Translated from *Uspekhi Khimii* **60** 45–68 (1991) U.D.C. 536.653:547

# Thermochemistry of the solvation of organic non-electrolytes

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ABSTRACT. This review surveys experimental data on the thermochemistry of the solvation of organic non-electrolytes. An analysis of the enthalpy of solvation as the sum of the enthalpies of non-specific solvation and of specific interaction is presented. The various methods for isolating the contribution of the enthalpies of the complex formation reactions between the solute and the solvent are examined. The role of the dipole moment of the solute molecule in solvation is analysed in detail.

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## I. Introduction

The problem of the thermodynamics of the dissolution and solvation of organic compounds has always aroused the interest of investigators working in various fields of science where the problems of the behaviour of species in a liquid medium were raised. At the present time, the study of this problem is prosecuted in two directions. On the one hand, the "purely solution" problems are solved—for example liquid–vapour and extraction equilibria have been investigated, which is a subject of classical physical chemistry. Extensive experimental and theoretical data have accumulated in this field and generalisations have been made. These have already been reflected in the monographs of Morachevskii and co-workers.[1,2]

The quantitative features relating the thermodynamic parameters of the dissolution and solvation of organic compounds to their structural characteristics as well as the macroscopic properties of the solvents have been studied within the framework of the second aspect of the chemistry of solutions. Studies on these lines have been associated as a rule with the solution of the problem of the influence of the medium on various physicochemical processes.

Abraham and co-workers[3] have worked fruitfully on the analysis of the activity coefficients within the framework of multiparameter correlations with the properties of the medium. As a result of the efforts by Fuchs, Arnett, Krestov, the authors of the present review, as well as other investigators, extensive data have accumulated during the last two decades on the enthalpies of solution and solvation of organic non-electrolytes. It is therefore necessary to survey the existing data and to examine them from a single standpoint. In the present review, this has been done within the framework of the empirical approach developed previously.[4,5]

Problems of the solvation of compounds in binary solvents as well as problems of the thermochemistry of the hydration of organic non-electrolytes are not discussed in the present review. They have been dealt with in the monographs of Krestov and co-workers[6] and Belorusov and Panov.[7] Nor does the present review deal with the theoretical approaches to the analysis of the thermodynamic parameters of solvation, because these problems have already been described in monographs.[8,9]

## II. Phenomenological description

The stability of a solute molecule $A_i$ depends on its interaction with the molecules of the surrounding medium, i.e. with solvent molecules and with other solute molecules. Henceforth, we shall discuss only the situation where the interactions between the molecules of the solute $A_i$ in solution have been ruled out. The thermodynamic transfer functions are used to characterise such infinitely dilute solutions. Thus the enthalpy of the transfer of the substance $A_i$ to an infinitely dilute solution ($\Delta H_t^{A_i}$) is equal to the difference between the partial molar enthalpy of the solute $A_i$ in the infinitely dilute solution ($\overline{H}^{A_i}$) and the partial molar enthalpy of $A_i$ in the standard state ($\overline{H}_{st}^{A_i}$):

$$\Delta H_t^{A_i} = \overline{H}_{\infty}^{A_i} - \overline{H}_{st}^{A_i}. \quad (1)$$

If one uses the pure substance (p.s.) $A_i$ at a temperature $T$ and a pressure of 1 atm as the standard state [$H_{st}^{A_i}$ (p.s.)], then the enthalpy of the transfer of $A_i$ to the infinitely dilute solution from this state represents the enthalpy of solution of compound $A_i$ in the solvent S ($\Delta H_s^{A_i/S}$):

$$\Delta H_s^{A_i/S} = \overline{H}_{\infty}^{A_i} - \overline{H}_{st}^{A_i}\ (\text{p.s.}). \quad (2)$$

When the vapour of the pure non-electrolyte, which has the properties of an ideal gas and is at a temperature $T$ and a pressure of 1 atm, is adopted as the standard state [$\overline{H}_{st}^{A_i}$(G)], the enthalpy of transfer represents the enthalpy of solvation of compound $A_i$ in the solvent S ($\Delta H_{solv}^{A_i/S}$) and can be defined as follows:

$$\Delta H_{solv}^{A_i/S} = \overline{H}_{\infty}^{A_i} - \overline{H}_{st}^{A_i}\ (\text{G}). \quad (3)$$

According to Eqns. (2) and (3), the difference between the enthalpies of solution and solvation of compound $A_i$ in the two standard states is in its turn equal to the enthalpy of evaporation of $A_i$ ($\Delta H_{vap}^{A_i}$):

$$\Delta H_s^{A_i/S} - \Delta H_{solv}^{A_i/S} = \overline{H}_{st}^{A_i}(G) - \overline{H}_{st}^{A_i}(p.s.) = \Delta H_{vap}^{A_i}. \quad (4)$$

The enthalpy of transfer from one solvent to another $\{\delta H_s^{A_i}\}_{S_0}^{S}$, with the enthalpy of solution of $A_i$ in the solvent $S_0$ adopted as the standard state, is also used in studies on the thermochemistry of dissolution and solvation:

$$\{\delta H_s^{A_i}\}_{S_0}^{S} = \Delta H_s^{A_i/S} - \Delta H_s^{A_i/S_0} = \Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{A_i/S_0}. \quad (5)$$

In most cases the enthalpies of solvation of substances are determined from the differences between two experimentally measured quantities: the enthalpy of solution and the enthalpy of evaporation. Recommendations concerning the determination of the enthalpies of solution may be found in original communications, for example that of Izaat et al.[10] The methods used for the measurement, the estimation of errors, and the analysis of the enthalpy of evaporation data have been described in the monograph of Lebedev and Miroshnichenko.[11]

## III. Enthalpies of solvation of alkanes in various media

Systems where the solute is an alkane (Y) are relatively simple from the standpoint of the study of the nature of the forces of the intermolecular interaction which determines the solvation of alkanes. Frequent attempts have been made to calculate the enthalpies of solvation of alkanes in different, media representing it in the form of dispersion and induction interactions.[12]

The problem of the study of the thermodynamics of the solvation of alkanes usually reduces in essence to seeking the increment per $-CH_2-$ group.[12-14] This increment is found by determining the slope of the linear relation between the enthalpies of solvation of alkanes in a solvent S and the number of carbon atoms $n_C$ in the molecule of the dissolved alkane.

The influence of the branching of the alkane on the enthalpy of its solvation has been investigated[15] and it has been shown that the enthalpy of solvation of a normal hydrocarbon is greater in absolute magnitude than that of a branched hydrocarbon with the same number of carbon atoms in the molecule. The authors[15] explained this effect by the fact that steric hindrance arises in the interaction of the quaternary carbon atom with solvent molecules.

The dependence of the enthalpies of solution and evaporation of alkanes on their molar volumes [$V_M^{Y_i}$] and molecular refractions

$$[MR^{Y_i} = V_M^{Y_i}(n^2-1)/(n^2+2)],$$

has been investigated[4,5] and correlations have been established for the enthalpies of solution:

$$\Delta H_s^{Y_i/S} = k_S^{V_M} V_M^{Y_i}, \quad (6)$$

$$\Delta H_s^{Y_i/S} = k^{MR} MR^{Y_i}. \quad (7)$$

The proportionality coefficients $k_S^{V_M}$ and $k^{MR}$ in Eqns. (6) and (7) represent individual characteristics of the solvent and their significance will be revealed below. It is noteworthy that Eqns. (6) and (7) are applicable to liquid alkanes. If the enthalpies of solution of solid alkanes are analysed, then, according to Eqns. (6) and (7), the ratio of the enthalpies of transfer of alkanes is equal to the ratio of their molar volumes and molecular refractions, because the contribution of the enthalpy of fusion of the same substance to the enthalpy of its solution in a series of solvents is constant.

In contrast to the enthalpies of solution, the enthalpies of evaporation of alkanes $\Delta H_{vap}^{Y_i}$ depend significantly on the degree of branching of the carbon skeleton, groups of hydrocarbons with the same degree of branching giving rise to several almost parallel lines on the plot of $\Delta H_{vap}^{Y_i}$ against $MR^{Y_i}$:[4]

$$\Delta H_{vap}^{Y_i} = a_Y + bMR^{Y_i}, \quad (8)$$

where $a_Y$ is a constant term which depends on the structure of the alkane (kJ mol$^{-1}$) and $b$ = 1.05 kJ cm$^{-3}$. For linear alkanes, $a_Y$ = 0.91 ± 0.94 kJ mol$^{-1}$ and for monocyclic hydrocarbons, $a_Y$ = 4.39 ± 0.62 kJ mol$^{-1}$. the appearance in the alkane molecule of one tertiary or one quaternary carbon atom leads to a decrease in the enthalpy of evaporation by 1.31 ± 0.41 or 4.60 ± 0.93 kJ mol$^{-1}$ respectively compared with the value for the unbranched hydrocarbon with the same number of carbon atoms. Here one should bear in mind that the degree of branching of hydrocarbons hardly alters their molecular refraction.

