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Termochemistry of Aniline Solution in Mixtures of Alcohols with Dihexyl Ether

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Abstract—The heats of solution of aniline and cyclohexane in mixtures of methanol, 1-butanol, and 1-octanol with dihexyl ether at 25°C in the entire range of compositions of the mixed solvents were measured. The enthalpies of transfer of aniline and cyclohexane from dihexyl ether to its mixtures with alcohols were calculated. It was suggested that, in methanol-based systems, the major factor is the interaction of the alcohol as an acid with aniline as a base, whereas in butanol- and octanol-based system the larger contribution is made by the interaction of the alcohol as a base with aniline as an acid.

Our previous systematic studies of aniline solvation in mixed solvents concerned aqueous-organic solvents, namely, mixtures of water with methanol, *tert*-butanol [1], isomeric butyl alcohols [2], and some aprotic solvents [3, 4]. Mixtures of two nonaqueous solvents were not studied.

In this work we chose as binary solvents mixtures of alcohols with dihexyl ether. Ethers are an interesting class of solvents. In some parameters (cohesion energy density, Dimroth–Reichardt parameter E_T^N), ethers are similar to alkanes. However, in contrast to alkanes, ethers exhibit relatively high basicity and are capable of specific interactions with alcohols. Also, for the sake of comparison, we performed experiments with another solute, cyclohexane, which is incapable of specific interactions with solvents.

The heats of solution ($\Delta_s H^0$) of cyclohexane and aniline in mixtures of methanol, 1-butanol, and 1-octanol with dihexyl ether are listed in Table 1. The experimental data were approximated by polynomials (1); their coefficients A_i are listed in Table 2.

$$\Delta_s H^0 = A_0 + A_1 X_2 + A_2 X_1 X_2. \qquad (1)$$

Here, X_2 is the mole fraction of alcohol. For the Hex_2O–MeOH system with *cyclo*-C_6H_{12} as a solute, we used Eq. (2):

$$\Delta_s H^0 = A_0/(A_1 - X_2). \qquad (2)$$

The empirical parameters of polarity of the compounds are listed in Table 3. The parameters *A* and *B* for 1-octanol were not determined in [8]. Extrapolation of the dependences of *A* and *B* on the number of carbon atoms in the alcohol molecules is complicated

Table 1. Integral enthalpies of solution of cyclohexane and aniline in mixed solvents at 25°C (kJ mol^{-1})[a]

X_2	$m \times 10^3$	$\Delta_s H^m$	X_2	$m \times 10^3$	$\Delta_s H^m$
n-Hex_2O–MeOH, *cyclo*-C_6H_{12}			*n*-Hex_2O–MeOH, $PhNH_2$		
0.00	32	0.98	0.00	89	3.33
	47	0.92		162	3.33
0.20	52	0.95	0.31	120	1.84
	89	0.97		218	1.82
0.50	107	1.30	0.81	86	–1.15
	157	1.28		163	–1.11
0.80	87	1.88	0.97	59	–2.02
	150	1.93		146	–2.04
1.00	172	4.93	1.00	127	–2.37
	406	4.92		205	–2.41
n-Hex_2O–1-BuOH, *cyclo*-C_6H_{12}			*n*-Hex_2O–1-BuOH, $PhNH_2$		
0.20	41	1.12	0.22	82	2.21
	90	1.11		151	2.17
0.50	83	1.35	0.50	103	2.12
	125	1.34		208	2.06
0.80	44	1.68	0.80	93	2.34
	107	1.67		177	2.34
1.00	33	1.65	1.00	121	3.31
	78	1.66		192	3.34
n-Hex_2O–1-OctOH, *cyclo*-C_6H_{12}			*n*-Hex_2O–1-OctOH, $PhNH_2$		
0.50	76	1.28	0.21	129	2.00
	104	1.28		298	2.21
1.00	17	1.61	0.52	92	2.05
	34	1.59	1.00	129	4.19
				284	4.15

[a] X_2, mole fraction of alcohol; *m*, molal concentration of the solute, mol kg^{-1}.

