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Apparent molar volumes and enthalpies of solution of tetracyanoethylene in some solvents and of butan-1-ol in *n*-octane at different concentrations

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The effects of specific solute–solvent and solute–solute interactions on the change in the apparent molar volumes and in the enthalpies of solution, were found to be proportional in the title solutions at 25 °C.

The partial molar volume of a solute can be calculated at infinite dilution using the following equations:

$$\bar{V}_A = 1000(d_0 - d)/c_A d_0 + M_A/d_0 \quad (1)$$

$$\bar{V}_A = 1000(d_0 - d)/m_A\, d d_0 + M_A/d \quad (2)$$

$$\bar{V}_A = (d_0 - d)M_S(1 - x_A)/x_A d d_0 + M_A/d \quad (3)$$

Here, M_A and M_S are the molecular masses of the solute and the solvent, respectively; d and d_0 are the densities of the solution and the solvent, respectively; c_A, m_A and x_A are the concentration scales in molarity, molality and mole fraction, respectively. The partial molar volume of a solute from equations (1)–(3) includes the structural volume of the solute in this solvent and the volume change of the solvent in the process of shell formation around the solute.[1] The last part depends on the difference between solute–solvent and solvent–solvent interaction energies. In the case of strong ion–solvent interactions, the value of solvent electrostriction can be larger than the value of the structural volume of the solute, and the partial molar volume may be negative.[1] The change of the heat of solution and the molar volume of a solute at infinite dilution through the range of solvents reflect the changes of properties of both solute and solvent in the dissolving process, except the case of ideal solutions. All these changes of solute–solvent and solute–solute interactions define the changes of the apparent molar volume and the enthalpy of solution. In general, specific interactions can sharply affect the activation volumes and reaction volumes, and from these details the nature of high-pressure effects on the rates and equilibria can be better estimated.[2]

Appreciable volume changes can be expected from the specific solute–solvent interaction of the strong -acceptor, tetracyanoethylene (TCNE) (E_A = 2.88 eV),[3] with -donor alkylbenzenes. It is well known that the heat of solution of all alcohols in nonpolar solvents has unusually high curvature, and for the range of concentrations less than 0.02 mol dm^{-3} there is saturation due to the total monomerization. Similarly, S-shaped curves can be expected for the apparent molar volume of alcohols in dilute alkane solutions. However, the apparent molar volumes of alcohols in the alkane solutions were determined[4–7] for the range of concentrations above 0.02–0.04 mol dm^{-3}. The calculation of partial molar volumes of alcohols from the data of this concentration range cannot be correct.

Tetracyanoethylene (Merck) was sublimed in a vacuum (50 Pa) at 110 °C as white crystals, mp 198–200 °C (lit.,[8] 200 °C). Butan-1-ol and all solvents were purified by known methods.[9] The enthalpies of solution were measured at 25 °C using a differential calorimeter (the solvent volume was 180 cm^3) as reported previously.[10] Calibration of the calorimeter by the heat of solution of KCl in water at 25 °C gave 17.4±0.2 kJ mol^{-1} (precise data[11] 17.51±0.01 kJ mol^{-1}). Three to five measurements with sequentially dissolving samples (30–100 mg) of TCNE were carried out. The integral heats of solution of butanol in *n*-octane were obtained by sequentially dissolving samples in three independent sets of experiments. Apparent molar volumes of solutes in solutions were determined by means of a digital vibrating-tube densimeter (A. Paar, DMA 602) with an accuracy of (1–2)× 10^{-6} g cm^{-3}. The high level of thermostatic control [25± ±(1–2)×10^{-3} °C] was achieved using a triple cascade of water thermostats (22, 24.5 and 25 °C) with a reduced heater power in the last one (15 W, 20 dm^3 of water).[2] The densimeter was placed in a box at a constant temperature of air (25±0.2 °C). The apparent molar volume of TCNE in each of solutions (Table 1) was invariable in the concentration range 0.02–0.05 mol dm^{-3}. The apparent molar volume of butan-1-ol in octane solutions depends on concentration in the whole range examined. Three to five measurements of the density were carried out for all concentrations of solutions. No change in the densities of TCNE and butanol solutions was observed in these solvents within few hours.

