	1.88	1.97
	1.00	1.00	1.74	1.74	1.74
MeOH—Bu ⁿ OH, C ₁₀ H ₂₂	0.00	0.00	8.37	8.15	8.15
	0.11	0.21	6.33	6.59	6.37
	0.31	0.50	4.72	4.58	4.76
	0.57	0.75	0.34	3.40	3.47
	1.00	1.00	2.82	2.82	2.82
MeOH—Bu ⁿ OH, C ₁₆ H ₃₄	0.00	0.00	13.50	13.32	13.32
	0.10	0.20	10.87	11.08	11.30
	0.31	0.50	7.98	7.87	8.03
	0.57	0.75	5.96	5.98	6.20
	1.00	1.00	5.24	5.23	5.23
MeOH—Bu ⁿ OH, C ₁₆ H ₃₄	0.00	0.00	13.50	13.48	13.48
	0.20	0.36	9.50	9.80	9.20
	0.40	0.60	8.07	7.89	8.20
	0.80	0.90	6.53	6.67	6.70
	1.00	1.00	6.75	6.69	6.69
MeOH—Bu ⁿ OH, C ₁₆ H ₃₄	0.00	0.00	13.50	13.46	13.46
	0.10	0.21	11.74	11.78	20.88
	0.18	0.34	10.88	10.71	13.41
	0.30	0.50	9.31	9.59	13.35
	0.51	0.70	8.86	8.64	13.14
	0.56	0.75	8.61	8.57	15.31
	0.70	0.84	8.38	8.62	12.53
	0.80	0.90	8.74	8.81	11.99
	1.00	1.00	9.19	9.28	9.28

Note. $V_m/\text{cm}^3 \text{mol}^{-1}$ is the molar volume: cyclohexane, 108.8; heptane, 147.5; decane, 195.8; hexadecane, 294.1; MeOH, 40.7; BuⁿOH, 92.0; BuⁱOH, 92.9; and Bu^tOH, 94.9.

^a Experimental values.

^b Polynomial approximation.

^c Calculated using Eq. (1).

Previously,⁵ solutions of alkanes in mixtures with nonspecific solvent—solvent interactions have been studied. Based on a simple mixing model, the following equation was proposed:

$$\Delta_{\text{sol}}H^\circ = \Phi_1\Delta_{\text{sol}}H_1^\circ + \Phi_2\Delta_{\text{sol}}H_2^\circ - (V_3H^E/(X_1V_1 + X_2V_2)), (1)$$

where X_1 , X_2 , and Φ_1 , Φ_2 are the mole and volume fractions of the components of the mixed solvent, respectively; $\Delta_{\text{sol}}H_1^\circ$ and $\Delta_{\text{sol}}H_2^\circ$ are the enthalpies of dissolution of alkanes in the components of the mixture; and V_1 , V_2 , and V_3 are the molar volumes of the solvent components and the solute.

The sum of the first and second terms in Eq. (1) corresponds to the additive (with respect to the volume fraction) enthalpy of dissolution, while the third term is

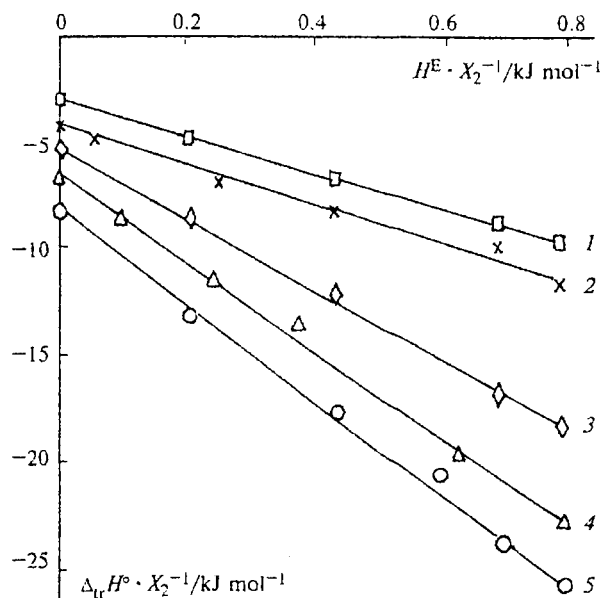


Fig. 1. Dependences of $\Delta_{\text{tr}}H^\circ \cdot X_2^{-1}$ on $H^E \cdot X_2^{-1}$ for C₆H₁₂ (1), C₇H₁₆ (2), C₁₀H₂₂ (3), and C₁₆H₃₄ (5) in the MeOH—BuⁿOH system and C₁₆H₃₄ (4) in the MeOH—BuⁱOH system.

equal to its deviation from the additivity.

We were interested in finding out whether Eq. (1) can be used to describe the enthalpies of dissolution of alkanes in those systems in which specific solvent—solvent interactions are possible and, hence, the enthalpies of mixing of various systems acquire different charges. It was also important to answer the question of whether the size of the alkane molecule influences the accuracy of the description.

We measured the enthalpies of dissolution of cyclohexane, heptane, decane, and hexadecane in mixtures of methanol with 1-butanol and hexadecane in mixtures of methanol with the isomers of butyl alcohol.

