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A new method for the extraction of specific interaction enthalpy from the enthalpy of solvation

Boris N. Solomonov,* Vladimir B. Novikov, Mikhail A. Varfolomeev and Natalia M. Mileshko

Department of Chemistry, Kazan State University, Kremlevskaja St. 18, Kazan 420008, Russia

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ABSTRACT: A new, simple method for the extraction of specific interaction enthalpy from the enthalpy of solvation is proposed. It is based on empirical but very general relationships describing the non-specific solvation enthalpy. The specific interaction enthalpy is calculated from the solution enthalpies in the solvent under consideration, cyclohexane and tetrachloromethane. The solution enthalpy of at least one linear alkane in the solvent must also be available. The solution enthalpies of a 'model compound' or homomorph are not required. This method is applicable not only for proton-donor solutes but also for acceptor solutes such as iodine. It can be used also for solvents associated by hydrogen bonding (e.g. alcohols). The enthalpies of specific interaction for 280 solute–solvent systems were calculated. Solution enthalpy data were mainly obtained from the literature and partially measured by the authors. The results were compared with literature data on complexation enthalpy. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: specific interactions; hydrogen bonds; enthalpy of solution; solvent scales

INTRODUCTION

The behavior of molecules in various chemical and biological processes is greatly affected by the solvent. Such an influence is commonly described in terms of intermolecular interactions which may be of non-specific or specific type. We will consider the latter as the localized donor–acceptor interactions (including hydrogen bond formation). One of the tools for the investigation of solute–solvent intermolecular interaction is the study of transfer of the solute molecules from the ideal gas phase to the solvent at infinite dilution. This transfer is named the 'solvation' and the 'solution' means the transfer to the same state but from the standard state of the solute at a given temperature (solid, liquid or vapor). The standard molar enthalpies of these processes are interrelated by a simple equation:

$$\Delta_{\mathrm{solv}}H^{\mathrm{A/S}} = \Delta_{\mathrm{soln}}H^{\mathrm{A/S}} - \Delta_{\mathrm{vap}}H^{A} \qquad (1)$$

where $\Delta_{\mathrm{solv}}H^{\mathrm{A/S}}$ is the solvation enthalpy of the solute A in the solvent S, $\Delta_{\mathrm{soln}}H^{\mathrm{A/S}}$ is the solution enthalpy and $\Delta_{\mathrm{vap}}H^{\mathrm{A}}$ is the standard molar vaporization enthalpy of the solute. On the other hand, the solvation enthalpy can be regarded as the sum of non-specific solvation enthalpy [$\Delta_{\mathrm{solv(nonsp)}}H^{\mathrm{A/S}}$] and the enthalpy of solute–solvent specific interactions [$\Delta_{\mathrm{int(sp)}}H^{\mathrm{A/S}}$]:

$$\Delta_{\mathrm{solv}}H^{\mathrm{A/S}} = \Delta_{\mathrm{solv(nonsp)}}H^{\mathrm{A/S}} + \Delta_{\mathrm{int(sp)}}H^{\mathrm{A/S}} \qquad (2)$$

**Correspondence to:* B. N. Solomonov, Department of Chemistry, Kazan State University, Kremlevskaja St. 18, Kazan 420008, Russia. E-mail: boris.solomonov@ksu.ru

It should be kept in mind that the augend in this equation contains not only the non-specific solvent–solute interaction enthalpy [$\Delta_{\mathrm{int(nonsp)}}H^{\mathrm{A/S}}$] but also the cavity formation term ($\Delta_{\mathrm{cav}}H^{\mathrm{A/S}}$), which reflects the partial disconnexion of solvent–solvent interactions (both non-specific and specific in some extent) during the solvation:[1,2]

$$\Delta_{\mathrm{solv(nonsp)}}H^{\mathrm{A/S}} = \Delta_{\mathrm{cav}}H^{\mathrm{A/S}} + \Delta_{\mathrm{int(nonsp)}}H^{\mathrm{A/S}} \qquad (3)$$

The second term in Eqn (2) is more clear and comprehensible. It is often of particular interest because it can be compared with the data obtained by other methods (IR, UV, calorimetric titration, etc.). On the other hand, in some cases the solvent–solute specific interaction enthalpy is the only source of information about the hydrogen bonding energies. Furthermore, the data on specific interaction enthalpy can be used for the development of solvent basicity and acidity scales.[3–6]

There exist a number of approaches for the extraction of specific interaction enthalpies from solvation enthalpy data. They include the pure base method[7] and its modification,[3] the non-hydrogen bonding baseline method[8] and the method of base solutes.[9,10] These methods are actually based on estimation of non-specific solvation enthalpy in Eqn (2) using 'model' solutes or 'model' solvents. The essential inadequacy of such an approach is the poorly founded choice of 'models', i.e. the substances having the same properties as the explored solute (or solvent) except for its ability to undergo specific interaction. This problem has been substantially solved in the method of base solutes, but the application of this method

requires the analysis of a number of solvation enthalpy values.[10]

In this paper, we propose a new, very general method for the extraction of specific interaction enthalpy from the enthalpy of solvation. It requires the minimum of experimental solution enthalpy data and does not require the choice of certain 'model' compounds for a given solute.