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Table 2. Coefficients of the polynomials $\Delta_s H^0 = A_0 + A_1X_2 + A_2X_1X_2$ describing the enthalpies of solution of cyclohexane and aniline in mixed solvents at 25°C (kJ mol^{-1})[a]

System	A_0	A_1	A_2	R	S
n-Hex$_2$O–MeOH, *cyclo*-C_6H_{12}	0.79	1.16	–	0.997	0.18
n-Hex$_2$O–1-BuOH, *cyclo*-C_6H_{12}	0.97	0.77	–	0.963	0.07
n-Hex$_2$O–1-OctOH, *cyclo*-C_6H_{12}	0.95	0.65	–	0.999	0.004
n-Hex$_2$O–MeOH, $PhNH_2$	3.45	–5.70	–	0.998	0.14
n-Hex$_2$O–1-BuOH, $PhNH_2$	3.27	0.03	–5.43	0.960	0.18
n-Hex$_2$O–1-OctOH, $PhNH_2$	3.23	1.00	–6.88	0.978	0.18

[a] For the Hex$_2$O–MeOH system with *cyclo*-C_6H_{12} as solute, the equation $\Delta_s H^0 = A_0/(A_1 - X_2)$ was used; X_2, mole fraction of alcohol; R, correlation coefficient; and S, standard deviation.

by the fact that these dependences are nonlinear. It was shown previously [13] that the parameters E_N^T, α, and β in the series of 1-alkanols linearly correlate with the molar density (ρ_m), a quantity inverse to the solvent molar volume ($\rho_m = 1/V_m$). We found that, for four lower 1-alkanols (from MeOH to *n*-BuOH), the parameters *A* and *B* are also linear in ρ_m:

$$A = 0.492 + 10.364\rho_m;\ R\ 0.991,\ S\ 0.007, \quad (3)$$

$$B = 0.370 + 5.155\rho_m;\ R\ 0.970,\ S\ 0.007. \quad (4)$$

Using Eqs. (3) and (4), we calculated the parameters *A* and *B* for 1-octanol (Table 3).

The parameter E_T^N is known for three ethers; Et_2O, *i*-Pr_2O, and *n*-Bu_2O. This quantity is also linear in ρ_m:

$$E_T^N = 0.077 + 4.688\rho_m;\ R\ 0.897,\ S\ 0.004. \quad (5)$$

From relationship (5), we determined the parameter E_T^N for dihexyl ether (Table 3).

The parameters β, *A*, and *B* are known for only two ethers (Table 3). Therefore, for Hex$_2$O these parameters (Table 3) were calculated assuming that they are also linear in ρ_m:

$$\beta = 0.440 + 2.720\rho_m, \quad (6)$$

$$A = -0.036 + 16.349\rho_m, \quad (7)$$

$$B = 0.184 + 16.349\rho_m. \quad (8)$$

As already noted, ethers are similar to alkanes in many characteristics. The high solvating power of ethers with respect to alkanes is clearly illustrated by the fact that the enthalpies of solution of, e.g., cyclohexane in dibutyl ether and heptane are 0.84 and 0.79 kJ mol^{-1}, respectively [14].

Alcohols and ethers are isomers ($C_nH_{2n+2}O$), but ethers, in contrast to alcohols, cannot self-associate by hydrogen bonding. Data on the strength of ethers as bases are contradictory. As judged from the basicity parameter β, dibutyl ether is a two times weaker base than 1-octanol (Table 3). According to the *B* scale, diethyl ether is also a weaker base than 1-butanol. However, as judged from *DN*, alcohols and ethers are bases of similar strength. It should be noted in this connection that, according to [15], the energy characteristics of hydrogen bonds alcohol–alcohol and alcohol–ether are similar.

Table 3. Empirical parameters of polarity of compounds at 25°C[a]

Compound	E_T^N [5]	α [6]	*AN* [7]	*A* [8]	β [6]	*DN* [9]	*B* [8]	V_m
MeOH	0.765	0.93	41.3	0.75	0.62	18.9	0.50	40.7
1-BuOH	0.602	0.79	30.7[b]	0.61	0.88	19.5	0.43	92.0
1-OctOH	0.543	0.63	30.4[b]	0.56[c]	0.97	20.3	0.40[d]	158
Et_2O	0.120	0	3.9	0.12	0.47	19.2[e]	0.34	105
n-Bu_2O	0.102	0	–	0.06	0.46	25.0[f]	0.28	170
n-Hex$_2$O	0.097[g]	0	–	0.03[h]	0.46[i]	–	0.25[j]	235
$PhNH_2$	0.420	–	28.8[k]	0.36	–	33.0[l]	1.19	91.5
cyclo-C_6H_{12}	0.077	0	–	0.02	0	–	0.06	109

[a] E_T^N, normalized Dimroth–Reichardt parameter; α and β, Kamlet–Taft acidity and basicity parameters; *AN*, Gutmann–Mayer acceptor number; *DN*, Gutmann donor number; *A* and *B*, Swain acity and basity parameters. [b] Data of [10]. [c,d] Calculated by Eqs. (3) and (4) (see text). [e] Data of [11]. [f] Calculated [12]. [g] Calculated by Eq. (5) (see text). [h,j] Calculated by Eqs. (7) and (8) (see text). [i] Calculated by Eq. (6) (see text). [k] Calculated [1]. [l] Determined using correlation in [7]. V_m, molar volume, cm^3 mol^{-1}.