Solute–solvent interactions. The correlation coefficient of the empirical relationship between the value of V_{TCNE} and the enthalpies of solution of TCNE in alkylbenzenes [$\bar{V}_{TCNE}$ = (100.76±0.63) + (0.413±0.021) $_{sol}H$; R = 0.9620, S_V = 1.17, N = 6] is less than that with the values of ionization potentials of alkylbenzenes [$\bar{V}_{TCNE}$ = (14.5±7.6) + (10.25±0.35)IP; R = = 0.9823, S_V = 0.80, N = 6] and the free energy of complex formation [$\bar{V}_{TCNE}$ = (109.40±0.66) + (1.536±0.062) G_0; R = = 0.9763; S_V = 0.93, N = 6]. Because of a large difference of the effects of chlorine and methyl groups on the IP values and complex formation (Table 1), chlorobenzene can be withdrawn

Table 1 Ionization potentials of solvents (IP), the partial molar volume of tetracyanoethylene ($\bar{V}_{TCNE}$), the enthalpies of solution ($_{sol}H$) and solvation ($_{solv}H$), the free energy (G_0) of complex formation of TCNE with alkylbenzenes and the rate constants (k_2) of the Diels–Alder reaction of TCNE with anthracene at 25 °C.

Solvent	IP^a/eV	$\bar{V}_{TCNE}$/cm^3 mol^{-1}	$_{sol}H$/kJ mol^{-1}	– $_{solv}H^b$/kJ mol^{-1}	G_0^a/kJ mol^{-1}	k_2^c/dm^3 mol^{-1} s^{-1}
Chlorobenzene	9.10	109.23±0.14	23.1±0.3	58.1±0.3	–0.65	1.82
Benzene	9.25	108.40±0.26	14.9±0.4	66.3±0.4	1.72	0.38
Toluene	8.82	104.56±0.37	9.7±0.5	71.5±0.5	3.24	0.13
o-Xylene	8.58	102.06±0.32	1.4±0.1	79.8±0.1	4.81	0.061
p-Xylene	8.48	101.46±0.25	0.0±0.5	81.2±0.5	5.04	—
Mesitylene	8.14	98.07±0.10	–2.7±0.4	83.9±0.4	7.07	0.01
Acetonitrile	12.12	109.97±0.12	15.2±0.2	66.0±0.2	—	2.18
Ethyl acetate	9.54	112.09±0.06	9.2±0.5	72.0±0.5	—	0.24
Cyclohexanone	9.14	110.42±0.35	7.6±0.3	73.6±0.3	—	0.20
p-Dioxane	9.13	105.72±0.16	4.3±0.2	76.9±0.2	—	0.34
1,2-Dichloroethane	11.12	107.81±0.20	21.3±0.3	59.9±0.3	—	3.82
Dichloromethane	11.35	107.50±0.20^d	23.4±0.5	57.8±0.5	—	4.28

^{a}From ref. 12 for alkylbenzenes and from ref. 13 for other solvents. ^{b}Calculated using the value $_{subl}H$ 81.2 kJ mol^{-1}.[14] ^{c}From ref. 15. ^{d}From ref. 16.

Table 2 Apparent molar volumes (φ) and the integral enthalpies of solution ($_{\rm sol}H$) of butan-1-ol in *n*-octane at 25 °C.

$C_{\rm butanol}$/ mol dm^{-3}	$_{\rm sol}H^a$/ kJ mol^{-1}
0	(23.2)^c
0.00348	23.0
0.00659	22.6
0.0107	22.4
0.0156	22.1
0.0214	21.6
0.0278	20.9
0.0349	19.8
0.0422	18.8
0.0537	17.2
0.0681	15.5
0.0853	13.8
0.107	12.2
0.145	10.2
0.190	8.7
0.232	7.7
0.275	7.0

$C_{\rm butanol}$/ mol dm^{-3}	φ^b/ cm^3 mol^{-1}	φ^b/ cm^3 mol^{-1}
0	(99.27)^c	(7.30)^c
0.0146	98.95	6.98
0.0285	98.50	6.53
0.0353	98.20	6.23
0.0536	97.64	5.67
0.0845	96.81	4.84
0.115	96.23	4.26
0.524	94.08	2.11
0.977	93.57	1.60
10.87^d	91.97	0
0.0332	97.19^e	5.66
0.0766	96.08^e	4.55
0.144	94.82^e	3.29
0.182	94.58^e	3.05

[a] Accuracy of ±0.15 kJ mol^{-1}. [b] Accuracy of ±0.20 cm^3 mol^{-1}. [c] The calculated limiting values (see the text) are given in parentheses. [d] For pure butanol. [e] The apparent molar volume of butanol in *n*-heptane at 20 °C from ref. 7.