RESULTS AND DISCUSSION

In a previous paper,[11] we deduced the equation for calculation of the enthalpy of non-specific solvation [$\Delta_{solv(nonsp)}H^{A/S}$]. This equation is based on our presupposition that the difference between the enthalpies of non-specific interactions for some solvent S and cyclohexane (as a solvent) is proportional to the same difference for tetrachloromethane and cyclohexane (as a solvents):

$$\Delta_{int(nonsp)}H^{A/S} - \Delta_{int(nonsp)}H^{A/C_6H_{12}} = q\left[\Delta_{int(nonsp)}H^{A/CCl_4} - \Delta_{int(nonsp)}H^{A/C_6H_{12}}\right] \quad (4)$$

where the proportionality factor q is the constant for any range of solutes (A) in each solvent (S). It is generally accepted that the non-specific interaction enthalpy of any solute with saturated hydrocarbon is minimal in a range of solvents. Therefore, the term $\Delta_{int(nonsp)}H^{A/C_6H_{12}}$ can be considered as the common dispersion interaction enthalpy. Accordingly, the term $\Delta_{int(nonsp)}H^{A/S} - \Delta_{int(nonsp)}H^{A/C_6H_{12}}$ is the additional non-specific interaction enthalpy of a solute A with the solvent S.

The assumption formularized by Eqn (4) is not rigorously deduced from any physical model but is based on the results of our previous work. In particular, it was shown that dipole[12,13] and multipole[14] moments of the solutes have no effect on the non-specific solvation enthalpy, and the dependences of the non-specific solvation enthalpies in different solvents (excluding alkanes) on the solute molar refraction are similar to one for tetrachloromethane.[12,13,15]

Cyclohexane in Eqn (4) is the reference solvent. It is essential because the calculation of the non-specific interaction enthalpy according to Eqn (3) requires the absolute values of cavity formation enthalpy. These data are experimentally inaccessible but there is a method[1,2] for the determination of this value relative to certain reference solvents. Using the McGowan characteristic volume[16] (V_x^A) as the measure of the volume of a solute molecule, this method gives the equation for calculation of relative cavity formation enthalpy:

$$\Delta_{cav}H^{A/S} - \Delta_{cav}H^{A/C_6H_{12}} = \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)V_x^A \quad (5)$$

where $\delta_{cav}h^S$ and $\delta_{cav}h^{C_6H_{12}}$ are the specific relative cavity formation enthalpies for solvent S and cyclohexane, respectively. This value can be obtained using the solution enthalpy of any linear alkane in the solvent:

$$\delta_{cav}h^S = \frac{\Delta_{soln}H^{Alkane/S}}{V_x^{Alkane}} \quad (6)$$

Saturated hydrocarbons do not interact specifically with a solute. The absence of specific interactions with tetrachloromethane as a solvent is also a widely used assumption,[3,7–10] so

$$\Delta_{solv(nonsp)}H^{A/C_6H_{12}} = \Delta_{solv}H^{A/C_6H_{12}} \quad \text{and} \quad \Delta_{solv(nonsp)}H^{A/CCl_4} = \Delta_{solv}H^{A/CCl_4} \quad (7)$$

By combining Eqns (3), (4), (5) and (7), the equation for non-specific solvation enthalpy was obtained:[11]

$$\Delta_{solv(nonsp)}H^{A/S} = \Delta_{solv}H^{A/C_6H_{12}} + \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)V_x^A + q\left[\Delta_{solv}H^{A/CCl_4} - \Delta_{solv}H^{A/C_6H_{12}} - \left(\delta_{cav}h^{CCl_4} - \delta_{cav}h^{C_6H_{12}}\right)V_x^A\right] \quad (8)$$

The proportionality factor q in this equation must be calculated for each solvent by regression analysis.

To verify this equation, we applied it to solvation enthalpy data obtained from the literature. Since Eqn (8) describes the enthalpy of non-specific solvation, we selected systems in which specific solute–solvent interactions can be neglected. On this account, proton donor solutes and solvents (water, alcohols, carbonic acids, aniline, formamide) were excluded from the analysis. Pyridine interacts with tetrachloromethane specifically,[17] so we excluded the data where pyridine is the solute. Tetrahydrofuran, dioxane, dialkyl ethers and triethylamine probably also interact specifically with tetrachloromethane because the enthalpy of solution for these solutes is exothermic.

The list of base solutes, their solution enthalpies in cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$) and tetrachloromethane ($\Delta_{soln}H^{A/CCl_4}$), characteristic volumes (V_x^A) and vaporization enthalpies ($\Delta_{vap}H^A$) are given in Table 1. Table 2 gives the specific relative cavity formation enthalpies ($\delta_{cav}h^S$) obtained by Eqn (6). This value was calculated as the average for all available solution enthalpies of alkanes (N is a number of such alkanes). The values of the parameter q calculated by regression analysis using Eqn (8) are given in Table 3. N is the number of solutes for each solvent, S_0 is the standard deviation and R is the

Table 1. Base solutes and their parameters for the analysis of non-specific solvation enthalpy using Eqn (8)