If Eqns. (4) and (8) are valid, then the enthalpy of solvation of an alkane $Y_i$ in a solvent S is linearly related to the molar refraction of the dissolved hydrocarbon:

$$-\Delta H_{solv}^{Y_i/S} = a_Y + k_S' MR^{Y_i}. \quad (9)$$

An example of such relations is presented in Fig. 1. The constant term $a_Y$ in Eqn. (9) is almost independent of the type of solvent and is determined solely by the structural characteristics of the dissolved hydrocarbon. The coefficient $k_S'$ depends on the properties of the solvent and can be estimated from the equation

$$k_S' = b - k_S^{MR(V_M)}. \quad (10)$$

Fuchs and Stephenson[14] found an empirical relation between the enthalpies of solvation of the methylene group in various solvents and solvent parameters such as the Taft–Kamlert $\pi^*$ constant and a polarisability [function] $(n^2-1)/(2n^2+1)$:

$$\Delta H_{solv}^{-CH_2-} = -3.68 + 1.61(\pi^*)^2 - 5.99(n^2-1)/(2n^2+1). \quad (11)$$

By adding together several empirical correlations,[7,9,11] it is possible to obtain an expression which permits the estimation of the enthalpy of solvation of any alkane from its molar refraction, structural characteristics ($A_Y$), and the empirical parameters of the solvents:

$$\Delta H_{solv}^{Y_i/S} = a_Y + \left\{0.79 + 0.347(\pi^*)^2 + 1.29\frac{(n^2-1)}{(2n^2+1)}\right\} MR^{Y_i}. \quad (12)$$

The results presented in Table 1 show that there is agreement between the enthalpies of solvation calculated by Eqn. (12) and the experimental values.

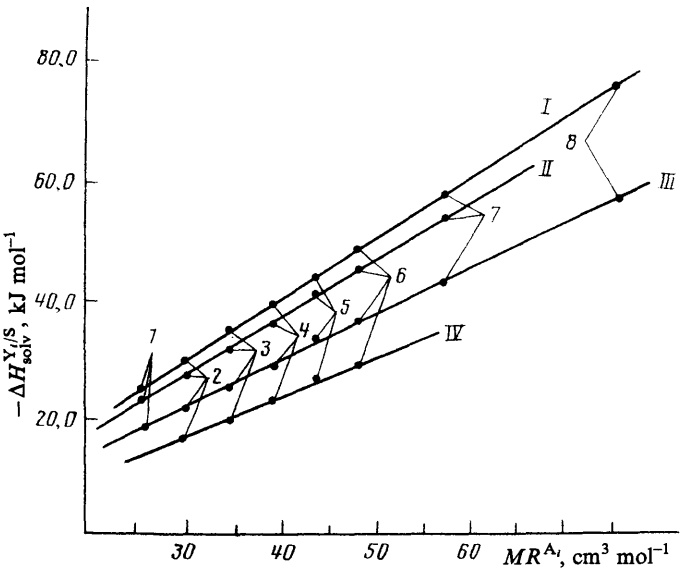



**Figure 1.** Relation between the enthalpies of solvation of alkanes and their molecular refractions in various solvents; (I) n-heptane; (II) n-butyl chloride; (III) dimethylformamide (DMF); (IV) dimethyl sulphoxide (DMSO). The numbers of the points correspond to the following compounds: *1*, n-pentane; *2*, n-hexane; *3*, n-heptane; *4*, n-octane; *5*, n-nonane; *6*, n-decane; *7*, n-dodecane; *8*, n-hexadecane. The enthalpies of solvation were taken from Fuchs and Stephenson.[14]

The relation obtained by Fuchs and Stephenson[14] is important also for the development of ideas about the solvation of organic compounds of different classes, because many organic compounds contain alkyl groups, the enthalpies of solvation of which enter additively into the enthalpy of solvation of the entire molecule.

The alkane solvation process can be subdivided arbitrarily into two stages:

(1) the creation in the solvent of a cavity whose size corresponds to the dimensions of the dissolved alkane molecule;

(2) the accommodation in this cavity of a molecule of the dissolved alkane and its interaction with solvent molecules.

Hence the enthalpy of solvation of an alkane can be represented by the sum of the enthalpies of formation of the cavity ($\Delta H_{cav}^{Y_i/S}$) and the enthalpy of the interaction of the alkane with the solvent ($\Delta H_{int}^{Y_i/S}$);

$$\Delta H_{solv}^{Y_i/S} = \Delta H_{cav}^{Y_i/S} + \Delta H_{int}^{Y_i/S}. \quad (13)$$

The problem of the subdivision of the solvation energy into the energy of formation of the cavity in the solvent and the energy of the interaction of the solute with the solvent has begun to be studied particularly vigorously during the last decade,[16–23] although this question had been raised already in the 1930's.[24,25] At the present time, there are two methods for calculating the energy of formation of the cavity. One of them is associated with the use of the theory of scaled particles (SPT) developed by Riess et al.[26] Another method for the calculation of the energy of formation of the cavity, based on the use of the concept of surface tension, was proposed by Sinanoglu.[27] It is noteworthy that the application of these methods to the calculation of the energy of the cavity leads to markedly divergent results.[18,19]

**Table 1.** Experimental enthalpies of solvation (kJ mol$^{-1}$) of cyclohexane and n-hexane in a series of solvents (298 K) and their values calculated by Eqn. (12).

| Solvent | $-\Delta H_{solv}^{C_6H_{12}/S}$ | | $-\Delta H_{solv}^{C_6H_{14}/S}$ | |
|---|---|---|---|---|
| | experiment | calculation | experiment | calculation |
| Hexane | 32.42 | 33.06 | 31.55 | 30.73 |
| Triethylamine | — | — | 31.20 | 31.14 |
| Dibutyl ether | 32.30 | 32.91 | 31.22 | 30.55 |
| Cyclohexane | 33.05 | 33.76 | 30.43 | 31.51 |
| 1-Octanol | — | — | 30.34 | 30.36 |
| Mesitylene | — | — | 30.29 | 30.64 |
| Carbon tetrachloride | 32.34 | 33.25 | 29.92 | 30.93 |
| 1-Chlorobutane | — | — | 29.54 | 29.59 |
| 2-Propanol | 31.05 | 30.94 | 29.77 | 28.46 |
| 1,1,1-Trichloroethylene | — | — | 29.04 | 29.17 |
| Toluene | 30.75 | 31.75 | 29.00 | 29.33 |
| Chlorobenzene | 30.59 | 30.00 | 29.04 | 27.49 |
| Tetrahydrofuran | 30.12 | 30.25 | 28.24 | 27.71 |
| 1,1,1-Trifluorotoluene | — | — | 28.20 | 27.11 |
| Fluorobenzene | 30.00 | 30.57 | 28.43 | 28.06 |
| Cyclohexanone | 29.70 | 28.43 | 27.16 | 25.79 |
| 1-Butanol | — | — | 27.07 | 29.26 |
| Benzene | 29.53 | 30.39 | 26.91 | 28.82 |
| Benzonitrile | 28.57 | 27.06 | — | — |
| Anisole | 28.16 | 29.64 | — | — |
| Methanol | 28.11 | 29.05 | 25.86 | 26.42 |
| Acetophenone | 27.99 | 27.13 | 26.53 | 24.38 |
| Ethyl acetate | 27.94 | 30.17 | 26.68 | 27.63 |
| Nitrobenzene | 27.15 | 25.34 | — | — |
| 1,2-Dichloroethane | 26.73 | 27.66 | 24.20 | 24.93 |
| 1,4-Dioxane | 26.48 | 30.77 | 24.04 | 28.54 |
| Dimethylformamide | 25.65 | 26.35 | 23.64 | 23.54 |
| Acetonitrile | 24.03 | 25.70 | 21.13 | 22.84 |
| Dimethyl sulphoxide | 21.67 | 24.68 | 18.24 | 21.74 |
| Nitromethane | 20.25 | 26.24 | 17.79 | 23.41 |

Note. The enthalpies of solvation of the alkanes were taken from Refs.14, 15, and 29.

