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Comparative Study of Solvation of CCl_4 in Alcohol–Alcohol and Alcohol–Alkane Systems

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Abstract—The behavior of CCl_4 in methanol–1-butanol, methanol–1-decanol, and 1-butanol–1-decanol is determined by an interaction like CCl_4 (base)–solvent (acid).

Effects sometimes observed in nonaqueous systems have previously been considered intrinsic in aqueous systems. Earlier we studied [1] solutions of CCl_4 in alkane–alcohol binary mixtures and revealed an effect silimar to the effect of stabilization of water structure by nonelectrolyte additives. Solution of CCl_4 in an alcohol was less endothermic than in an alkane. Addition of an alcohol, a component stronger solvating CCl_4 than an alkane, was expected to make solution of CCl_4 less endothermic. It was found, however, that the endothermicity of solution first increased and then, with increasing alcohol content, began to decrease. Thus, the composition dependence of the enthalpy of solution of CCl_4 had a maximum at X ~0.3 (X is the molar fraction of alcohol).

In the referred work we also established one more interesting fact. It is known [2] that CCl_4 as electron-acceptor is capable to forming weak complexes with electron-donor compounds, such as alcohols. We, however, showed that the observed trend in the enthalpy of solution of CCl_4 in a series of alcohols is explained by an interaction in which CCl_4 plays the role of proton acceptor. In other words, alcohols enter hydrogen bonding with CCl_4.

The above observations prompted us to proceed with stidues in this field. In the present work as binary solvents we chose alcohol–alcohol systems: methanol–1-butanol, metanol–1-decanol, and 1-butanol–1-decanol. 1-Butanol and 1-decanol entered into the compositions of the alcohol–alkane systems we studied in [1].

The experimental results obtained in the present work are listed in Table 1. The $\Delta H_0 = f(X)$ dependences were fitted by Eq. (1) [3] whose coefficients are given in Table 2.

$$\Delta H_0 = A_0 + A_1X_2 + X_1X_2\Sigma A_iX_2^{1-2}, \quad i = 2. \tag{1}$$

Here ΔH_0 is the enthalpy of solution of CCl_4 to infinite dilution and X is molar fraction.

Table 1. Entalpies of solution of CCl_4 in mixed solvents at 25°C (kJ/mol)[a]

m	ΔH_m	m	ΔH_m	m	ΔH_m
MeOH–1-BuOH		MeOH–1-DecOH		1-BuOH–1-DecOH	
X_2 0.000		X_2 0.048		X_2 0.246	
0.1228	–0.58	0.1022	–0.76	0.1112	0.32
ΔH_0 –0.58		ΔH_0 –0.76		0.2225	0.35
X_2 0.250		X_2 0.093		ΔH_0 0.335	
0.1092	–0.88	0.1312	–0.80	X_2 0.491	
0.2338	–0.80	ΔH_0 –0.80		0.0949	0.56
ΔH_0 –0.84		X_2 0.173		0.1955	0.60
X_2 0.350		0.1174	–0.66	ΔH_0 0.58	
0.1216	–0.85	ΔH_0 –0.66		X_2 0.747	
0.2538	–0.83	X_2 0.252		0.0957	0.89
ΔH_0 –0.84		0.1811	–0.45	0.1918	0.86
X_2 0.492		ΔH_0 –0.45		ΔH_0 0.88	
0.0914	–0.78	X_2 0.525		X_2 1.000	
0.3878	–0.74	0.1258	0.19	0.0744	1.07
ΔH_0 –0.76		ΔH_0 0.19		0.1643	1.07
X_2 0.761		X_2 0.530		ΔH_0 1.07	
0.1191	–0.39	0.1236	0.17		
0.2333	–0.38	0.2152	0.20		
ΔH_0 –0.385		ΔH_0 0.19			
X_2 1.000		X_2 0.746			
0.0575	–0.06	0.1092	0.59		
0.0911	–0.10	0.2154	0.61		
ΔH_0 –0.08		ΔH_0 0.60			

[a] (X_2) Molar fraction of the second specified component and (m) molality (mol/kg solvent).