Solute (A)	$\Delta_{soln}H^{A/C_6H_{12}}$, 298 K (kJ mol^{-1})	$\Delta_{soln}H^{A/CCl_4}$, 298 K (kJ mol^{-1})	V_{x1}^{A} (cm^3 mol^{-1} × 10^{-2})	$\Delta_{vap}H^{A}$, 298 K (kJ mol^{-1})
Acetone	9.75[43]	2.70[29]	0.5470	30.84[33]
Acetonitrile	15.00[38]	7.57[35]	0.4042	32.93[44]
Acetophenone	10.73	3.31[35]	1.0139	53.39[44]
Anisole	7.20[28]	1.55[35]	0.9160	46.82[39]
Anthracene	29.70[45]	24.52[45]	1.4540	101.70[46]
Benzaldehyde	10.29[13]	3.35[47]	0.8730	50.21[48]
Benzene	3.19[38]	0.54[28]	0.7164	33.85[49]
Benzonitrile	11.53[13]	4.20	0.8711	52.30[48]
Bromobenzene	4.48[40]	0.84[12]	0.8914	43.81[46]
Butanone	8.20[43]	1.76[29]	0.6879	34.89[33]
tert-Butyl methyl ether	6.44[28]	1.63[28]	0.8718	30.42[49]
Chlorobenzene	3.77[40]	0.63[35]	0.8388	40.96[44]
1-Chlorobutane	2.89[38]	0.33[35]	0.7946	33.51[44]
p-Chloronitrobenzene	25.15[12 a]	18.91[47]	1.0130	70.29[12]
1-Chlorooctane	2.97[8]	0.84[8]	1.3582	54.43[48]
Cyclohexane	0.00	0.71[28]	0.8454	33.05[49]
Cyclohexanone	7.41[28]	0.38[35]	0.8611	45.06[49]
Cyclopentanone	9.08[33]	1.34[50]	0.7202	42.72[48]
n-Decane	2.16[38]	3.01[39]	1.5176	51.38[49]
1,2-Dichlorobenzene	5.22[51]	1.55[50]	0.9612	47.70[46]
1,4-Dichlorobenzene	22.20[51]	18.20[12]	0.9612	64.90[46]
N,*N*-Dimethylaniline	6.44[32]	0.84[32]	1.0980	52.83[46]
2,2-Dimethylbutane	0.54[49]	1.80[39]	0.9540	27.70[49]
Diphenyl	23.80[51]	18.54[12]	1.3242	81.60[46]
Dimethylformamide	13.60[31]	3.18[24]	0.6468	47.70[48]
Dimethyl sulfoxide	17.49[24]	7.91[26]	0.6130	52.89[46]
n-Dodecane	2.67[38]	3.64[39]	1.7990	61.30[49]
Ethyl acetate	7.28[26]	0.17[52]	0.7466	35.14[48]
Ethylbenzene	2.97[51]	0.54[53]	0.9982	42.37[54]
3-Ethylpentane	0.96[55]	1.34[55]	1.0949	35.23[55]
Fluorobenzene	4.60[40]	1.09[35]	0.7341	35.52[48]
n-Heptane	1.60[38]	2.09[28]	1.0949	36.57[49]
2-Heptanone	6.78[43]	1.05[39]	1.1106	47.45[49]
4-Heptanone	7.07[28]	1.05[39]	1.1106	46.69[33]
Hexachlorobenzene	27.20[12]	24.27[12]	1.4508	92.00[46]
n-Hexadecane	3.72[38]	4.69[39]	2.3630	81.38[39]
n-Hexane	1.17[38]	1.63[29]	0.9540	31.55[49]
2-Hexanone	6.74[43]	1.05[39]	0.9676	42.89[33]
Iodobenzene	5.48[40]	1.59[12]	0.9746	49.60[46]
Mesitylene	4.14[28]	0.75[28]	1.1391	47.49[39]
2-Methylbutane	0.63[49]	1.30[39]	0.8131	25.23[49]
N-Methylpyrrole	7.90[5]	1.59[32]	0.7183	40.58[48]
Naphthalene	23.00[13]	18.75[12]	1.0854	72.89[46]
Nitrobenzene	11.92[28]	4.81[47]	0.8906	55.02[39]
n-Nonane	1.97[28]	2.64[28]	1.3767	46.44[49]
2-Nonanone	6.60[43]	1.42[28]	1.3924	56.61[49]
5-Nonanone	6.00[43]	0.46[28]	1.3924	54.89[49]
n-Octane	1.75[38]	2.38[39]	1.2358	41.51[49]
2-Octanone	6.80[43]	1.15[29]	1.2515	51.80[33]
1-Octene	1.63[49]	1.00[39]	1.1928	40.58[49]
n-Pentane	1.03[38]	1.46[39]	0.8131	26.74[49]
2,4-Pentanedione	9.75[23]	3.22[23]	0.8445	43.10[48]
2-Pentanone	7.11[43]	1.34[50]	0.8288	38.41[33]
Tetrachloromethane	1.72[28]	0.00	0.7391	32.43[44]
2,2,4,4-Tetramethylpentane	0.29[28]	2.30[28]	1.3767	38.53[49]
2,2,4,4-Tetramethyl-3-pentanone	4.18[28]	0.46[28]	1.3924	45.35[49]
Toluene	2.94[38]	−0.13[39]	0.8573	37.99[49]
Trifluoromethylbenzene	6.95[28]	3.22[28]	0.9104	37.57[28]
Tri-*n*-butylamine	2.09[25]	0.88[56]	1.8992	69.60[48]

[a] Solvent: *n*-hexane.

Table 2. Relative cavity formation enthalpies per unit of McGowan characteristic volume

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	*N*
Acetone	7.65	8[2]
Acetonitrile	10.66	6[21,29,34,38]
Acetophenone	5.31	2[2]
Anisole	5.69	1[2]
Benzene	5.02	9[8,28,37,39]
Benzonitrile	4.01	4
Benzylamine	7.85	1[20]
Chlorobenzene	2.56	2[2]
1-Chlorobutane	2.07	7[28]
Cyclohexane	1.42	9[28,38]
Cyclohexanone	4.66	2[2]
Dibutyl ether	0.53	7[8,28]
1,2-Dichlorobenzene	3.47	1[2]
N,*N*-Dimethylacetamide	7.66	3[34]
1,4-Dioxane	7.57	8[2]
Dipropyl ether	0.70	1
Dimethylformamide	8.62	9[8,28,34,37]
Dimethyl sulfoxide	13.87	6[8,28,34,36]
Ethyl acetate	5.98	9[28]
Mesitylene	1.10	7[8,28,39]
Nitrobenzene	4.99	5
Nitromethane	13.74	4[34,38]
Pyridine	6.66	4
Tetrachloromethane	1.91	8[28,29,39]
Toluene	2.65	7[8,28,39]
1,1,1-Trichloroethane	2.57	5[8,28]
Triethylamine	0.43	8[8,28]
Trifluoromethylbenzene	3.50	6[28,39]
p-Xylene	1.31	2[2]