We have measured the enthalpies of solution of methanol, 1-butanol, and 1-octanol in dihexyl ether. These data, along with published enthalpies of solution of alcohols in dibutyl ether and heptane, are listed in Table 4. It is seen that the enthalpy of solution of methanol in dihexyl ether is lower than that in ethyl acetate (5.65 kJ mol^{-1} [18]) but higher than that in DMSO (–1.42 kJ mol^{-1} [18]). This fact shows that dihexyl ether is a stronger base than ethyl acetate but a weaker base than DMSO. It is interesting that the endothermic effect of solution of alcohols in both $n\text{-Bu}_2\text{O}$ and $n\text{-Hex}_2\text{O}$ increases in going from methanol to 1-butanol and somewhat decreases in going from 1-butanol to 1-octanol. The enthalpy of solution of 1-octanol in three solvents ($n\text{-Bu}_2\text{O}$, $n\text{-Hex}_2\text{O}$, C_7H_{16}) is proportional to that of 1-butanol in the same solvents, with the proportionality coefficient slightly lower than unity and a very high correlation coefficient:

$$\Delta_s H^0(\text{1-OctOH}) = 0.97\Delta_s H^0(\text{1-BuOH}),\ \text{kJ mol}^{-1};\quad R\ 0.9998,\ S\ 0.13. \tag{9}$$

It is also interesting that there is a linear correlation, with a small positive slope and almost zero deviations, between the enthalpy of solution of cyclohexane in heptane, dibutyl ether, and dihexyl ether, on the one hand (see below), and the number of carbon atoms in the solvent molecules (N_s), on the other hand:

Solvent	C_7H_{16}	$n\text{-Bu}_2\text{O}$	$n\text{-Hex}_2\text{O}$
$\Delta_s H^0$, kJ mol^{-1} (25°C)	0.79 [16]	0.84 [16]	0.95 (this work)

$$\Delta_s H^0 = 0.58 + 0.031 N_s,\ \text{kJ mol}^{-1};\ R\ 0.986,\ S\ 0.014. \tag{10}$$

This correlation includes heptane, which is in line with the "alkane-like" behavior of ethers. Thus, we can conclude that the ether oxygen atoms do not take part in the solvation of cyclohexane with ethers, and interaction of an alkane with ethers is determined by interaction with their hydrocarbon groups.

The enthalpies of transfer of cyclohexane and aniline from dihexyl ether to its mixtures with methanol, 1-butanol, and 1-octanol are plotted in Fig. 1.

Let us first consider cyclohexane solutions. Figure 1 shows that mixtures of 1-butanol and 1-octanol with dihexyl ether exhibit approximately equal solvating power with respect to cyclohexane. In these systems, solvation of cyclohexane only slightly weakens with increasing content of alcohol. A sharp increase in the enthalpy of cyclohexane transfer is observed only in the methanol-based system at the methanol mole fraction $X > 0.8$. Apparently, in this range of composition, methanol starts to form its intrinsic structure by self-association of molecules, which prevents solvation of the alkane. It is quite natural that this range is fairly narrow. Dihexyl ether molecules are very large (V_m 235 $\text{cm}^3\ \text{mol}^{-1}$), and the ratio of the molar volumes of methanol and dihexyl ether is 1 : 6; therefore, in a mixture of methanol with dihexyl ether the latter occupies most of the volume.

Table 4. Enthalpies of solution of alcohols in individual solvents at 25°C (kJ mol^{-1})

Solvent	MeOH	1-BuOH	1-OctOH
$n\text{-Hex}_2\text{O}^a$	4.20	6.97	6.55
$n\text{-Bu}_2\text{O}$	–	8.37^b	8.12^c
C_7H_{16}	15.83^d	24.05^b	23.39^c

[a] Data of this work. [b] Data of [16]. [c] Data of [17]. [d] Data of [18].