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Table 2. Coefficients of the polynomial $\Delta H_0 = A_0 + A_1X_2 + X_1X_2\Sigma A_iX_2^{1-2}$ ($i = 2$) (kJ/mol) describing the enthalpy of solution of CCl_4 in mixed solvents at 25°C

Components	A_0	A_1	A_2	A_3	A_4	A_5	R	S
MeOH–BuOH	–0.62	0.58	–1.72	–	–	–	0.964	0.070
MeOH–DecOH	–0.58	1.66	–7.29	37.4	–67.07	39.59	0.999	0.008
ßuOH–DecOH	0.07	1.14	0.49	–	–	–	0.997	0.040
BuOH–C_6H_{14}	1.05	–0.97	2.11	–	–	–	0.998	0.020
BuOH–$C_{10}H_{22}$	1.24	–1.17	2.44	–	–	–	0.983	0.060
MeOH–BuOH[a]	4.91	–3.20	–6.70	5.20	–	–	0.999	0.030

[a] Solute cyclohexane.

The sum of the first and second terms of Eq. (1) is additive enthalpy, and the third term, excess ($\Delta\Delta H_0$).

Figure 1 shows the enthalpies of CCl_4 transfer ($\Delta_{tr}pH_0$) from methanol to methanol–1-butanol and methanol–1-decanol mixtures, calculated by Eq. (1). For the sake of comparison, in the same figure are given the enthalpies of cyclohexane transfer from methanol to a methanol–1-butanol mixture [4]. As seen from Fig. 1, 1-butanol stronger, than methanol, solvates cyclohexane which nonspecifically interacts with the solvent.

With respect to CCl_4, a stronger solvating agent is methanol which is the most acidic among monoatomic alcohols, as concertedly evidenced by their Kamlet–Taft acidity parameters α, Swain acidity parameters *A*, and acceptor numbers *AN* (Table 3). The *A* and *B* (Swain basicity parameter) values for 1-decanol were not detected in [6]. The dependences of *A* and *B* on the number of carbon atoms in the alcohol molecule are nonlinear and thus difficult to extrapolate. Earlier we showed [1] that the Dimroth–Reichardt parameters E_T^N, α, and β in the 1-alkanol series are linearly related to the molar density of alcohols (ρ_m), a value reverse to the molar volume of solvents (V_m^{-1}). We found that the *A* and *B* parameters of four 1-alkanols (MeOH–1-BuOH), too, are linearly related to ρ_1.

$$A = 0.492 + 10.364\ \rho_1;\ R\ 0.991,\ S\ 0.007, \qquad (2)$$

$$B = 0.370 + 5.155\ \rho_1;\ R\ 0.970,\ S\ 0.007. \qquad (3)$$

By Eqs. (2) and (3) we calculated *A* and *B* for 1-decanol (Table 3).

Solvation of cyclohexane strengthens over the entire range of compositions of the methanol–1-butanol system, whereas CCl_4 is first solvated stronger and then weaker. Methanol additives to 1-decanol produce similar effect on solvation of CCl_4. Addition to methanol of more basic (Kamlet–Taft basicity parameter β) but less acidic solvents [1-butanol and 1-decanol (Table 3)] should enhance an interaction like solvent (base)–CCl_4 (acid) but weaken an interaction like solvent (acid)–CCl_4 (base).

The slightly enhanced solvation of CCl_4 solvation in going from methanol to methanol solutions of 1-butanol and 1-decanol can be explained by prevailing contribution of the first of the above two interactions. On the right side of the minimum of the $\Delta_{tr}H_0(X)$ function, the second interaction becomes to prevail. Since 1-decanol is a weaker proton donor than 1-butanol, the minimum of the $\Delta_{tr}H_0(X)$ function is displaced to smaller 1-decanol fractions. However, it should be noted that the acidity parameters of alcohols are nicely consistent with each other and offer a clear view of the H-donor ability order of 1-alkanols, but this is not true of the basicity parameters. For instance, the Swain basicity parameter *B*, unlike β and *DN*, decreases in going from shorter to longer chain alcohols. One should not ignore this fact, since the nonzero basicity of CCl_4 on this scale (*B* 0.34) agrees (unlike β and *DN*) with our results for interaction of CCl_4 with alcohols.

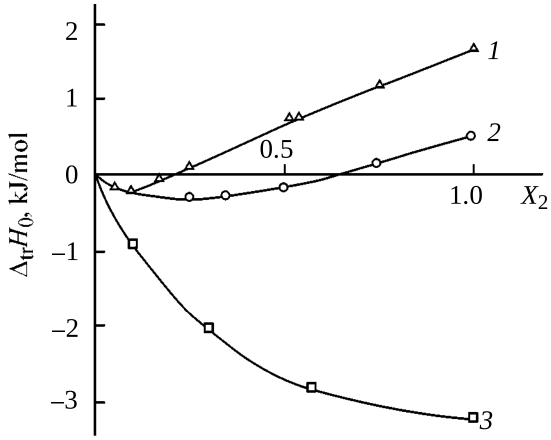

Fig. 1. Enthalpies of transfer of (*1, 2*) CCl_4 and (*3*) cyclohexane from methanol to (*1*) methanol–1-decanol and (*2, 3*) methanol–1-butanol mixtures. Here and hereinafter, X_2 is the molar fraction of the second component.