Table 3. Parameters of linear regression upon Eqn (8) for the range of solvents

Solvent (*S*)	*N*	*q*	S_0	*R*
Acetone	28	2.04 ± 0.05	1.52	0.969
Acetonitrile	31	2.28 ± 0.04	1.11	0.983
Acetophenone	9	1.72 ± 0.05	0.84	0.992
Anisole	7	1.96 ± 0.10	1.39	0.974
Benzene	53	1.60 ± 0.02	0.92	0.983
Benzonitrile	21	1.62 ± 0.03	0.69	0.988
Benzylamine	7	2.18 ± 0.07	1.23	0.978
Chlorobenzene	16	1.40 ± 0.07	1.10	0.910
1-Chlorobutane	10	1.16 ± 0.04	0.28	0.995
Cyclohexanone	7	1.56 ± 0.09	1.04	0.979
Dibutyl ether	27	0.61 ± 0.04	1.04	0.883
1,2-Dichlorobenzene	7	1.44 ± 0.06	0.93	0.984
N,*N*-Dimethylacetamide	15	2.12 ± 0.10	2.33	0.944
1,4-Dioxane	27	2.14 ± 0.09	2.18	0.930
Dipropyl ether	13	0.94 ± 0.06	1.31	0.848
Dimethylformamide	50	2.24 ± 0.07	2.54	0.927
Dimethyl sulfoxide	48	2.56 ± 0.08	2.88	0.924
Ethyl acetate	48	1.82 ± 0.05	1.83	0.939
Mesitylene	30	0.98 ± 0.05	1.12	0.946
Nitrobenzene	18	1.67 ± 0.07	1.60	0.969
Nitromethane	12	2.44 ± 0.11	1.37	0.979
Pyridine	29	2.01 ± 0.06	1.70	0.944
Toluene	43	1.38 ± 0.03	0.98	0.972
1,1,1-Trichloroethane	8	1.38 ± 0.07	0.43	0.993
Triethylamine	30	0.65 ± 0.06	1.54	0.816
Trifluoromethylbenzene	27	1.57 ± 0.04	0.95	0.982
p-Xylene	13	1.14 ± 0.06	0.89	0.947

correlation coefficient. The experimental values of solvation enthalpy were calculated using Eqn (1) and literature data on enthalpy of solution.[1–3,5,8,10,12,13,18–42] It must be noted that in the majority of cases the standard deviation of calculated value of solvation enthalpy from the experimental value is <2 kJ mol^{-1}.

The parameter q is a solvent property and it would be more convenient to calculate its value from correlation with any solvent property. We analyzed the correlations of q values in Table 3 with some solvent parameters,[89] namely: function of refractive index $[f(n) = (n^2 - 1)/(n^2 + 1)]$, function of relative permittivity $[g(\varepsilon_r) = (\varepsilon_r - 1)/(\varepsilon_r + 1)]$, their difference $[g(\varepsilon_r) - f(n)]$, Dimroth–Reichardt $[E_T(30)]$ and Kamlet–Abboud–Taft (π^*) solvatochromic parameters and Hildebrand solubility parameter (δ_H). The correlation coefficients/standard deviations were found to be −0.07/0.53, 0.62/0.42, 0.62/0.42, 0.85/0.28, 0.79/0.33 and 0.87/0.27, respectively. The last three solvent parameters do have some correlation with q values, the Hildebrand solubility parameter showing a slightly better correlation. Nevertheless, a substantially better correlation (correlation coefficient 0.98 and standard deviation 0.09) can be found for the square root of specific relative cavity formation enthalpies ($\sqrt{\delta_{cav}h^S}$). The correlation between q and $\sqrt{\delta_{cav}h^S}$ is shown in Fig. 1.

This parameter is to some extent the analogue of the Hildebrand solubility parameter because in regular solution theory δ_H^2 characterizes the specific cavity formation energy. The Hildebrand parameter reflects the overall breaking of solvent–solvent interactions, being calculated from the vaporization enthalpy, whereas for cavity formation the breaking of some part of such interactions only is required. The parameter $\sqrt{\delta_{cav}h^S}$ probably reflects better just this part of the interactions.

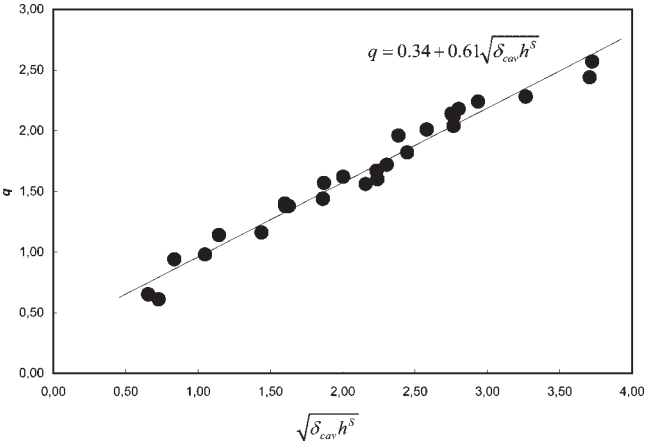

Figure 1. Correlation of q (Table 3) with square root of specific relative cavity formation enthalpy (calculated from data in Table 2)

The empirical correlation between q and $\sqrt{\delta_{cav}h^S}$ permits the simplification of Eqn (8) for new solvents:

$$\begin{aligned}\Delta_{solv(nonsp)}H^{A/S} = {} & \Delta_{solv}H^{A/C_6H_{12}} \\ & + \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)V_x^A \\ & + \left(0.34 + 0.61\sqrt{\delta_{cav}h^S}\right) \\ & \times \left[\Delta_{solv}H^{A/CCl_4} - \Delta_{solv}H^{A/C_6H_{12}} \right. \\ & \left. - \left(\delta_{cav}h^{CCl_4} - \delta_{cav}h^{C_6H_{12}}\right)V_x^A\right] \qquad (9)\end{aligned}$$