Attempts have been made to estimate experimentally the energy of formation of the cavity.[15,28–30] This was done most logically in the studies of the present authors and their co-workers.[28,29] The method proposed[28,29] was based on the following assertions: (1) the energy of formation of the cavity depends only on the energy of the solvent–solvent interaction and on the size of the solute molecules; (2) the energy of the interaction of the alkane with the solvent per unit volume of the latter is constant. The validity of the second postulate has been demonstrated in a series of studies.[31–34]

The enthalpy of solution of an alkane $Y_i$ in a solvent S is described by the expression

$$\Delta H_s^{Y_i/S} = \Delta H_{vap}^{Y_i} + \Delta H_{cav}^{Y_i/S} + \Delta H_{int}^{Y_i/S}. \quad (14)$$

Taking into account the postulate that the energy of the interaction of the alkane with different organic non-electrolytic solvents is

constant, the differences between the enthalpies of solution of alkanes in a series of solvents are then determined by the differences between the enthalpies of formation of the cavity in these solvents:

$$(\delta H_s^{Y_i})_{S_h}^S = (\delta H_{cav}^{Y_i})_{S_h}^S, \quad (15)$$

where $S_h$ is a hypothetical solvent in which the heats of solution of all saturated hydrocarbons are zero. It has been suggested[28,29] that each solvent be characterised by the specific relative enthalpy of formation of the cavity ($\delta h_{cav}^S$), which is equal to the proportionality coefficient $k_S$ in Eqns. (6) and (7). Knowing $k_S$ and the molecular refraction or molar volume of the substance $A_i$, it is possible to calculate the relative enthalpy of formation of the cavity generated by $A_i$ in the solvent and to determine the enthalpy of the interaction of the solute with the solvent by an equation analogous to Eqn. (15).

The solvation energy has been represented[35] by three terms; the energy of formation of the cavity, the energy of the interaction of the solute with the solvent, and the energy of the reorganisation of the solvent molecules around the cavity in the solvent. The last term can be regarded as the "response" of the solvent to the replacement in the latter of a hypothetical molecule, not interacting with the solvent, by the real molecule which is capable of entering into various intermolecular interactions of the solvent–solute type.

Kiselev et al.[36] proposed a rigorous axiomatic approach to the consideration of the solvation process, which make it possible to justify theoretically the existing ideas in the literature concerning solvation as a multistage process and to estimate the limits of its applicability.

## IV. Enthalpies of solvation of various compounds in alkanes

The thermochemistry of solvation of various compounds in alkanes has been studied in a number of investigations.[31,32,37–49] A universal relation between the enthalpies of solvation of compounds in cyclohexane and their molecular refractions was obtained on the basis of the results. It holds for most varied classes of compounds (Fig. 2). It is noteworthy that Fig. 2 presents data for compounds whose molecules contain an unbranched hydrocarbon skeleton. For cases where the solute molecule has a branched hydrocarbon skeleton, regularities have been found in the deviations from the linear relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$. An attempt has been made[5] to explain the universal relation between the enthalpies of solvation of compounds in cyclohexane and their molecular refractions on the basis of existing ideas about intermolecular interaction. It was verified if the molecular refraction is the only parameter of a substance to which its enthalpy of solvation in an alkane is linked by such a simple relation. For this purpose, correlations were drawn between $\Delta H_{solv}^{A_i/C_6H_{12}}$ and the molar volume ($V_M^{A_i}$), the molar magnetic susceptibility ($\chi_M^{A_i}$), and the surface area ($A_W$) calculated by Bondi's method:[50]

$$-\Delta H_{solv}^{A_i/C_6H_{12}} = 13.13 + 0.207 V_M^{A_i},$$
$$n = 72,\ r = 0.92,\ S_0 = 26.6;$$

$$-\Delta H_{solv}^{A_i/C_6H_{12}} = 15.21 + 1.995 \chi_M^{A_i},$$
$$n = 41,\ r = 0.95,\ S_0 = 16.4;$$

$$-\Delta H_{solv}^{A_i/C_6H_{12}} = 6.4 + 3.51 A_W,$$
$$n = 74,\ r = 0.80,\ S_0 = 7.99.$$

Comparison of the correlation parameters of the equation shows that the best description of the enthalpies of solvation in an alkane can be obtained with the aid of molecular refraction:

$$-\Delta H_{solv}^{A_i/C_6H_{12}} = 5.09 + 1.03 MR^{A_i}, \quad (16)$$
$$n = 102,\ r = 0.994,\ S_0 = 1.56.$$

Molecular refraction is known to be a thermodynamically invariant quantity.[51] Furthermore, the solvent exerts only a weak influence on it.[52] Molecular refraction and polarisability are sometimes regarded as measures of the "intrinsic volume" of molecules[53] or as the factors responsible for dispersion interactions. In the thermodynamics of solutions, the volume properties of the solute molecules are expressed in terms of the limiting values of the partial molar volumes ($\overline{V}_M^{A_i}$). It is believed that $\overline{V}_M^{A_i}$ is mainly made up of two quantities: the intrinsic volume of the molecule and the change in the volume of the solution as a result of the influence of the dissolved molecule on the packing of the solvent molecules in the perturbed part of the solution.[54]

The concept of the "intrinsic volume" of the molecule in a liquid is highly indefinite. The molecular size is sometimes expressed in terms of the molar volume, the van der Waals volume, the parachor, or the molar refraction. The interpretation of the observed relation between $\Delta H_{solv}^{A_i/C_6H_{12}}$ and $MR^{A_i}$ would be greatly simplified if there were a relation between $MR^{A_i}$ and $\overline{V}_M^{A_i}$. However, there are too few data for the partial molar volumes of different compounds in alkanes to reach any serious conclusions and the small amount of information available indicates the absence of a general relation between $MR^{A_i}$ and $\overline{V}_M^{A_i}$.[5]

The interaction of alkanes with organic compounds has been discussed[12,38] within the framework of not only dispersion but also induction interactions. The existence of a relation between $\Delta H_{solv}^{A_i/C_6H_{12}}$ and $MR^{A_i}$ in cyclohexane shows that, when solvation phenomena involving alkanes are considered, the induction interactions can be neglected, since, if it were the case that the contribution of these interactions plays a significant role, then for compounds having the same $MR^{A_i}$ but different dipole moments, for example, for cyclooctane ($\mu$ = 0 D, $MR^{A_i}$ = 36.5 cm$^3$ mol$^{-1}$) and acetophenone ($\mu$ = 3 D, $MR^{A_i}$ = 36.5 cm$^3$ mol$^{-1}$), the enthalpies of solvation would not be the same, as indicated by experimental data. The molecular dipole moments of compounds dissolved in cyclohexane (Fig. 2) differ by several units. Since there is no general relation between molecular refraction and the dipole moment, the linear relation between $\Delta H_{solv}^{A_i/C_6H_{12}}$ and $MR^{A_i}$ implies that, within the limits of experimental error, the enthalpies of solvation of compounds in alkanes are determined by forces related to the polarisability of molecules. It is believed that these forces are induced by dispersion interactions. Experimental enthalpies of solvation of compounds in cyclohexane have been compared[5] with the energies of dispersion interactions calculated in different ways. It has been shown that only the Kirkwood–Muller equation[16] reproduces the observed relation between $\Delta H_{solv}^{A_i/C_6H_{12}}$ and $MR^{A_i}$ to an adequate degree of approximation.

The universal relation discovered[31,32] between the enthalpies of solvation of compounds in cyclohexane and their refractions created new possibilities for the determination of the enthalpies of solvation of compounds in other solvents. The point is that, in the present stage of the experimental determination of enthalpies of solvation, this is primarily the problem of measuring the enthalpy of evaporation of the solute. The problem consists not only in the fact that it is extremely difficult to measure $\Delta H_{vap}^{A_i}$ but also in the