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

Compound	α [5]	β [5]	*A* [6]	*B* [6]	*AN* [7]	*DN* [8]	α_m [9]	β_m [9]
MeOH	0.93	0.62	0.75	0.50	41.3	79.1	0.33	0.47
BuOH	0.79	0.88	0.61	0.43	30.7	81.6	0.33	0.47
DecOH	0.71[b]	0.99[b]	0.55[c]	0.40[c]	–	–	–	–
CCl_4	0	0	0.09	0.34	8.6	0	–	–
cyclo-C_6H_{12}	0	0	0.02	0.06	0	0	–	–
C_6H_{14}	0	0	0.01	–0.01	0	0	–	–
$C_{10}H_{22}$	0	0	–	–	–	0	–	–

[a] α and β are the Kamlet–Taft acidity and basicity parameters; *A* and *B* are the Swain acidity and basicity parameters; *AN* is the Gutmann–Maier acceptor number, *DN* is the Gutmann donor number, kJ/mol; and α_m and β_m are the acidity and basicity parameters of monomeric alcohols. [b] Calculated by the equations proposed in [1]. [c] Calculated by Eqs. (2) and (3).

On the assumption that *B* correctly reflects basicity trends, another mechanism can be proposed. Addition to methanol of 1-butanol or 1-decanol result in destruction of the intrinsic methanol structure, thus enhancing solvation of solutes, on account of decreased endo contribution of void formation and, probably, enhanced nonspecific solvation of solutes with longer chain alcohols. Apparently, a combined effect of these two factors is responsible for the enhanced solvation of cyclohexane over the entire range of compositions of the methanol–1-butanol mixture. 1-Decanol produces a more profound destruction of the methanol structure compared with 1-butanol, as evidenced by the enthalpies of mixing for the alcohol–alcohol systems (see below).

Figure 2 displays the enthalpies of CCl_4 transfer from 1-butanol to 1-butanol–methanol and 1-butanol–1-decanol mixtures. For the sake of comparison, we gave in the same figure the enthalpies of CCl_4 transfer in alcohol–alkane systems, calculated with data in [1]. Addition to 1-butanol of a more acidic solvent (methanol) enhances solvation of CCl_4 and, what is notable, to a greater extent than expected by the additivity condition. Other additives weaken solvation of CCl_4 in the following order: 1-decanol, hexane, and decane. In the latter cases, solvation, too, weakens to a greater extent than expected by the additivity condition. In the BuOH–DecOH system, however, the deviation of the enthalpy of CCl_4 transfer from additivity is small (no more than 0.1 kJ/mol). Systems BuOH–alkane–CCl_4 are appreciably less additive. Note that BuOH–DecOH and BuOH–C_6H_{14} mixtures exhibit similar solvating ability with respect to CCl_4 at *X* ~0.8.

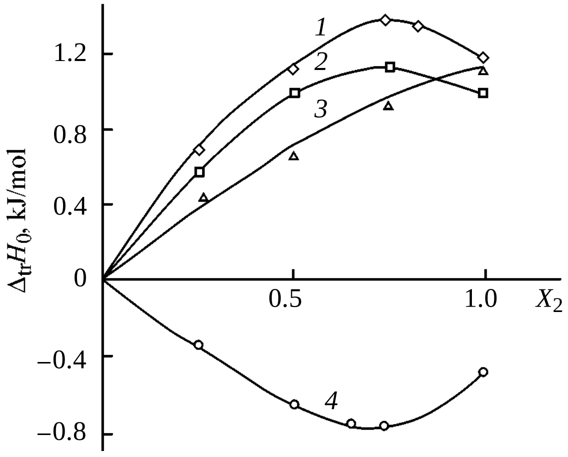

Fig. 2. Enthalpies of transfer of CCl_4 for 1-butanol to its mixtures with (*1*) decane, (*2*) hexane, (*3*) 1-decanol, and (*4*) methanol.