By combining Eqns (2) and (9), the specific interaction enthalpy can be calculated. The difference in solvation enthalpies for solute A is equal to the difference in solution enthalpies. Hence the resulting equation is

$$\begin{aligned}\Delta_{int(sp)}H^{A/S} = {} & \Delta_{soln}H^{A/S} - \Delta_{soln}H^{A/C_6H_{12}} \\ & - \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)V_x^A \\ & - \left(0.34 + 0.61\sqrt{\delta_{cav}h^S}\right) \\ & \times \left[\Delta_{soln}H^{A/CCl_4} - \Delta_{soln}H^{A/C_6H_{12}} \right. \\ & \left. - \left(\delta_{cav}h^{CCl_4} - \delta_{cav}h^{C_6H_{12}}\right)V_x^A\right] \qquad (10)\end{aligned}$$

Hence the enthalpies of solution in this solvent ($\Delta_{soln}H^{A/S}$), cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$) and tetrachloromethane ($\Delta_{soln}H^{A/CCl_4}$) must be available for calculation the enthalpy of solute–solvent specific interaction. The enthalpy of solution of at least one alkane in the solvent under consideration (for calculation of $\delta_{cav}h^S$) must also be known.

We calculated the enthalpy of solute–solvent specific interaction for all systems whose solution enthalpy data were available in the literature. Partially these data and also some solution enthalpies in cyclohexane and tetrachloromethane and solution enthalpies of alkanes in some solvents were measured by authors. The results are given in Table 4, where $\Delta_{int}H^{A/S}(sp)$ is the calculated enthalpy of specific interaction, $\delta_{cav}h^S$ is the specific enthalpy of cavity formation, $\Delta_{soln}H^{A/S}$ is the experimental value of solution enthalpy and $\Delta_cH^{A\cdots S}$ is the complexation enthalpy obtained from literature. For each solute the enthalpy of solution in cyclohexane ($\Delta_{soln}H^{A/C_6H_{12}}$) and tetrachloromethane ($\Delta_{soln}H^{A/CCl_4}$) and the characteristic volume (V_x^A) are shown. The specific interaction of iodine with different solvents is charge-transfer complexation; for other solutes it is hydrogen bonding.

The enthalpies of solute–solvent specific interaction calculated using Eqn (10) are generally in good correspondence with the literature data for complexation enthalpy. The standard deviation of $\Delta_{int}H^{A/S}(sp)$ from the middle of $\Delta_cH^{A\cdots S}$ is 2 kJ mol^{-1} for 82 compared points (excluding three points for *N*-methylaniline). In our opinion, some of the disagreements in these values can be explained by the following reasons:

- The specific interaction enthalpy and complexation enthalpy are calculated per mole of solute and complex, respectively. These values must be equal only if the degree of complexation is unity.
- Some solutes, such as aniline, probably form 1:2 complexes with solvents, whereas literature complexation enthalpies correspond to 1:1 complexes.
- Complexation enthalpy data obtained from the literature are often ambiguous. Discrepancies amounting 5–10 kJ mol^{-1} are often found between the results obtained by different workers studying the same systems by the same or different methods.
- The inaccuracy of Eqn (10) is highly affected by inaccuracies in $\Delta_{soln}H^{A/C_6H_{12}}$ and $\Delta_{soln}H^{A/CCl_4}$, especially for solvents with high $\delta_{cav}h^S$. The precise determination of solution enthalpies in cyclohexane and tetrachloromethane may be a non-trivial task for some weakly soluble substances.
- In some cases the presence of specific interactions of the solute with tetrachloromethane may not be completely excluded. Such interactions should decrease the results for other solvents obtained using Eqn (10).
- Despite certain model concepts, which underlie this method, Eqn (10) is principally an empirical one.

Catalan *et al.*[3] proposed a 'pure solvent method' for accurate estimation of the basicity of solvents. Being based on solution enthalpies of pyrrole, *N*-methylpyrrole, benzene and toluene, it yields $\delta\Delta H^0_{solv}$ values. We compared our results for pyrrole with these data. The correlation is shown in Fig. 2. The largest deviation can be seen for chloroform, but it is not surprising because in our method chloroform is a proton donor whereas $\delta\Delta H^0_{solv}$ is a basicity scale (unlike the methods based on homomorphs, our method gives the overall enthalpy of all possible solute–solvent specific interactions). Except for this point, the correlation coefficient and standard deviation are 0.98 and 1.3 kJ mol^{-1}, respectively. The intercept of the correlation is about 2.1 kJ mol^{-1}. This non-zero value is comprehensible considering that the 'pure solvent method' gives non-zero basicities for cyclohexane and tetrachloromethane. The slope is almost unity, confirming the similarity of the methods. However, our method seems to overestimate the specific interaction enthalpies with hexametapol and somewhat with tetrahydrofuran.

The rationality of the results obtained by Eqn (10) can be confirmed by correlation with the solvent basicity (SB) scale.[6] These correlations for two solutes, 1-butanol and chloroform, are shown in Fig. 3. The correlation coefficient/standard deviation were found to be 0.97/1.6 and 0.98/0.7, respectively.