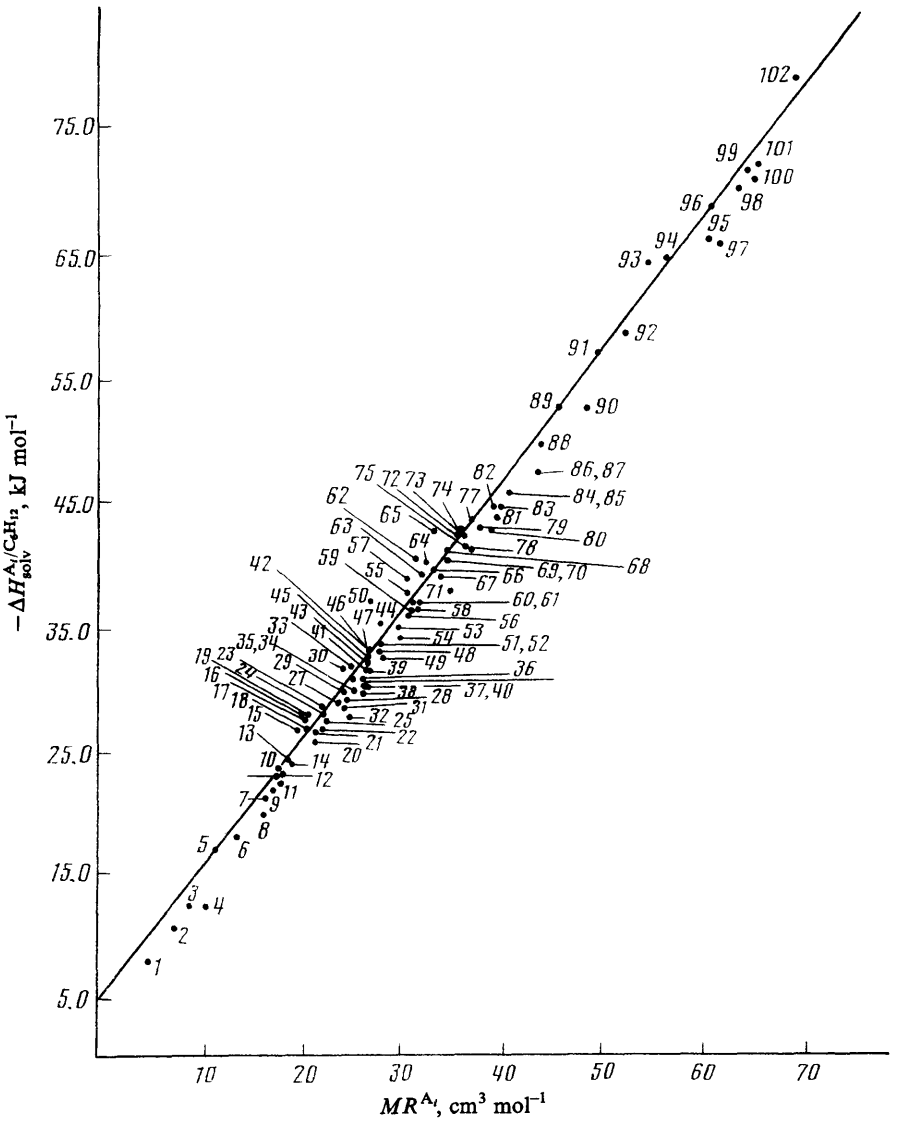



**Figure 2.** Relation between the enthalpies of solvation of compounds in cyclohexane and their molar refractions. The numbers of the points correspond to the following compounds: *1*, water; *2*, hydrogen chloride; *3*, methanol; *4*, hydrogen bromide; *5*, propionitrile; *6*, ethanol; *7*, propanal; *8*, propanone; *9*, 1-cyano-2-propene; *10*, 2-propen-1-ol; *11*, 1-propanol; *12*, methyl acetate; 13, 1-amino-2-propene; *14*, iodomethane; *15*, ethyl nitrate; *16*, tetrahydrofuran; *17*, chloroform; *18*, *cis*-1,2-dichloroethylene; *19*, *trans*-1,2-dichloroethylene; *20*, butanone; *21*, carbon disulphide; *22*, 1-butanol; *23*, methyl propionate; *24*, ethyl acetate; *25*, dimethyl sulphite; *26*, 1,4-dioxane; *27*, propane-1-thiol; *28*, 1-aminobutane; *29*, 1,2-dimethoxyethane; *30*, pyridine; *31*, thiophen; *32*, hexafluorobenzene; *33*, cyclopropyl methyl ketone; *34*, 2-pentanone; *35*, 3-pentanone; *36*, trichloroethylene; *37*, 1-chlorobutane; *38*, 1,4-difluorobenzene; *39*, fluorobenzene; *40*, benzene; *41*, carbon tetrachloride; *42*, piperidine; *43*, 1-pentanol; *44*, ethyl chloroacetate; *45*, methyl butyrate; *46*, n-propyl acetate; *47*, cyclohexane; *48*, 1-bromobutane; *49*, iodine; *50*, phenol; *51*, butane-1-thiol; *52*, 1-iodopropane; *53*, 2-hexanone; *54*, 3-hexanone; *55*, aniline; *56*, 1,1-dichlorobutane; *57*, 1,1,2,2-tetrachloroethane; *58*, 1-hexanol; *59*, chlorobenzene; *60*, n-butyl acetate; *61*, methyl valerate; *62*, benzonitrile; *63*, benzaldehyde; *64*, methyl trichloroacetate; *65*, nitrobenzene; *66*, methyl phenyl ether; *67*, bromobenzene; *68*, thiophenol; *69*, 2-heptanone; *70*, 4-heptanone; *71*, phenylacetylene; *72*, 1,4-dichlorobenzene; *73*, 1,2-dichlorobenzene; *74*, heptanol; *75*, vinylbenzene; *76*, acetophenone; *77*, ethyl trichloroacetate; *78*, phenyl acetate; *79*, methyl benzoate; *80*, 2-octanone; *81*, iodobenzene; *82*, 1,3-dinitrobenzene; *83*, methyl phenyl sulphide; *84*, 1-octanol; *85*, *N*,*N*-di-methylaniline; *86*, 2-nonanone; *87*, 5-nonanone; *88*, naphthalene; *89*, 1,2,4,5-tetrachlorobenzene; *90*, 2-decanone; *91*, 1-decanol; *92*, biphenyl; *93*, hexachlorobenzene; *94*, benzophenone; *95*, *cis*-azobenzene; *96*, phenanthrene; *97*, benzil; *98*, *trans*-azobenzene; *99*, anthracene; *100*, 1-bromodecane; *101*, 1,2-diphenylethylene; *102*, diphenylmercury. The enthalpies of solution and solvation were taken from Refs. 5, 31, 32, and 37–49.

fact that traditionally this problem is dealt with by specialists who use the values of $\Delta H_{vap}^{A_i}$ to determine the enthalpy of formation of a substance in the gas phase. It is quite natural that the set of experimental enthalpies of evaporation produced by them is suitable in the first place for the solution of problems in this field. Among the investigators known to us only Fuchs[47] and Suvorov and Kondrat'ev[55] measured enthalpies of evaporation in order to study solvation phenomena.

We proposed[4,31,32] a version of what is in our view an extremely convenient method for the determination of $\Delta H_{vap}^{A_i}$, which for many compounds is not inferior to dissolution calorimetry as regards its productivity and simplicity of its application. It is based on the use of the observed relation between the enthalpies of solvation of compounds in cyclohexane and their molar refractions. The determination of the enthalpy of evaporation in this method reduces to measurements of the enthalpy of solution of the given compound in cyclohexane and of its molecular refraction:

$$\Delta H_{vap}^{A_i} = \Delta H_s^{A_i/C_6H_{12}} + 4.39 + 1.05 MR^{A_i}. \quad (17)$$

For compounds with a branched hydrocarbon skeleton, it is necessary to introduce the appropriate corrections.[32] Unfortunately, it is difficult to determine the error of the measurement of $\Delta H_{vap}^{A_i}$ by the method described,[31,32] because the existing significant discrepancies with literature data may be caused either by the limited applicability of Eqn. (17) or by the not always correct measurement of $\Delta H_{vap}^{A_i}$ by direct methods (the errors in the measurement of the enthalpies of solution of compounds in cyclohexane are not so great).

We shall now discuss the advantages of the method based on Eqn. (17). Firstly, in this method the molecular weight and the state of aggregation of the substance do not have such a significant influence on the accuracy of the measurement of $\Delta H_{vap}^{A_i}$ because the enthalpy of solution in alkane does not depend greatly on these parameters. An increase in the molecular weight of the substance leads in essence to a decrease in the relative error in the determination of the enthalpy of evaporation. Secondly, the determination of $\Delta H_{vap}^{A_i}$ for involatile compounds by classical methods requires fairly high temperatures. Many organic and organoelement compounds tend to decompose at these temperatures. Therefore, for compounds of this kind our method[31,32] may prove to be virtually the only one suitable at the present time.

There is no doubt that the direct experimental measurement of the enthalpy of evaporation is more promising from the standpoint of the accuracy of its determination. However, bearing in mind the difficulties in the determination of the enthalpy of formation at the present stage, the method based on the use of Eqn. (17) is, in our view, an essential instrument for the investigation of the thermochemistry of solvation over a wide range of organic compounds. Fuchs et al.[56] recently improved the equation relating the enthalpy of solvation and the molar refraction and put forward the following two parameter equation:

$$-\Delta H_{solv}^{A_i/S} = a + bMMR^{A_i} + cV_M^{A_i}, \quad (18)$$

where

$$MMR^{A_i} = V_M^{A_i} \quad (n^2-1)/(n^2+2),$$

is a function of polarisability. It was shown[56] that, for the range of compounds investigated (carbon tetrachloride, perfluoroheptane, diiodomethane, benzene, hexane, decane, hexadecane, cyclohexane, toluene, and mesitylene), Eqn. (18) describes the enthalpy of solvation better than Eqn. (17).