The general reason for the weakening solvation of CCl_4 on dilution of 1-butanol both with 1-decanol and with alkanes lies in decreasing acidity of the solvent. The dependence of the acidity of the BuOH–DecOH mixture on its composition is likely to be close to linear, which results in an almost linear $\Delta_{tr}H_0(X)$ dependence for CCl_4. Alkanes, unlike 1-decanol, are «inert» solvents. Their addition to alcohols decreases the association degree of the latter. The basicity (β_m) and acidity (α_m) of monomeric alcohols are much lower that the basicity and acidity of associated forms (Table 3). Therefore, as the association degree of alcohols is reduced by dilution, their ability to specific interactions with a third component gets weaker. However, this reasoning cannot explain the endothermicity maximum of CCl_4 transfer at high concentrations of alkanes. We suggest that in this concentration range alcohol–alkane mixtures contain the maximal amount of cyclic associates (for instance, tetramers [10]). Such associates, unlike linear, have no terminal OH groups and cannot act as proton donors unless the alcohol–alcohol bond is cleaved. Further increase of the alkane contents of alcohol–

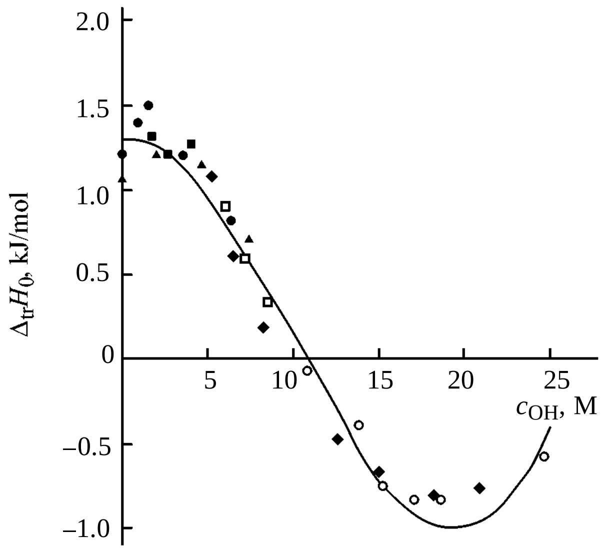

Fig. 3. Dependence of the enthalpy of solution of CCl_4 in alcohol–alcohol and alcohol–alkane mixtures on the molar concentration of hydroxy groups in the systems [calculation by Eq. (4)].

alkane mixtures results in appearance of monomeric alcohols and slightly enhanced solvation of CCl_4.

Since the behavior of CCl_4 in alcohol–alcohol and alcohol–alkane mixtures is determined by specific solute–solvent and solvent–solvent interactions involving alcohol OH groups, we suggested that there is some common dependence for these two systems. Such dependence in shown in Fig. 3, where the enthalpies of solution of CCl_4 are plotted as ordinates and the molar concentrations of hydroxy groups, as abscissas. The molar concentrations of hydroxy groups in mixtures were calculated assuming the additivity of volume [V(mixture) = $X_1V_1 + X_2V_2$, where V_i is the molar volume of component i]. In Fig. 3. $c_{ON} = 0$ corresponds to alkanes and the rightmost point, to methanol. The 7 systems (4 alkane–alcohol and 3 alcohol–alcohol) represented in the figure all are fairly accurately described by polynomial (4).

$$\Delta H_0 = 1.31 + 7.208\times10^{-3}s_{ON} - 18.65\times10^{-3}s^2_{ON} + 62.56\times10^{-5}s^3_{ON},\ \text{kJ/mol}; \quad (4)$$

$$R\ 0.973,\ S\ 0.13.$$

For the 3 alcohol–alcohol systems the correlation is much better [Eq. (5)].

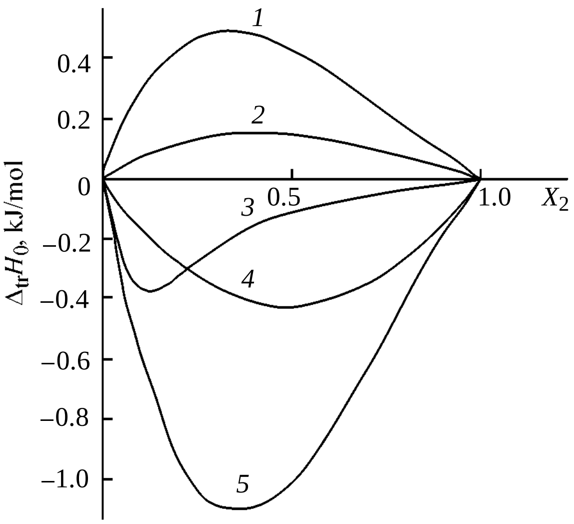

Fig. 4. Excess enthalpies of (*1*) methanol–1-decanol and (*2*) methanol–1-butanol mixtures and the excess enthalpies of solution of CCl_4 in (*3*) methanol–1-decanol and (*4*) metanol–1-butanol mixtures and of cyclohexane in (*5*) metanol–1-butanol mixtures [polynomial fits (Tables 2, 4)].