Table 4. Enthalpies of specific interaction $[\Delta_{int}H^{A/S}(sp)]$ (298 K) calculated using Eqn (10)

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}(sp)$ (kJ mol^{-1})	$\Delta_cH^{A\cdots S}$ (kJ mol^{-1})
Solute (A): aniline; $\Delta_{soln}H^{A/C_6H_{12}} = 15.6$;[57] $\Delta_{soln}H^{A/CCl_4} = 8.7$;[28] $V_x^A = 0.816$				
Acetone	7.65	−5.4[58]	−11.2	−10.5[28]
Acetonitrile	10.66	0.0[58]	−6.0	−7.1[28]
Anisole	5.69	1.5[58]	−4.3	−7.9[59]
Benzene	5.02	5.2[28]	−0.7	−1.0;[28] −6.9[59]
Chloroform	3.47	0.7[32]	−5.7	
Dibutyl ether	0.53	2.9[28]	−6.1	−7.5[28]
1,2-Dichloroethane	8.56	2.1[28]	−3.7	
1,4-Dioxane	7.57	−4.6[58]	−10.3	
Dimethylformamide	8.62	−11.2[28]	−17.0	−14.2[28]
Dimethyl sulfoxide	13.87	−10.9[28]	−17.4	−15.5[28]
Ethyl acetate	5.98	−3.5[28]	−9.3	−10.0;[28] −12.9[59]
Mesitylene	1.10	7.9[28]	−0.2	−1.7[28]
Pyridine	6.66	−7.4[32]	−13.1	−10.0;[28] −14.3[59]
Toluene	2.65	5.9[28]	−0.9	−0.9[28]
Triethylamine	0.43	−1.8[28]	−11.2	−13.8[28]
Solute (A): anthracene; $\Delta_{soln}H^{A/C_6H_{12}} = 29.7$;[13] $\Delta_{soln}H^{A/CCl_4} = 24.5$;[12] $V_x^A = 1.454$				
Chloroform	3.47	20.8[10]	−3.2	
Solute (A): benzene; $\Delta_{soln}H^{A/C_6H_{12}} = 3.2$;[38] $\Delta_{soln}H^{A/CCl_4} = 0.5$;[28] $V_x^A = 0.7164$				
Chloroform	3.47	−2.0[3]	−2.2	
Solute (A): bromobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 4.5$;[40] $\Delta_{soln}H^{A/CCl_4} = 0.8$;[12] $V_x^A = 0.8914$				
Chloroform	3.47	−0.9[10]	−1.2	
Solute (A): 1-butanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.5$;[13] $\Delta_{soln}H^{A/CCl_4} = 19.2$;[28] $V_x^A = 0.7309$				
Acetone	7.65	7.2[10]	−10.3	−9.2[59]
Acetonitrile	10.66	10.8[10]	−7.2	
Benzene	5.02	16.9[28]	−0.5	−2.2[59]
Benzylamine	7.85	−4.4[18]	−21.9	
Dibutyl ether	0.53	8.5[28]	−10.9	
1,2-Dichloroethane	8.56	16.1[28]	−1.5	
Dichloromethane	7.43	14.4[38]	−3.1	
Diethyl Ether	1.59	5.3[38]	−13.0	−12.4;[59] −15.9[59]
N,*N*-Dimethylacetamide	7.66	1.0[34]	−16.4	
1,4-Dioxane	7.57	8.1[13]	−9.4	−13.0[59]
Dimethylformamide	8.62	2.5[10]	−15.1	−14.6;[60] −16.7[59]
Dimethyl sulfoxide	13.87	4.1[27]	−14.6	
Ethyl acetate	5.98	8.5[10]	−8.9	−10.0[59]
Hexametapol	4.45	−5.9[18]	−23.3	
Mesitylene	1.10	16.2[28]	−2.4	
3-Methylsulfolane	9.87	10.0[34]	−7.8	
Nitromethane	13.74	16.0[38]	−2.7	
Propylene carbonate	10.14	10.6[36]	−7.3	
Pyridine	6.66	1.3[35]	−16.1	−17.2;[60] −14.6[59]
Toluene	2.65	16.9[28]	−0.9	
Triethylamine	0.43	−4.8[18]	−24.4	−23.0;[59] −20.5[59]
Solute (A): chlorobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 3.8$;[40] $\Delta_{soln}H^{A/CCl_4} = 0.6$;[35] $V_x^A = 0.8388$				
Chloroform	3.47	−0.9[10]	−1.1	
Solute (A): chloroform; $\Delta_{soln}H^{A/C_6H_{12}} = 2.9$;[38] $\Delta_{soln}H^{A/CCl_4} = 0.9$;[61] $V_x^A = 0.6167$				
Acetone	7.65	−5.0[61]	−7.1	−7.0[62]
Acetonitrile	10.66	−1.5[38]	−4.8	
Diethyl ether	1.59	−8.1[38]	−8.6	−7.7[62]
1,4-Dioxane	7.57	−4.9[61]	−7.0	−6.9;[62] −9.2[59]
Dimethyl sulfoxide	13.87	−5.5[27]	−10.2	
Nitromethane	13.74	1.1[38]	−3.5	
Pyridine	6.66	−5.5[61]	−7.3	−10.7;[62] −10.0[59]
Tetrahydrofuran	3.28	−8.4[61]	−9.2	−8.2;[62] −15.0[59]
Triethylamine	0.43	−13.0	−13.5	−16.0;[62] −16.7[59]
Solute (A): *m*-cresol; $\Delta_{soln}H^{A/C_6H_{12}} = 25.2$;[28] $\Delta_{soln}H^{A/CCl_4} = 15.6$;[63] $V_x^A = 0.916$				
Benzene	5.02	10.8[28]	−0.5	−2.7[28]
Dibutyl ether	0.53	−5.3[28]	−21.8	−23.8;[28] −19.2[63]
1,2-Dichloroethane	8.56	9.4[28]	−0.9	
Dimethylformamide	8.62	−14.0[28]	−24.4	−24.5;[28] −23.0[63]
Dimethyl sulfoxide	13.87	−12.8[28]	−23.2	−24.9;[28] −26.4[63]
Ethyl acetate	5.98	−5.6[28]	−16.5	−19.9;[28] −13.4[63]