## V. The influence of the polarity of the medium on the enthalpy of the non-specific solvation of organic non-electrolytes

Before proceeding to the description of this problem, it appears to be necessary to discuss the concept of the polarity of a non-electrolyte. The dipole moment of a molecule is the most widely used measure of the polarity of a non-electrolyte when solvation phenomena are considered. However, there exists also another viewpoint on the determination of the polarity of solute molecules which has been most fully formulated by Claessens et al.[57] These authors believe that the postulate that any polar molecule should possess a dipole moment is incorrect. Thus a molecule may have no dipole moment owing to the complete compensation of two systems of the distribution of charge density in the molecule, each of which is characterised by a dipole moment. The molecules having such a charge distribution have a quadrupole moment and are polar. The same considerations can be applied when oppositely directed quadrupoles are considered, etc. The authors[57] therefore suggest that the expression "polar molecule" be replaced by the expressions "dipolar molecule", "quadrupolar molecule", etc. The energies of electrostatic interactions for such molecules can be calculated by the equation[57]

$$\Delta G_{int} = -N_{A_i}\left[\frac{1}{2}\frac{2(\varepsilon_S-1)}{2\varepsilon_S+1}\frac{\mu_\alpha^2}{a^3} + \frac{1}{6}\frac{6(\varepsilon_S+1)}{3\varepsilon_S+2}\frac{\theta_{\alpha\beta}}{a^5} + \frac{1}{30}\frac{24(\varepsilon_S-1)}{4\varepsilon_S+3}\frac{\Omega_{\alpha\beta\gamma}}{a^7} + \ldots\right], \quad (19)$$

where $\varepsilon_S$ is the dielectric constant of the solvent, $\mu_\alpha$ a component of the dipole moment, $a$ the radius of the cavity in which the molecule has been placed, $\theta_{\alpha\beta}$ a component of the quadrupole moment, and $\Omega_{\alpha\beta\gamma}$ a component of the octupole moment.

The idea of the polarity of the substance as a combination of the properties of dipolarity and polarisability appears less definite.[58] We adopt the dipole moment of the solute molecule as a measure of its polarity. The dielectric constant is adopted as a measure of the solvent polarity. Hence the problem of polarity reduces to the elucidation of the influence of these parameters on the energy of non-specific solvation.

The contribution of polar interaction is usually estimated by applying the homomorph principle, according to which the enthalpy of non-specific solvation, determined by dispersion forces for a compound capable of specific $[\Delta H_{int}^{A_i/S}(sp)]$ or polar $[\Delta H_{int}^{A_i/S}(or)]$ interactions is set equal to the enthalpy of solvation of a compound incapable of such interactions. An alkane $Y_i$ with a molar volume equal to that of the solute $A_i$ is usually selected as the homomorph:

$$\Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{Y_i/S} = \Delta H_{int}^{A_i/S}(sp) + \Delta H_{int}^{A_i/S}(or). \quad (20)$$

If the polar molecule does not enter into a complex formation reaction with the solvent, the difference on the left-hand side of Eqn. (20) represents in this case the enthalpy of orientation interaction.

As can be seen from Eqn. (20), the homomorph method is based on the hypothesis that the dispersion interactions are determined

solely by the size of the solute molecules. However, it has been shown[4,59] that this hypothesis is incorrect, and the contributions of orientation interaction to the enthalpy of solvation, calculated by Eqn. (20), therefore represent overall quantities.

In this section, we shall attempt to show, using both our own and literature data, that the molecular dipole moment of the solute does not exert a significant influence on the enthalpy of solvation. The existence of a relation between the enthalpies of solvation of compounds of different polarity in cyclohexane (Fig. 2) and their molar refraction shows that the dipole–induction interactions do not make a significant contribution to the enthalpy of solvation.

The enthalpies of solvation of benzene and its halo-derivatives in cyclohexane and dimethyl sulphoxide are compared in Table 2. As can be seen from the results presented in Table 2, the difference between the enthalpies of solvation of chlorobenzene and benzene in cyclohexane and dimethyl sulphoxide ($\varepsilon_{C_6H_{12}} = 2.02$, $\varepsilon_{(CH_3)_2SO} = 46.6$) is approximately the same despite the fact that the polarities of the two solutes differ ($\mu_{C_6H_5Cl} = 1.7$ D, $\mu_{C_6H_6} = 0$ D). The enthalpies of solvation of these compounds are determined by dispersion forces. Relatively small differences between the $\Delta H_{solv}^{A_i/S}$ for halobenzenes in the two solvents can therefore be attributed, in principle, to their orientation interaction with dimethyl sulphoxide. However, the small size of the postulated orientation interaction of halobenzenes with the polar dimethyl sulphoxide is a major embarrassment. The results of Krichnan and Friedman[35] and Fuchs et al.[45] therefore stimulated our interest in the problem of solvation of aromatic hydrocarbons and their halo-derivatives.[59–61] It was found that, despite the difference between the polarities ($\Delta\mu = 2.5$ D) of the solutes and solvents ($\Delta\varepsilon_S = 59$), in all the cases investigated there is an excellent linear relation between $\Delta H_{solv}^{A_i/S}$ and the molar refraction of the solute:

$$-\Delta H_{solv}^{A_i/S} = a_S + b_S MR^{A_i}. \qquad (21)$$

**Table 2.** Enthalpies of solvation (kJ mol$^{-1}$) of benzene and fluoro-, chloro-, and bromo-benzenes in dimethyl sulphoxide and cyclohexane (298 K).

| Solvent | $-\Delta H_{solv}^{C_6H_5X/S}$ | | | | Refs. |
|---|---|---|---|---|---|
| | X=H | X=F | X=Cl | X=Br | |
| Dimethyl sulphoxide | 31.1 | 34.2 | 38.1 | 41.6 | [35] |
| Cyclohexane | 29.9 | 30.9 | 36.5 | 39.3 | [45] |

These results imply that the contribution of orientation interactions to the enthalpies of solvation of the test compounds is insignificant.

Another method of estimating the contribution of orientation interactions to the enthalpy of solvation has also been used[59–61] — comparison of the enthalpies of solution and solvation of compounds differing only in dipole moment. Such compounds are, in particular, the *o*-, *m*-, and *p*-isomers of disubstituted benzenes and the *cis*- and *trans*-isomers of disubstituted ethylenes. Pairwise comparison of the enthalpies of solution of these compounds in a series of solvents yielded a straight line with a slope close to unity.[59–61] The solvent polarity was varied within wide limits (from carbon tetrachloride to dimethyl sulphoxide). According to Eqn. (5), the difference between the enthalpies of solvation of compounds is equal to the difference between their enthalpies of solution. Hence it follows that the relative enthalpy of solvation is independent of the dipole moment ($\Delta\mu = 6.0$ D) of the solute molecule.

The absence of an influence of the molecular dipole moment of the solute on the enthalpies of solvation of the organic non-electrolytes investigated may be due to several causes. Firstly, it is possible that not the dipole moment of the molecule as a whole but the dipole moments of individual groups or bonds in the molecule are important for solvation. This hypothesis makes it possible to explain the identical enthalpies of solvation of isomers. Secondly, the molecules investigated in the studies mentioned above [35,45,59–61] are fairly large and the continuous theory with the aid of which the contribution of electrostatic interactions to the solvation energy is estimated requires allowance not only for the dipole moment of the molecule but also for the size of the latter,[62] which was not done. Thirdly, it is possible that the contributions of polar interactions to the enthalpy of solvation are compensated by the energy of reorganisation of the solvent.[4,59] A detailed analysis of the causes which induced such an unusual phenomenon is therefore necessary.

The version which states that, for the analysis of the factors determining the solvation energy one must take into account not the dipole moment of the molecule as a whole but the dipole moments of its individual groups, appeared many years ago and was based on the study of different physicochemical characteristics of halobenzenes.[63]

The influence of the dipole moment of the $C_{Ar}-Hal$ bond on the enthalpies of solvation of halobenzenes was tested.[4,59] Since the dipole moment of the $H-C_{Ar}$ bond (0.7 D [64]) is approximately equal in absolute magnitude to the dipole moment of the $C_{Ar}-Hal$ bond (1.0 D [65]), the substitution of hydrogen atoms by halogen atoms in the molecule should not alter significantly the "polarity" of the latter. From this standpoint, the "polarities" of halobenzenes and benzene are the same. On the other hand, naphthalene, diphenyl, and anthracene are more "polar" than benzene, because they contain a larger number of polar bonds. If there is a linear relation between $\Delta H_{solv}^{A_i/S}$ for aromatic hydrocarbons and polyhalobenzenes and their $MR^{A_i}$ while the dipole moments of individual bonds in the solute molecule influence its enthalpy of solvation, then at least a parallel variation should be observed between the characteristic of the "polarity" of the solute

$$n\sum_{i=1}^{n}\mu_i(C_{Ar}-H) \quad \text{or} \quad n\sum_{i=1}^{n}\mu_i(C_{Ar}-Hal),$$

and its molecular refraction. However, it has been shown[4,59] that such parallel variation is not observed. This means that the dipole moment of the $C_{Ar}-H$ or $C_{Ar}-Hal$ bond does not influence significantly the enthalpies of solvation of halobenzenes.