With aniline as a solute (Fig. 1), the methanol-based system differs from the other two systems. These sys-

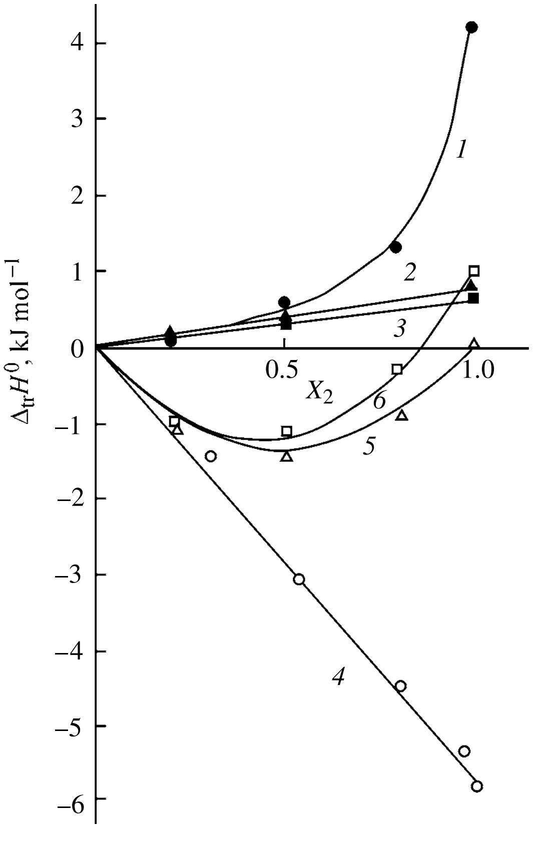

Fig. 1. Enthalpies of transfer of (*1–3*) cyclohexane and (*4–6*) aniline from dihexyl ether to its mixtures with (*1, 4*) methanol, (*2, 5*) 1-butanol, and (*3, 6*) 1-octanol. (X_2) Mole fraction of alcohol. Lines are calculated by Eq. (1) (see text).

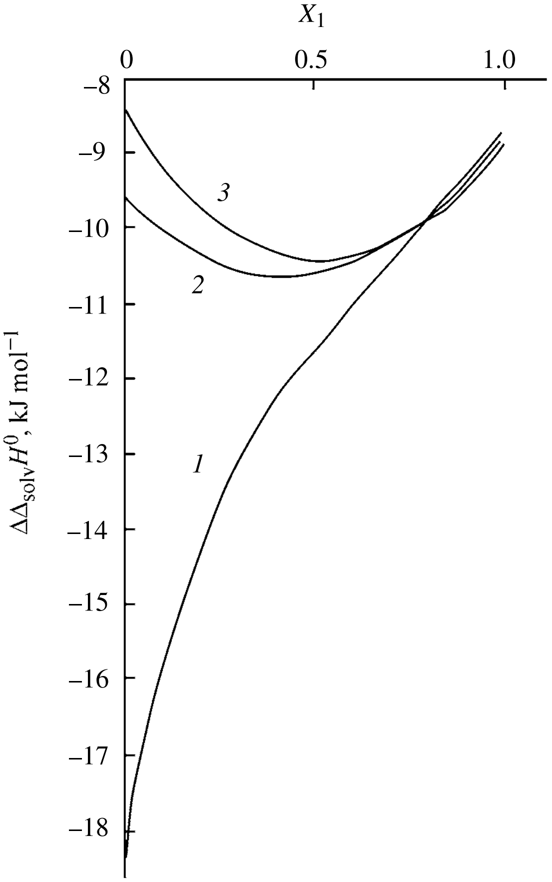

Fig. 2. Difference between the enthalpies of solvation of aniline and cyclohexane in mixtures of dihexyl ether with (*1*) methanol, (*2*) 1-butanol, and (*3*) 1-octanol as a function of the solvent composition. (X_1) Mole fraction of dihexyl ether. Lines are calculated (see text).