Continues

Table 4. Continued

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}$(sp) (kJ mol^{-1})	$\Delta_c H^{A\cdots S}$ (kJ mol^{-1})
Mesitylene	1.10	9.6[39]	−5.4	−6.5[28]
Toluene	2.65	10.5[28]	−2.4	−3.5[28]
1,1,1-Trichloroethane	2.57	10.8[64]	−2.1	
Triethylamine	0.43	−20.2[28]	−37.0	−39.5[28]
Solute (A): 1,2-dichlorobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 5.2$;[13] $\Delta_{soln}H^{A/CCl_4} = 1.5$;[50] $V_x^A = 0.9612$				
Chloroform	3.47	−0.2[10]	−1.2	
Solute (A): 1,4-dichlorobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 22.2$;[13] $\Delta_{soln}H^{A/CCl_4} = 18.2$;[12] $V_x^A = 0.9612$				
Chloroform	3.47	17.4[10]	−0.2	
Solute (A): *cis*-1,2-dichloroethene; $\Delta_{soln}H^{A/C_6H_{12}} = 3.7$;[13] $\Delta_{soln}H^{A/CCl_4} = 1.6$;[13] $V_x^A = 0.5922$				
Acetone	7.65	−3.1[13]	−5.6	
Acetonitrile	10.66	0.0[13]	−3.6	
Benzene	5.02	−0.7[65]	−2.4	
Chlorobenzene	2.56	−0.2[65]	−1.4	
1,2-Dichlorobenzene	3.47	0.3[65]	−1.1	
1,4-Dioxane	7.57	−2.7[13]	−5.2	
Dimethylformamide	8.62	−4.8[13]	−7.7	
Dimethyl sulfoxide	13.87	−3.3[65]	−8.1	
Pyridine	6.66	−2.0[65]	−4.2	
Solute (A): *trans*-1,2-dichloroethene; $\Delta_{soln}H^{A/C_6H_{12}} = 2.4$;[13] $\Delta_{soln}H^{A/CCl_4} = 0.5$;[13] $V_x^A = 0.5922$				
Acetone	7.65	−2.5[13]	−4.2	
Acetonitrile	10.66	0.5[13]	−2.3	
Benzene	5.02	0.2[65]	−0.6	
Chlorobenzene	2.56	0.0[65]	−0.2	
1,2-Dichlorobenzene	3.47	0.3[65]	−0.1	
1,4-Dioxane	7.57	−2.6[13]	−4.2	
Dimethylformamide	8.62	−4.8[13]	−6.8	
Dimethyl sulfoxide	13.87	−3.0[65]	−7.1	
Pyridine	6.66	−1.4[65]	−2.7	
Solute (A): *N*,*N*-dimethylaniline; $\Delta_{soln}H^{A/C_6H_{12}} = 6.4$;[13] $\Delta_{soln}H^{A/CCl_4} = 0.8$;[32] $V_x^A = 1.098$				
Chloroform	3.47	−5.4[32]	−5.0	
Solute (A): diphenyl; $\Delta_{soln}H^{A/C_6H_{12}} = 23.8$;[13] $\Delta_{soln}H^{A/CCl_4} = 18.5$;[12] $V_x^A = 1.3242$				
Chloroform	3.47	14.1[10]	−3.6	
Solute (A): diphenylamine; $\Delta_{soln}H^{A/C_6H_{12}} = 29.1$;[66] $\Delta_{soln}H^{A/CCl_4} = 21.9$;[66] $V_x^A = 1.424$				
Acetonitrile	10.66	18.0[66]	−5.7	
1,4-Dioxane	7.57	9.2[66]	−12.6	−9.6[62]
Dipropyl ether	0.70	12.1[13]	−9.2	
Dimethylformamide	8.62	5.9[66]	−16.5	
Dimethyl sulfoxide	13.87	8.8[66]	−17.3	
Ethyl acetate	5.98	11.3[66]	−9.7	
Pyridine	6.66	5.4[66]	−15.9	−15.1[62]
Tetrahydrofuran	3.28	5.0[66]	−15.3	
Toluene	2.65	17.1[66]	−3.1	
Solute (A): 2.6-di-*tert*-butylphenol; $\Delta_{soln}H^{A/C_6H_{12}} = 19.7$;[67] $\Delta_{soln}H^{A/CCl_4} = 16.1$;[67] $V_x^A = 1.9023$				
Acetone	7.65	12.5[67]	−9.8	
Acetonitrile	10.66	17.2[67]	−9.4	
Benzene	5.02	16.6[67]	−2.2	
1,4-Dioxane	7.57	11.2[67]	−11.0	
Dimethylformamide	8.62	7.1[67]	−16.6	
Dimethyl sulfoxide	13.87	11.4[67]	−20.1	
Ethyl acetate	5.98	12.2[67]	−7.8	
Tetrahydrofuran	3.28	5.0[67]	−11.6	
Solute (A): Dimethylformamide; $\Delta_{soln}H^{A/C_6H_{12}} = 13.6$;[31] $\Delta_{soln}H^{A/CCl_4} = 3.2$;[24] $V_x^A = 0.6468$				
Chloroform	3.47	−12.3[31]	−11.2	
Solute (A): Dimethyl sulfoxide; $\Delta_{soln}H^{A/C_6H_{12}} = 17.5$;[24] $\Delta_{soln}H^{A/CCl_4} = 7.9$;[26] $V_x^A = 0.613$				
Chloroform	3.47	−13.8[24]	−17.8	
Solute (A): ethanol; $\Delta_{soln}H^{A/C_6H_{12}} = 23.3$;[38] $\Delta_{soln}H^{A/CCl_4} = 18.4$;[68] $V_x^A = 0.4491$				
Acetone	7.65	5.3[10]	−10.3	
Acetonitrile	10.66	8.0[34]	−7.4	−10.5[69]
Acetophenone	5.31	7.0[13]	−9.1	
Benzonitrile	4.01	8.2[13]	−8.2	
Benzylamine	7.85	−6.2[13]	−21.9	
1,2-Dichloroethane	8.56	13.5	−2.0	
Dichloromethane	7.43	12.7[38]	−3.0	