## VI. Enthalpy of complex formation as a component of the enthalpy of solvation

The enthalpy of solvation of a substance can be represented by the sum of the enthalpies of non-specific solvation $\Delta H_{solv}^{A_i/S}$ and specific interaction $\Delta H_{int}^{A_i/S}$ (sp):

$$\Delta H_{solv}^{A_i/S} = \Delta H_{solv}^{A_i/S}(\text{non-sp}) + \Delta H_{int}^{A_i/S}(\text{sp}). \qquad (22)$$

The enthalpy of the specific interaction of the solute with the solvent represents the enthalpy of the complex formation reaction ($\Delta H_c^{A_i/S}$) (of the type of reaction involving the formation of hydrogen or donor–acceptor bonds between the solute and solvent molecules) per mole of the solute.

There are conflicting points of view in the literature on the relative contributions of the enthalpies of non-specific solvation and specific interaction to the enthalpy of solvation. Before proceeding to the discussion of the question of the subdivision of the enthalpy of solvation into components [Eqn. (22)], we shall demonstrate that these relative contributions may be different (Table 3).

**Table 3.** Relation between the enthalpies of non-specific solvation and the enthalpies of specific solvation (kJ mol$^{-1}$) for a series of compounds (at 298 K).[66]

| Solute $A_i$ in a solvent S | $-\Delta H_{solv}^{A_i/S}$(non-sp) | $-\Delta H_{int}^{A_i/S}$(sp) |
|---|---|---|
| Phenol in benzene | 44.3 | 4.6 |
| Iodine in chlorobenzene | 37.7 | 4.6 |
| Pyrrole in dimethylformamide | 37.2 | 13.4 |
| Phenol in pyridine | 44.1 | 30.4 |
| Water in tetrahydrofuran* | 18.3 | 20.2 |
| Water in dimethyl sulphoxide* | 16.4 | 32.6 |

*Data taken from Somonov et al.[67] are quoted.

The development of a method for the subdivision of $\Delta H_{solv}^{A_i/S}$ into components consists in finding general principles of some kind which govern the determination of the enthalpy of non-specific solvation. Thus, from the difference between the enthalpies of solvation and non-specific solvation, we obtain the enthalpy of specific interaction, which may be compared with the enthalpy of complex formation, determined, for example, by spectroscopic methods. The agreement between the latter quantities may be a test of the validity of the method of subdivision of the enthalpy of solvation. Naturally, the most general principles governing the determination of the enthalpy of non-specific solvation can be deduced only when the principal quantitative relations involving the variation of the enthalpy as a function of the structural characteristics of the solute have become clear. Apparently the above problem cannot be fully solved at the present time but the search for ways of solving the problem of the subdivision of $\Delta H_{solv}^{A_i/S}$ into components by deducing the general principles governing the determination of the enthalpy of non-specific solvation nevertheless appears more progressive than the search for partial solutions.[44,68,69]

The simplest method of estimating the enthalpy of specific interaction consists in determining the difference between the enthalpies of solution in a solvent S and in a solvent I (usually carbon tetrachloride or an alkane) which is inert from the standpoint of the possibility of the formation of specific bonds with the solute:

$$\Delta H_{int}^{A_i/S}(sp) = \Delta H_s^{A_i/S} - \Delta H_s^{A_i/I} = \Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{A_i/I}. \quad (23)$$

The disadvantages of this method as well as its modified version[70] have been discussed.[66] The method for the determination of $\Delta H_{int}^{A_i/S}$ (sp) according to which the enthalpy of specific interaction is determined from the difference between the enthalpies of solvation in a solvent S of the test compound $A_i$ and of a compound $M_i$, which resembles $A_i$ as regards molecular size, structure, and the parameters responsible for the non-specific interaction but is incapable of entering into specific interactions with the solvent S is free from fundamental disadvantages:

$$\Delta H_{int}^{A_i/S}(sp) = \Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{M_i/S}. \quad (24)$$

Since the enthalpy of solvation of the compound $M_i$ models the enthalpy of the non-specific solvation of compound $A_i$, $M_i$ is referred to as a model compound.

The method based on Eqn. (24) has been used to determine the enthalpies of formation of hydrogen bonds between the molecules of pyridine, water, and methanol,[71] diazines, water, and methanol,[72] and oct-1-yne and a series of proton-accepting solvents.[73]

In order to obviate the difficulty involving the determination of $\Delta H_{vap}^{A_i}$, Arnett and co-workers[44,68,69] suggested that the enthalpy of specific interaction be determined from the equation

$$\Delta H_{int}^{A_i/S}(sp) = [\Delta H_s^{A_i/S} - \Delta H_s^{A_i/CCl_4}] - [\Delta H_s^{M_i/S} - \Delta H_s^{M_i/CCl_4}]. \quad (25)$$

This method, known as the "pure base method", has been used in numerous investigations.[74–80]

Spencer et al.[78] proposed an equation which makes it possible to calculate the enthalpy of specific interaction from the enthalpies of the transfer of compounds from one solvent to another.

Two further new methods for isolating the contribution of the enthalpy of specific interaction have been developed recently.[4,66,67,81–85] One of them[4,66,67,81] is based on the study of the dependence of the enthalpies of solvation of compounds in carbon tetrachloride on the molecular refraction, which makes it possible to classify the solutes in terms of the type of non-specific solvation: for example, aromatic hydrocarbons and their halo-derivatives; monofunctional aromatic compounds containing the nitrile, carbonyl, nitro-, amino-, and hydroxy-groups. This classification makes it possible to find the enthalpies of non-specific solvation of various compounds from the relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$ established for compounds of the same type but incapable of specific interaction with the solvent.

Fig. 3 presents the relation between the enthalpies of solvation of some of the compounds investigated in the above studies[4,66,67,81] and their molecular refractions in carbon tetrachloride and in acetonitrile. The enthalpies of solvation of compounds in carbon tetrachloride are non-specific. In acetonitrile the picture is somewhat different: the points corresponding to compounds capable of specific interaction with the solvent deviate from the general relation. The magnitudes of the deviation of these points, determined from the plot of $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$ (Fig. 3*a*), is virtually equal to the enthalpy of complex formation between the solute† and the solvent determined in an inert solvent.

†The data for water are an exception, because the water molecule contains two hydrogen atoms capable of complex formation with the solvent.[67]

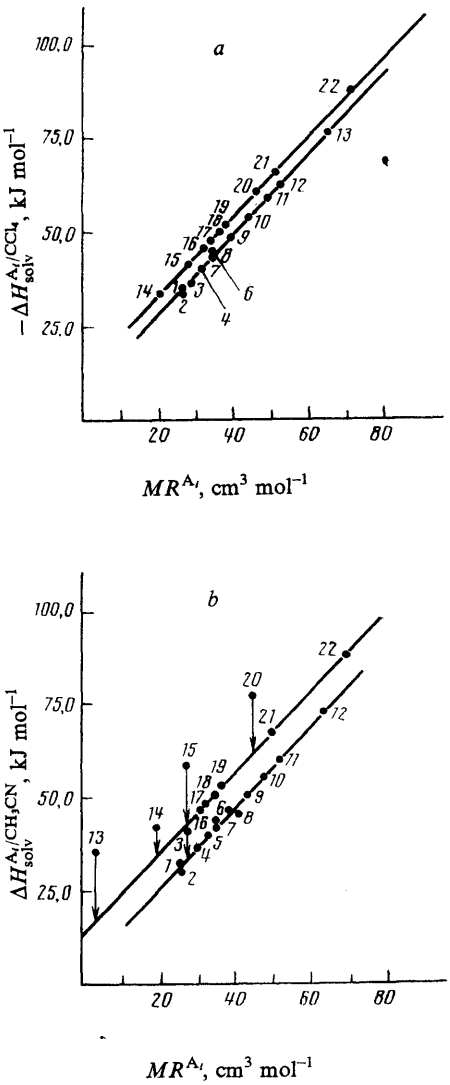



**Figure 3.** Relation between the enthalpies of solvation of compounds in carbon tetrachloride (*a*) and acetonitrile (*b*) and their molar refractions. The numbers of the points correspond to the following compounds: *1*, fluorobenzene; *2*, benzene; *3*, iodine; *4*, chlorobenzene; *5*, bromobenzene; *6*, *o*-dichlorobenzene; *7*, *p*-dichlorobenzene; *8*, iodobenzene; *9*, naphthalene; 10, 1-chloronaphthalene; *11*, biphenyl; *12*, anthracene; *13*, water; *14*, pyrrole; *15*, phenol; *16*, benzaldehyde; *17*, nitrobenzene; *18*, *p*-chlorobenzaldehyde; *19*, *p*-chloronitrobenzene; *20*, 1-naphthol; *21*, 1-nitronaphthalene; *22*, 9-anthraldehyde. The enthalpies of solvation were taken from Refs. 59, 66, and 67.