$$\Delta H_0 = 2.70 - 3.73\times10^{-1}c_{OH} + 1.04\times10^{-1}c^2_{OH} - 3.16\times10^{-5}c^3_{OH},\ \text{kJ/mol}; \quad (5)$$

$$R\ 0.987,\ S\ 0.08.$$

Equations (4) and (5) are interesting theoretically but call for comprehension. There practical value is obvious, since they allow estimation of the enthalpy of solution of CCl_4 in yet unexplored alkane–alcohol and alcohol–alcohol systems.

Intermolecular interactions in binary systems are characterized by the heat of mixing H^E, and in ternary systems, by the excess enthalpy of solution $\Delta\Delta H_0$. Therefore, it seemed interesting to compare these two characteristics for the systems in question.

Figure 4 compares the dependences of the $\Delta\Delta H_0$ of CCl_4 in methanol–1-butanol and methanol–1-decanol and of *cyclo*-C_6H_{12} in methanol–1-butanol [3] on the composition of the mixture with the corresponding dependences of the H^E of these mixtures. The H^E values were taken from [11–13]. The $H^E = f(X)$ dependences were fitted by polynomials of degrees X_2 (molar fraction of the second component), whose coefficients are listed in Table 4. The table also lists the coefficients for calculating H^E for the 1-butanol–hexane and 1-butanol–decane systems studied in [1]. As seen from Fig. 4, both the systems studied have positive enthalpies of mixing. Therewith, as the length

Table 4. Coefficients of the polynomials fitting the enthalpies of alcohol–alcohol and alcohol–alkane mixing at 25°C, kJ/mol

System	b_0	b_1	b_2	b_3	R	S
MeOH–BuOH	0.030	0.494	–0.547	–	0.904	0.016
MeOH–DecOH	0.042	2.932	–5.773	2.826	0.979	0.025
1-BuOH–DecOH	0.049	1.735	0.423	–2.022	0.975	0.039
1-BuOH–C_6H_{14}	0.035	0.726	1.864	–2.505	0.952	0.052
1-BuOH–$C_{10}H_{22}$	0.048	1.750	0.390	–1.990	0.974	0.039

of the hydrocarbon radical in the second component increases, mixing becomes more endothermic. The excess enthalpies of solution of CCl_4 in methanol–1-butanol and methanol–1-decanol mixtures are negative, and if the $\Delta\Delta H_0(X)$ dependence for CCl_4 in the methanol–1-butanol system is symmetrical, than in the MeOH–DecOH–CCl_4 system it has a well-defined minimum at the 1-decanol molar fraction X 0.1. Comparison of the $\Delta\Delta H_0(X)$ dependences for CCl_4 and cyclohexane in methanol–1-butanol shows that $\Delta\Delta H_0$ are similar in sign, but much differ in absolute value (the $\Delta\Delta H_0$ values for cyclohexane are more negative).

Figure 5 shows compares the $\Delta\Delta H_0(X)$ dependences for CCl_4 in 1-butanol–1-decanol with the corresponding $H^E(X)$ dependences for this solvent mixture. In the same figure we show the $\Delta\Delta H_0(X)$ dependences for CCl_4 in 1-butanol–hexane and 1-butanol–decane mixtures [1] and the corresponding $H^E(X)$ dependences for these mixtures. As seen from the figure, the $\Delta\Delta H_0$ and H^E values of these systems exhibit similar positive deviations from additivity, and the H^E values for 1-butanol–alkane mixtures get more positive with increasing hydrocarbon chain length in the alkane.

Figure 6 represents the enthalpy of specific solvation of CCl_4 in the methanol–1-butanol mixture, calculated as a difference of the enthalpies of solvation of CCl_4 and cyclohexane. The enthalpies of solvation were calculated by Eq. (6):

$$\Delta_{solv}H_0 = \Delta H_0 - \Delta_{vap}H_0. \qquad (6)$$

Here $\Delta_{vap}H_0$ is the enthalpy of vaporization of CCl_4 (32.2 kJ/mol) and cyclohexane (32.8 kJ/mol) [13]. The ΔH_0 values for CCl_4 and cyclohexane in the methanol–1-butanol mixture were calculated by Eq. (1) with the coefficients from Table 2.