from consideration with alkylbenzenes.[12] In this case a better correlation is observed [$\bar{V}_{\rm TCNE} = (22.43\pm1.4) + (9.299\pm0.073){\rm IP}$; $R = 0.9994$; $S_{\rm V} = 0.13$, $N = 5$]. It is clear (Table 1) that the changes in the rate constants of the Diels–Alder reaction with TCNE, the heat of solution of TCNE in alkylbenzenes and the free energy of complex formation are connected with changes in the specific energy of interaction between TCNE and these aromatic solvents. From the correlations obtained, we can conclude that the variation of the partial molar volume of TCNE in alkylbenzenes is conditioned by the same cause. Inert solvents such as alkanes and carbon tetrachloride were excluded due to the very low solubility of TCNE. For chlorobenzene, dichloromethane and 1,2-dichloroethane, the heats of solution are more endothermic, and the enthalpies of TCNE solvation are only –(58–60) kJ mol^{-1} (Table 1). The heat of solution of TCNE is exothermic in mesitylene, the strongest -donor among aromatic solvents of this series (Table 1), and the enthalpy of this complex formation is equal[12] to –18.9 kJ mol^{-1}. Even in this solution, the enthalpy of specific interaction contributes only one third of the enthalpy of nonspecific interaction (Table 1). Note that the enthalpies of interaction of TCNE in the crystal state and in a *p*-xylene solution are the same, and the molar volume of crystalline TCNE (lit.,[17] 102 cm^3) is nearly the same as in a *p*-xylene solution (Table 1). The rate constants go down by a factor of 400 with the change from 1,2-dichloroethane or dichloromethane to mesitylene (Table 1). The correlation between the free energy and the enthalpy of complex formation[12] of alkylbenzenes with TCNE with donor properties allows a prediction of the equilibrium constant (150 dm^3 mol^{-1}) and the enthalpy of complex formation (–30 kJ mol^{-1}) for the complex between TCNE and the strongest -donor, 9,10-dimethylanthracene (lit.,[18] IP = 7.04 eV). The strongest specific intermolecular interaction between TCNE and 9,10-dimethylanthracene in inert solutions may be a reason for the observed negative temperature coefficient of the rate constants of the Diels–Alder reaction.[19]

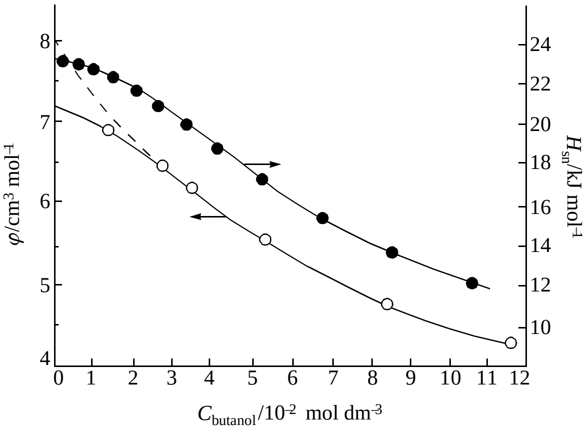

Figure 1 Concentration effect of butan-1-ol in an *n*-octane solution on the integral enthalpy of solution (●) and on the apparent molar volume of butan-1-ol (○). For dotted line, see the text.

Table 3 Partial monomer fraction (α) of butanol in an octane solution and calculated equilibrium constants for dimer ($K_{\rm D}$) and trimer ($K_{\rm T}$) processes.

$C_{\rm butanol}$/ mol dm^{-3}	α ($_{\rm sol}H_{\rm C}$/ $_{\rm sol}H_0$)	$K_{\rm D}$/ dm^3 mol^{-1}	$K_{\rm T}$/ dm^6 mol^{-2}	α^a ($\varphi_{\rm C}$/ V)	$K_{\rm D}$/ dm^3 mol^{-1}	$K_{\rm T}$/ dm^6 mol^{-2}
0.00659	0.9741	2.1	215	0.980	1.6	165
0.0107	0.9655	1.7	112	0.969	1.5	96
0.0156	0.9526	1.7	75	0.951	1.7	76
0.0214	0.9310	1.9	62	0.922	2.1	71
0.0278	0.9009	2.2	59	0.890	2.5	67
0.0349	0.8534	2.9	64	0.853	2.9	65
0.0422	0.8103	3.4	67	0.819	3.2	62
0.0537	0.7414	4.9	82	0.774	3.5	56
0.0681	0.6681	5.5	80	0.712	4.2	58
0.0853	0.5948	6.7	88	0.651	4.8	58
0.107	0.5259	8.0	95	0.599	5.2	54

[a] The values of $\varphi_{\rm C}$ were calculated for the same butanol concentrations as those used for calculating the value of $_{\rm sol}H_{\rm C}$.