Fuchs and Stephenson[82–85] suggested that the "base line" method be used for the determination of the energies of hydrogen bonds. Its essential feature involves the comparison of the difference between the enthalpies of solvation of compounds $A_i$ and $M_i$ in a series of solvents with the Taft–Kamlert $\pi^*$ constants. A "base line" is drawn through the points corresponding to inert solvents (n-heptane, cyclohexane, carbon tetrachloride, α,α,α-trifluorotoluene, and 1,2-dichloroethane). It takes into account the discrepancy between the enthalpies of solvation of the solute $A_i$ and the model compound $M_i$, which models the non-specific solvation of $A_i$ on passing from one solvent to another:

$$\Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{M_i/S} = m\pi^* + d, \qquad (26)$$

where $m$ and $d$ are the parameters of the correlation. If the complex formation reaction takes place between the solute and the solvent, then the plot of the relation between the relative enthalpy of solvation $\Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{M_i/S}$ and the $\pi^*$ constant shows deviations of the points for the corresponding solvents which are equal to the enthalpies of specific interaction.

It is noteworthy that the methods for the determination of $\Delta H_{int}^{A_i/S}$ (sp) described in the studies quoted[4,66,67,81–85] reflect, in essence, two approaches to the study of the thermochemistry of solvation of organic non-electrolytes. In one of them,[4] emphasis is laid on the study of the solvation of structurally different solutes in one solvent of some kind. In the other approach,[82–85] the structure of the solutes is fixed and the properties of the solvent are varied. In contrast to the method based on the study of the relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$, the "base line" method reproduces the variation of the difference $\Delta H_{solv}^{A_i/S}$ (non-sp) – $\Delta H_{solv}^{M_i/S}$ in a series of solvents. In this case, it is necessary to solve a further two problems; to plot a reliable "base line" and to select the model compound.

In order to plot the "base line", it is essential to have data for several inert solvents which have different $\pi^*$ constants, and this is not always possible. For example, it is difficult to determine the enthalpies of solution of carboxylic acids in cyclohexane, carbon tetrachloride, or benzene. One must be sure that the solvents employed are indeed inert. Since usually few such solvents are available, even a weak complex formation reaction with the solute can greatly distort the calculated results. If only two inert solvents are suitable for the test system, for example, cyclohexane and carbon tetrachloride, the probability of error increases.

The disadvantages of the existing methods for the determination of the enthalpy of specific interaction have been subjected to a thorough analysis.[66,86] This made it possible to formulate a series of measures whose application would permit the optimum determination of $\Delta H_{int}^{A_i/S}$ (sp). The essential features of these measures reduce to the following. In the initial stage, it is necessary to determine the enthalpy of the transfer of a molecule of compound $A_i$ from an inert solvent to a solvent S [see Eqn (22)]. This permits a rough estimate of $\Delta H_{int}^{A_i/S}$ (sp). Here one must bear in mind that carbon tetrachloride and not an alkane must be used as the inert solvent.

In the case where the solute $A_i$ contains an alkyl group the enthalpy of solvation of which varies significantly from solvent to solvent, the following equation has been proposed:

$$\Delta H_{int}^{A_i/S}(sp) = [\Delta H_s^{A_i/S} - \Delta H_s^{A_i/Y}] - [\Delta H_s^{M_i/S} - \Delta H_s^{M_i/S}] + \\ + MR^Y(\delta h_{cav}^S - \delta h_{cav}^Y). \qquad (27)$$

$\Delta H_{int}^{A_i/S}$ (sp) for proton donors not containing alkyl substituents can be determined by the "pure base" method having replaced the active hydrogen atom by the methyl group. It has been shown[74] that carbon tetrachloride, chloroform, or 1,2-dichloroethane can be used as the inert solvent. If none of the inert solvents can be used

but there is a possibility of determining the enthalpies of solvation of the proton donor and a model compound in which the active hydrogen can be replaced by the methyl group, then the enthalpy of specific interaction can be determined from the equation

$$\Delta H_{int}^{A_i/S}(sp) = \Delta H_{solv}^{A_i/S} - \Delta H_{solv}^{M_i/S} + 4.65k'_S, \quad (28)$$

where $k'_S$ is the slope of the relation between the enthalpies of solvation of alkanes and their molecular refractions in the solvent S.

If there is a possibility of determining the enthalpies of solvation of compounds in several inert solvents, then one may resort to the "base line" method. If the number of inert solvents is small, it is necessary in this case to select model compounds whose employment leads to a slope of the "base line" close to zero. This can be achieved by applying the method based on the study of the relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$.[4,86]

When the enthalpies of specific interaction of proton acceptors are determined, the choice of the inert solvent necessary for the construction of the "base line" is very wide and the requirements as regards the choice of the model compound are less stringent. This factor is important in the determination of $\Delta H_{int}^{A_i/S}$ (sp) in solvents associated via hydrogen bonds.[86]

It is noteworthy that the determination of the enthalpy of specific interaction in associated solvents occupies a special place in the thermochemistry of solvation of organic compounds, since in a solvent of this kind there are equilibria between different types of associated species and in the course of the solvation of the solute $A_i$ there is therefore the possibility of forming complexes consisting of the molecules of $A_i$ and of the associated species. This complex formation process may be accompanied by a shift of the association equilibria in the solvent, which influences the enthalpy of the specific interaction of the solute with the solvent and the enthalpy of solvation in conformity with Eqn. (22).

An approach to the estimation of the influence of the shift of association equilibria in solution on the enthalpy of solvation has been developed.[87–89] Comparison of the enthalpies of the specific interaction of compounds such as phenols, alcohols, acids, ketones, aromatic and aliphatic amines, and pyridines with solvents associated via hydrogen bonding with the enthalpies of formation of complexes $\Delta H_c^{A_i/S}$ between $A_i$ and S, measured in the absence of association of the molecules of the solvent S, showed that the relation between $\Delta H_{int}^{A_i/S}$(sp) and $\Delta H_c^{A_i/S}$ depends on whether the solute is an "acid" (proton donor or electron acceptor) or a "base" (proton acceptor or electron donor). There is a possibility of two situations (1) $\Delta H_{int}^{A_i/S}$ (sp) is almost identical with $\Delta H_c^{A_i/S}$ ("acids" in aliphatic alcohols and acetic acids); (2) $\Delta H_{int}^{A_i/S}$(sp) is appreciably smaller in absolute magnitude than $\Delta H_c^{A_i/S}$ and may be zero or positive ("bases" in aliphatic alcohols, acetic acids, formamide, and water; "acids" in water and formamide).

The results led to the development of ideas according to which the appearance of the reorganisation effect may be predicted from the nature of the solute—"acid" or "base"—and the ratio of the numbers of lone pairs and active hydrogen atoms in the solvent molecule.

## VII. The dipole moment and the enthalpy of solvation. Additional arguments

If the reduced dipole moment of the molecule (the ratio of the square of the dipole moment of the molecule to the cube of its radius is adopted as a measure of the polarity of the solute, then one of the most polar non-electrolytes is water.

Fig. 4 presents the relation between the enthalpies of non-specific solvation in a series of compounds (including water) and the molecular refractions in a polar solvent—acetonitrile. Similar relations can be obtained for the entire set of solvents used by Solomonov et al.[67] The enthalpy of non-specific solvation is determined from the difference between the enthalpy of solvation of the given compound and the enthalpy of its complex formation reaction with the solvent molecule.‡

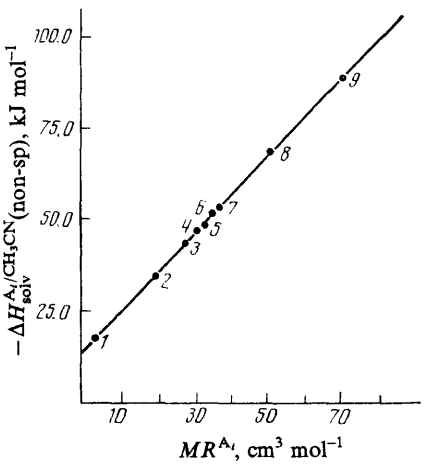



**Figure 4.** Relation between the enthalpies of non-specific solvation of a series of compounds in acetonitrile and their molar refractions. The numbers of the points correspond to the following compounds: *1*, water; *2*, pyrrole; *3*, phenol; *4*, benzaldehyde; *5*, nitrobenzene; *6*, *p*-chlorobenzaldehyde; *7*, *p*-chloronitrobenzene; *8*, 1-nitronaphthalene; *9*, 9-anthraldehyde.

Since the reduced dipole moments§ of molecules, presented in Fig. 4, differ significantly from one another, the existence of a relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$ shows that this factor does not exert a significant influence on the enthalpy of non-specific solvation.