Experimental

Integral heats of dissolution of cyclohexane, heptane, decane, and hexadecane were measured at 25 °C on a variable-temperature isothermic-shell ampule calorimeter with a volume of the reaction vessel of 60 cm³. The temperature was maintained with an accuracy of 0.0002 K; the thermometric and heat sensitivities of the setup were $5 \cdot 10^{-6}$ deg per mm and $5 \cdot 10^{-3}$ J per mm of the scale of the recording device. The solvents used in the study were purified by known procedures.⁶ "Chemically pure" grade alkanes for chromatography were used as received. Mixed solvents were prepared by the gravimetric method with an accuracy of 0.01 mole fractions. The enthalpies of dissolution were measured at solute concentrations $m < 0.5 \text{ mol kg}^{-1}$ of the solvent. The arithmetic mean values of the heat of dissolution ($\Delta_{\text{sol}}H^\circ$) were taken as standard enthalpies of dissolution, because the enthalpy of dissolution virtually does not depend on the alkane concentration (hexadecane in methanol: $m = 0.1346$, $\Delta_{\text{sol}}H^\circ = 13.48 \text{ kJ mol}^{-1}$; $m = 0.3045$, $\Delta_{\text{sol}}H^\circ = 13.44 \text{ kJ mol}^{-1}$). The obtained enthalp-

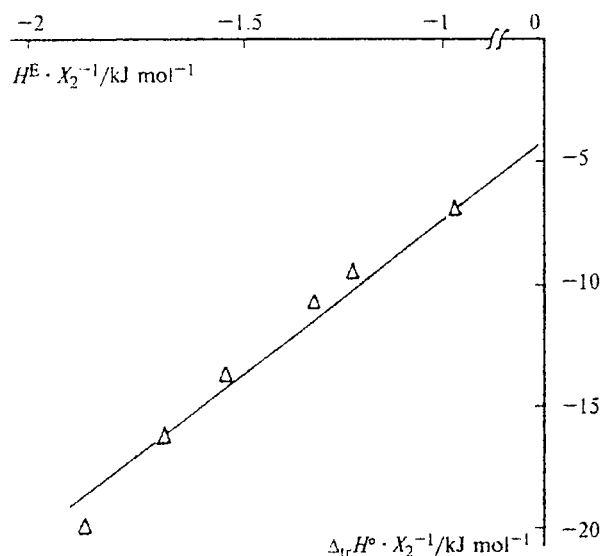


Fig. 2. Dependences of $\Delta_{tr}H^\circ \cdot X_2^{-1}$ on $H^E \cdot X_2^{-1}$ for $C_{16}H_{34}$ in the MeOH–BuⁱOH system.

ies of dissolution of heptane in BuⁿOH and cyclohexane in MeOH are in good agreement with the published data, which are given in parentheses: heptane 1.74 (1.76⁷) kJ mol^{−1}; cyclohexane 4.93 (4.94⁸) kJ mol^{−1}. The enthalpies of dissolution of decane and hexadecane in BuⁿOH fit well in the linear dependence

$$\Delta_{sol}H^\circ = a + bN_C,$$

where N_C is the number of carbon atoms in the alkane molecule (5–7, ⁷ 10, 14, ⁸ 16).

Results and Discussion

The experimental results and the published data⁴ on the excess enthalpies of mixing of the solvent components were approximated by polynomials in terms of the powers of X (where X is the mole fraction of butyl alcohol). The polynomial coefficients are listed in Table 1.

The results of our experiments and the values calculated from various equations demonstrate that Eq. (1) adequately describes the experimental data for the MeOH–BuⁿOH and MeOH–BuⁱOH systems (Table 2). The average relative difference for the description by the polynomial and Eq. (1) is 2.5%, and its maximum magnitude is 4%. In the case of dissolution of hexadecane in a mixture of methanol with *tert*-butyl alcohol, Eq. (1) gives unsatisfactory results, because the deviation of the enthalpy of dissolution of the alkane from additivity is negative (the same is true for all the other systems studied here), and the H^E value is also negative.

To interpret the processes occurring in solutions at the molecular level, various assumptions and model representations are used.^{9–12} A method proposed previously¹⁰ takes into account the contribution of the solute–solvent interactions and that of the solvent reorganization. In conformity with this assumption, in the absence of selective solvation, the linear dependence $\Delta_{tr}H^\circ \cdot X_2^{-1} = f(H^E \cdot X_2^{-1})$ should be observed. In fact, this linear dependence holds for most of the systems studied (Fig. 1). The correlation coefficients for these linear plots are no less than 0.999, and the standard deviation does not exceed 0.17. Apparently, in the mixture of MeOH with BuⁱOH, slight selective solvation occurs, because the correlation coefficient is lower (0.974), and the standard deviation is 0.92 (Fig. 2).

Apparently,⁹ preferential solvation is not realized if the $\Delta_{sol}H^\circ = f(X)$ plot is linear. It was suggested¹¹ that in this case, $\Delta_{sol}H^\circ = f(\Phi)$ should also be linear. It was found that the latter condition is fulfilled well for cyclohexane, heptane, and decane in the MeOH–BuⁿOH system. The correlation coefficients (R) are 0.998, 0.997, and 0.997, and the errors of approximation are 0.15, 0.20, and 0.30 kJ mol^{−1}, respectively. In the case of hexadecane in mixtures of MeOH with BuⁿOH, BuⁱOH, and Bu^tOH, the correlation coefficients of the linear dependences are 0.998, 0.997, and 0.798, and the approximation errors are 0.68, 0.70, and 0.80 kJ mol^{−1}, respectively.

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