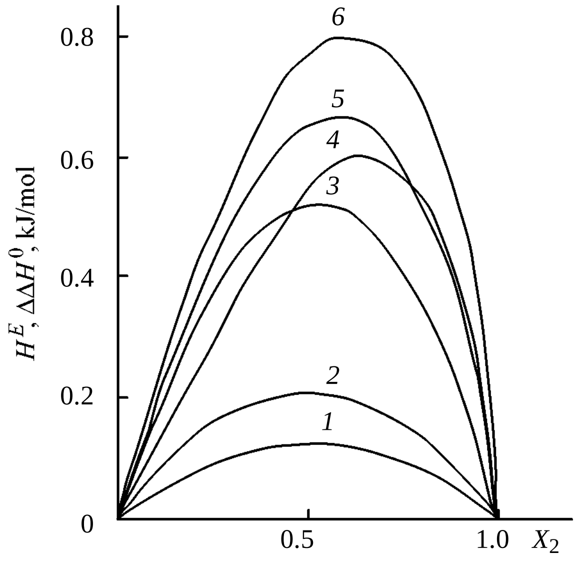

Fig. 5. Excess enthalpies of (*2*) 1-butanol–1-decanol, (*4*) 1-butanol–hexane, and (*6*) 1-butanol–decane mixtures and (*1, 3, 5*) excess enthalpies of solution of CCl_4 in these mixtures [polynomial fits (Tables 2, 4)].

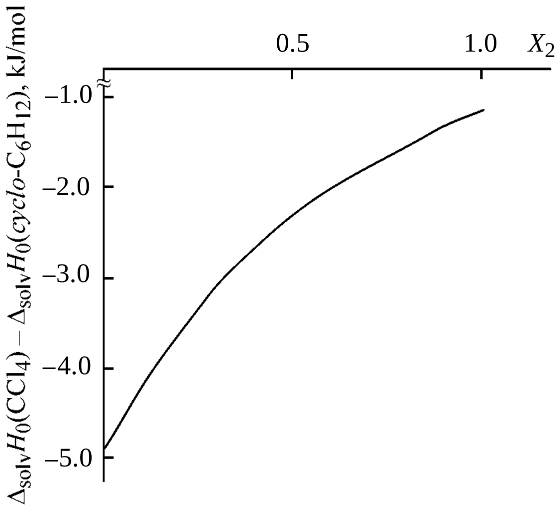

Fig. 6. Excess enthalpy of specific solvation of CCl_4 in the methanol–1-butanol mixture.

As seen from Fig. 6, the $\Delta_{solv}H_0(X)$ function is exothermic over the entire range of compositions of the mixed solvent, and, therewith, in methanol it is more exothermic than in 1-butanol, which agrees with the acidities of the solvents (Table 3). This dependence exhibits a positive deviation from additivity, unlike the $\Delta\Delta H_0(X)$ dependences (Fig. 4), which points to a greater role of universal solvent–solute interactions compared with specific.

Thus, the comparative study of solvation of CCl_4 in alcohol–alcohol and alcohol–alkane mixtures showed that the determining interaction of CCl_4 with these solvents is an interaction like CCl_4 (base)–solvent (acid). A common equation was obtained, relating the enthalpy of solution of CCl_4 in alcohol–alcohol and alcohol–alkane mixtures to the molar concentration of hydroxy groups in the mixed solvent.

EXPERIMENTAL

The intergral heats of solution of CCl_4 in alcohol–alcohol mixtures were measured at 25°C in a variable-temperature isothermic-shell ampule calorimeter, cell volume 60 cm^3. The thermometric and heat sensitivities of the calorimeter were 5×10^{-6} deg/mm recorder scale and 5×10^{-3} J/mm recorder scale.

1-Alkanols used were purified by known procedures [14]. Analytical grade CCl_4 was used as received. Mixed solvents were prepared gravimetrically with an accuracy of 0.001 molar fraction. For the standard enthalpies of solution at infinite dilution were taken the arithmetic mean heat effects of solution ΔN_m, since it was found the the enthalpies of solution are concentration-independent (Table 1).

Our value of the enthalpy of solution of CCl_4 in 1-butanol better agrees with the value –0.20 kJ/mol [2] than with the value 0.12 kJ/mol [15].

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