If benzaldehyde ($\mu$ = 2.6 D) or nitrobenzene ($\mu$ = 4.0 D) is adopted as the compound modelling the non-specific solvation of phenol ($\mu$ = 1.6 D) in the "pure base" method [Eqn. (25)], then, as shown by Solomonov and Konovalov[4] a correspondence is observed between the enthalpies of specific interaction and the enthalpies of complex formation determined in carbon tetrachloride for all the solvents investigated—proton acceptors, including highly polar ones (dimethyl formamide, dimethyl sulphoxide). This result also implies that the dipole moment of the solute molecule does not play a significant role.

Extensive experimental data on the thermochemistry of solvation of organic non-electrolytes show that the dipole moment of the

‡ In the case of water, twice the enthalpy of complex formation was adopted.

§ The ratio of the square of the dipole moment of the molecule to the electronic polarisability, which is proportional to the cube of the radius of the molecule, may be adopted as a measure of the reduced dipole moment.[90]

solute molecule does not influence significantly the enthalpy of solvation (at least for the compounds investigated).

Certain considerations have been put forward[4,59] concerning the possible compensation of the orientation interaction between solute and solvent molecules by the reorganisation of solvent molecules. However, if we accept that the energy of orientation interaction is compensated by the energy of the reorganisation of the solvent, then the next step must be taken — the recognition of the fact that in a physicochemical process occurring in solution, where the solvation shell "follows" reversibly (equilibrium process) the changes in the solute (for example, a chemical reaction), the contribution of the orientation interaction may not be observed because the experimental quantities reflect the overall solvent–solvent and solvent–solute interactions.

This view conflicts strongly with the existing ideas about the influence of the medium on various phyisochemical processes. Indeed, there exist a multiplicity of well established facts showing that the fraction of the more polar form of the solute increases in more polar solvents (for example, by virtue of tautomeric or conformational equilibria). Polar interactions are of decisive importance in the influence of the medium on the kinetics of reactions[91] and spectroscopic transitions.[92] The generally accepted Onsager–Böttcher model is in essence the only general physical model of the "test molecule–medium" system on the basis of which a large set of a wide variety of experimental data are analysed to this day.

Nevertheless, only the fact that, on passing from a less polar to a more polar solvent, certain parameters of the physicochemical process (reaction rate constants, activation energies, electronic transition energies, etc.) change has been reliably established experimentally. However, in the study of the influence of the medium on the thermodynamics of a process, the structure of the molecules of its final and initial states can be established and their dipole moments measured only in some cases. In the remaining instances, and these are in the vast majority, the polarity of the species (transition or excited state, non-isolatable complex) is unknown and is inferred from the influence of the solvent on the physicochemical process as a whole. It is therefore hardly possible to speak of the influence of the dipole moment on the solvation energy on the basis of "such" experimental data.

We shall now turn to the term "polarity of the medium". We shall not analyse the problem of which of the existing solvent polarity scales is best and shall only note that, on any of the solvent polarity scales known to us, acetonitrile, dimethyl formamide, and nitromethane are more polar than cyclohexane or carbon tetrachloride. It is also known that dimethyl formamide and dimethyl sulphoxide actually form the strongest hydrogen bonds with the solute, while acetonitrile and nitromethane are simultaneously proton donors and proton acceptors. These properties are absent from cyclohexane and carbon tetrachloride. The capacity of cyclohexane for dispersion interactions is also a minimum. Therefore an increase in the degree of interaction between the solvent and the solute may take place as a result of the increase in solvent "polarity". The parallel variation of the properties of the solvent has been frequently noted in the literature.[58,93] Hence it is entirely understandable that the observed changes in certain parameters of a physicochemical process on passing from a less polar to a more polar solvent are bound to be related to the change in the dipole moment of the species involved in this process.

The relative free energies of solvation of cryptate ion pairs have been investigated[94,95] in a series of solvents. Despite the large dipole moments of the solute molecules, the relative free energies of solvation of these compounds are comparable to the free energy of the transfer of polar neutral molecules in isodielectric solvents. Nevertheless, it has been shown[94,95] that the influence of the medium on the constants of the dissociation of the cryptate ion pairs into solvated ions and the absence of specific interactions with the solvent are due to polar forces. It may be that in this case the polar interaction plays a significant role only because the physicochemical processes are accompanied by the formation of ions.

The idea that the analysis of the solvation energy requires that account be taken of the contribution of quadrupole interactions together with that of dipole interactions has been developed in a number of studies.[57,96,97] This makes it possible to account for the enthalpies of solvation and solution of *cis*- and *trans*-dichloroethylenes,[96] dicyanoethylenes,[59] 1,3- and 1,4-dioxanes,[97] and *o*-, *m*-, and *p*-dinitrobenzenes.[59] Indeed, the absence of an effect of the dipole moment on the enthalpies of solvation of these compounds can be explained by approximately equal contributions of the dipole and quadrupole interactions to the enthalpy of solvation. The quadrupole moment is greater in the *trans*- and *para*-isomers, whereas the dipole moment is greater in the *cis*-, *meta*-, and *ortho*-isomers.

The importance of allowing for multipole interactions has been pointed out.[98] However, it has been shown[99] that the contribution of quadrupole and octupole interactions is negligible compared with the contribution of dipole interactions and the former should be regarded as corrections.

The experimental study of the influence of multipoles of a higher order than the dipole on the solvation energy is at present difficult, since the quadrupole and octupole moments are determined only with a very low accuracy.[57] Some doubts concerning a significant contribution of quadrupole interactions to the solvation energy have arisen from the relations obtained between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$ for aromatic hydrocarbons and their halo-derivatives.[5]

## VIII. Additivity in the enthalpies of the transfer and solvation of organic non-electrolytes

The question of the additivity of the solvation energies of organic compounds appears to be extremely important because, firstly, there is a prospect that the study of the solvation of complex organic compounds can be reduced to the study of simpler objects. Secondly, the possible deviations from the additivity of solvation energies may be caused by the mutual influence of atoms and groups in the solute molecule. The study of this question will help to improve our understanding of the inter-relation between the structure of the solute and its solvation energy.

The most significant argument in support of the additivity of the enthalpy of solvation of an alkyl group is the equality of the slopes of the relation between $\Delta H_{solv}^{A_i/S}$ and $MR^{A_i}$ found for alkanes, ketones, and aliphatic alcohols. This equality implies identical solvation of the alkyl substituent at the carbonyl, hydroxy-, and aliphatic groups.[4]

An interesting observation was made by Fuchs and co-workers,[15] who showed that the enthalpy of solvation of benzene is approximately additive, corresponding to the enthalpies of solvation of the three double bonds. Unfortunately, no numerical data were

quoted in their communication. Apparently Fuchs based his treatment on the equation

$$\Delta H_{solv}^{C_6H_6/S} = 3\Delta H_{solv}^{C_6H_{10}/S} - 2\Delta H_{solv}^{C_6H_{12}/S}. \quad (29)$$

Table 4 lists the experimental enthalpies of solvation of benzene in various solvents and their values calculated by Eqn. (29). The enthalpies of solvation of benzene, cyclohexane, and cyclohexene were taken from Solomonov.[5]

**Table 4.** Experimental enthalpies of solvation (kJ mol$^{-1}$) of benzene in a series of solvents (298 K) and their values calculated by Eqn. (29).

| Solvent | $-\Delta H_{solv}^{C_6H_6/S}$ | |
|---|---|---|
| | experiment | calculation |
| Dimethylformamide | 33.6 | 33.8 |
| 1,2-Dichloroethane | 32.7 | 33.3 |
| Methanol | 32.4 | 32.5 |
| Benzene | 33.9 | 34.0 |
| Carbon tetrachloride | 32.7 | 33.0 |

Fuchs and Rodewald[100] determined the enthalpies of solution of 95 aromatic compounds in methanol and dimethyl formamide and showed that in the vast majority of cases the enthalpies of transfer of aromatic compounds are additive relative to the group composition regardless of the positions of the substituents in the aromatic ring. These findings were explained by the fact that not the dipole moment of the molecule as a whole but the dipole moments of its individual groups are important for solvation.

When there is a specific interaction between the molecule of an aromatic compound and the solvent, additivity is not observed in the enthalpies of transfer.[101]

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During the last 15 years, an enormous amount of experimental data have been obtained on the thermochemistry of the dissolution and solvation of organic or non-electrolytes. These can be analysed within the framework of simple empirical relations between the enthalpies of solvation of compounds and their polarisabilities. These relations made it possible to develop an approach to the estimation of the enthalpies of non-specific solvation of organic non-electrolytes in various media.

Methods for the thermochemical determination of the energies of hydrogen and donor–acceptor bonds have been developed on the basis of the enthalpies of solution and solvation.

However, the question of the applicability of general ideas must be considered in each specific case and the simplified approaches are not always correct in the interpretation of thermochemical solvation data.

The extensive experimental data and the empirical relations found in the thermochemistry of solvation undoubtedly require a theoretical interpretation. Studies on these lines have already begun.[9,102–104]

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