tems are very complex because of the possibility of five kinds of solute–solvent and solvent–solvent specific interactions, even without taking into account specific interactions involving the phenyl ring of aniline, which are also quite possible. In dihexyl ether, aniline as an acid specifically interacts with the solvent as a base. This can be readily seen from the comparison of the heats of solution of aniline in heptane (15.02 kJ mol^{-1} [19]) and *n*-Hex$_2$O (3.33 kJ mol^{-1}) (Table 1). Solutions of alcohols in the ether hardly contain “free” (not involved in hydrogen bonding) protons, because proton acceptors (hydroxyl and ether oxygen atoms) are in excess. However, aniline is a stronger base than ether or alcohol, and its interaction with a proton is more favorable energetically. Specifically the interaction of aniline as a base with alcohol as an acid determines the shape of the dependence $\Delta_{tr}H^0 = f(X_2)$ in the entire range of compositions of the system *n*-Hex$_2$O–MeOH ($\Delta_{tr}H^0$ is the enthalpy of transfer of a solute from dihexyl ether to its mixtures with alcohol). Note that, as judged from any acidity parameter, methanol is a stronger acid than the other alcohols (Table 3). The acceptor numbers of 1-butanol and 1-octanol differ only slightly (Table 3), which is consistent with the shape of the curves $\Delta_{tr}H^0 = f(X_2)$ for the corresponding systems in Fig. 1. At the same time, the β values show that 1-butanol and especially 1-octanol are fairly strong bases. Therefore, it can be suggested that, in solutions of aniline in butanol–dihexyl ether and octanol–dihexyl ether, the interaction of aniline as an acid with the alcohol as a base will make a greater contribution against the background of the interaction of aniline as a base with the alcohol as an acid.

To obtain a clearer pattern of specific interactions of aniline with the solvents, it seems useful to follow the approach suggested in [20] for analysis of specific solvation of aromatic compounds in pure solvents. This approach involves calculation of the difference between the enthalpies of solvation of the solute in hand and cyclohexane. This difference corresponds to the enthalpy of specific solvation of the solute.

The enthalpies of solvation of aniline and cyclohexane were calculated as

$$\Delta_{solv}H^0 = \Delta_s H^0 - \Delta_{vap}H^0, \qquad (11)$$

where $\Delta_{vap}H^0$ is the enthalpy of vaporization (cyclohexane, 33.1 kJ mol^{-1} [14]; aniline, 55.40 kJ mol^{-1} [19]).

To calculate the enthalpies of solvation, we used the enthalpies of solution calculated by Eq. (1). The differences between the enthalpies of solvation of aniline and cyclohexane are plotted in Fig. 2 vs. the solvent composition. The curves resemble those in Fig. 1 in the shape, but the values of the enthalpy characteristics differ. The deviations of $\Delta\Delta_{solv}H^0$ from the additive values are positive in the methanol-based system and negative in the two other systems. Note that $\Delta\Delta_{solv}H^0$ includes all kinds of specific interactions of aniline with the solvents, i.e., interactions involving both the amino group and phenyl ring; it also includes the energy consumption for cleavage of hydrogen bonds in the solvent (except the case of pure dihexyl ether in which there are no hydrogen bonds). From $\Delta\Delta_{solv}H^0$ in pure *n*-Hex$_2$O, we can estimate the enthalpy of specific interaction of aniline as an acid with the ether as a base at about –9 kJ mol^{-1}. On the whole, Fig. 2 can be interpreted on the basis of three kinds of interactions considered when discussing Fig. 1.

Thus, analysis of the enthalpies of transfer of cyclohexane and aniline from dihexyl ether to its mixtures with alcohols shows that mixtures of dihexyl ether with methanol significantly differ from those with 1-butanol and 1-octanol in the solvation of both cyclohexane (at $X_2 > 0.8$) and aniline (at $X_2 > 0.3$).

EXPERIMENTAL

The integral heats of solution of cyclohexane and aniline were measured at 25°C in an ampule-type variable-temperature calorimeter equipped with an isothermal jacket; the reaction vessel volume was 60 cm^3. The thermometric and thermal sensitivities of the device (per millimeter of the recorder scale) were 5×10^{-6} deg and 5×10^{-3} J. The solvents were purified by common procedures [21]. Chromatographically pure cyclohexane was used without additional purification. Aniline purified by threefold vacuum distillation (moisture content < 0.5 wt % according to GLC) was stored for no more than a month in the dark. Mixed solvents were prepared gravimetrically with the accuracy of 0.01 (mole fraction scale). The enthalpies of solution were measured at the solute concentrations $m < 0.5$ mol kg^{-1} solvent. Since the enthalpy of solution was virtually independent of the solute concentration in this range (Table 1), the arithmetic mean values of the enthalpies of solution were taken as the standard enthalpies of solution ($\Delta_s H^0 = \Delta_s H^m$). The measured enthalpies of solution of cyclohexane in methanol and 1-octanol are in good agreement with the published data given in parentheses: cyclohexane in methanol, 4.93 kJ mol^{-1} (4.94 [14]); cyclohexane in 1-octanol, 1.60 kJ mol^{-1} (1.88 [14], 1.50 [22]).

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