The structure of *n*, -complexes differs from the coplanar structure of , -complexes of alkylbenzenes with TCNE.[20] All these types of correlation become poor in *n*-donor solvents (ethyl acetate, cyclohexanone, acetonitrile and dioxane). Solutions of TCNE in chloroalkanes are almost free from specific interactions, but partial molar volumes of TCNE in dichloromethane and dichloroethane are slightly lower than those in a benzene solution (Table 1).

Solute–solute interactions. The increase in the proportion of monomer alcohol molecules can be seen in the increase of the apparent molar volume and the enthalpy of solution (Table 2).

From experimental measurements[4–7] in the concentration range above 0.02–0.04 mol dm^{-3} the apparent molar volumes of alcohols increase sharply with decreasing concentration. However, the S-shape of the saturation curve appears from calorimetric measurements at concentrations less than 0.02 mol dm^{-3}. The fitting of experimental data in the usual way to the limit of concentration 0.0285 mol dm^{-3} gave an overestimated value for the partial molar volume of butanol (dotted line in Figure 1). It is difficult to do precise measurements of the density difference of solution and solvent at concentrations less than 0.01 mol dm^{-3} ($d < 8\times10^{-5}$ g cm^{-3}), but more sensitive calorimetric measurements extended here up to 0.003 mol dm^{-3} (Table 2). In the low concentration range (< 0.02 mol dm^{-3}), a greater part of *n*-butanol exists as the monomer, and the change in the heat of solution exhibits saturation. This S-shaped curve of the heat of solution of butan-1-ol in *n*-octane in the low concentration range is comparable to nearly the same S-shaped curve of the apparent molar volume of butan-1-ol in this concentration range. This saturation was realised taking into account an additional value of the apparent volume for a concentration of 0.0146 mol dm^{-3} (Figure 1), giving the partial molar volume of 99.27±0.20 cm^3 mol^{-1}. The limiting value of the heat of solution of butanol in *n*-octane evaluated here is 23.2 kJ mol^{-1}. Nearly the same values (23.6) were obtained by us for the limiting heat of solution of butan-1-ol in *n*-hexane and for ethanol in *n*-hexane (23.5 kJ mol^{-1}).[21]

With the assumption that the heat of solution and the change in the apparent molar volume of butanol caused by monomer formation, the monomer fraction of butanol in an octane solution can be calculated from the equation:

$$\alpha = C_{\rm M}/C = \ _{\rm sol}H_{\rm C}/\ _{\rm sol}H_0 = \ \varphi_{\rm C}/\ V \qquad (4)$$

where $C_{\rm M}$ and C are the monomer and total butanol concentrations in solution, respectively; $_{\rm sol}H_{\rm C}$ and $_{\rm sol}H_0$ are the enthalpies of solution at the working concentration and at the limiting low concentration, respectively; $\varphi_{\rm C}$ is the difference between the partial ($\bar{V}$) and apparent ($\varphi_{\rm C}$) molar volumes of butanol in octane solution, respectively; V is the volume difference between the partial molar volume of butanol in *n*-octane solution and the molar volume of pure butanol. The equilibrium constants for monomer–dimer (2M = D) and monomer–trimer (3M = T) equilibria can be calculated from the following equations:

$$K_\mathrm{D} = (1 - \alpha)/2C\alpha^2, \quad (5)$$

$$K_\mathrm{T} = (1 - \alpha)/3C^2\alpha^3. \quad (6)$$

The value of $\alpha = {}_\mathrm{sol}H_\mathrm{C}/{}_\mathrm{sol}H_0$ is based on the additional assumption that there are slight differences in nonspecific solute–solute and solute–solvent interactions. To check the last assumption, the heat of solution of diethyl ether (as a homomorph of butanol) in octane was measured. This value (1.6±0.2 kJ mol^{-1}) is low in comparison with the limiting value of the heat of solution of butanol in octane (23.2±0.2 kJ mol^{-1}), but does not change the results of calculations summarised in Table 3.

The attempt to distinguish these two types of equilibria has failed. We can suppose that in this range of concentrations both types of equilibria take place with different contributions. The data in Table 3 indicate that the value of K_D is nearly constant only in the low concentration range (≤ 0.02 mol dm^{-3}) and at higher concentrations (0.02–0.1 mol dm^{-3}) the trimer–monomer equilibrium can be the dominant process.

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