Continues

Table 4. Continued

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 100)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}$(sp) (kJ mol^{-1})	$\Delta_c H^{A\cdots S}$ (kJ mol^{-1})
Diethyl ether	1.59	5.2[38]	−12.5	
N,*N*-Dimethylacetamide	7.66	−0.5[34]	−16.1	−14.2[59]
Dimethylformamide	8.62	1.3[34]	−14.3	−16.3[59]
Dimethyl sulfoxide	13.87	1.2[27]	−14.3	
Ethyl acetate	5.98	7.4[10]	−8.5	
3-Methylsulfolane	9.87	7.8[34]	−7.7	
Nitrobenzene	4.99	12.3[13]	−3.8	
Nitromethane	13.74	12[38]	−3.5	
Propylene carbonate	10.14	8.5[36]	−7.0	
Pyridine	6.66	0.0[10]	−15.8	−15.9[59]
Solute (A): *N*-ethylaniline; $\Delta_{soln}H^{A/C_6H_{12}} = 9.9$;[32] $\Delta_{soln}H^{A/CCl_4} = 3.9$;[32] $V_x^A = 1.098$				
Chloroform	3.47	−2.5[32]	−5.0	
Pyridine	6.66	−5.2[32]	−8.3	
Solute (A): fluorobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 4.6$;[40] $\Delta_{soln}H^{A/CCl_4} = 1.1$;[35] $V_x^A = 0.7341$				
Chloroform	3.47	−0.9[10]	−1.2	
Solute (A): 3-fluorophenol; $\Delta_{soln}H^{A/C_6H_{12}} = 20.7$;[26] $\Delta_{soln}H^{A/CCl_4} = 15.9$;[26] $V_x^A = 0.7928$				
Benzene	5.02	7.5[26]	−7.1	−7.1[17]
1,2-Dichlorobenzene	3.47	11.1[26]	−3.5	
Solute (A): 1-hexanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.4$;[13] $\Delta_{soln}H^{A/CCl_4} = 18.7$; $V_x^A = 1.0127$				
Acetone	7.65	9.1[10]	−9.0	
Acetonitrile	10.66	13.4[10]	−5.8	
Acetophenone	5.31	8.2[13]	−9.2	
Benzonitrile	4.01	10.2[13]	−7.1	
Benzylamine	7.85	−3.1[13]	−21.3	
N,*N*-Dimethylacetamide	7.66	2.6[34]	−15.5	
Dimethylformamide	8.62	4.7[10]	−13.7	
Dimethyl sulfoxide	13.87	6.8[10]	−13.9	
Ethyl Acetate	5.98	9.4	−8.2	
3-Methylsulfolane	9.87	11.6[34]	−7.3	
Nitrobenzene	4.99	14.1[13]	−3.3	
Nitromethane	13.74	18.0[34]	−2.6	
Propylene Carbonate	10.14	12.6[36]	−6.4	
Pyridine	6.66	2.2[13]	−15.6	
Tetrahydrofuran	3.28	5.0	−12.3	
Solute (A): iodine; $\Delta_{soln}H^{A/C_6H_{12}} = 29.7$;[70] $\Delta_{soln}H^{A/CCl_4} = 26.7$;[70] $V_x^A = 0.625$				
Acetone	7.65	10.9[71]	−15.9	−15.3;[72] −15.3[73]
Acetonitrile	10.66	20.1[71]	−7.6	−9.6;[72] −7.9[74]
Benzene	5.02	18.8[75]	−7.5	−6.1[74]
Chlorobenzene	2.56	19.9[76]	−6.1	−5.0[74]
1,4-Dioxane	7.57	7.7[76]	−19.1	−15.8[74]
Dimethylformamide	8.62	0.4[71]	−26.7	−20.9;[72] −20.9[73]
Ethyl Acetate	5.98	13.0[76]	−13.4	−12.6;[72] −12.6[73]
Pyridine	6.66	−15.2[76]	−41.8	−31.3;[72] −37.2[77]
Tetrahydrofuran	3.28	2.5[71]	−23.5	−22.2;[72] −24.3[74]
Toluene	2.65	16.1[76]	−9.9	−7.5[74]
p-Xylene	1.31	14.6[71]	−11.6	−9.2[74]
Solute (A): iodobenzene; $\Delta_{soln}H^{A/C_6H_{12}} = 5.5$;[40] $\Delta_{soln}H^{A/CCl_4} = 1.6$;[12] $V_x^A = 0.9746$				
Chloroform	3.47	−0.4[10]	−1.4	
Solute (A): methanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.3$;[13] $\Delta_{soln}H^{A/CCl_4} = 18.2$;[78] $V_x^A = 0.3082$				
Acetone	7.65	3.6[10]	−10.0	−10.5[59]
Acetonitrile	10.66	6.2[10]	−6.4	−9.2[59]
Acetophenone	5.31	5.1[13]	−9.6	
Benzonitrile	4.01	7.0[13]	−8.3	
Benzylamine	7.85	−8.8[13]	−22.3	
Dichloromethane	7.43	11.6[38]	−2.1	
Diethyl ether	1.59	3.8[38]	−13.6	−15.5[59]
N,*N*-Dimethylacetamide	7.66	−2.3[34]	−15.9	
1,4-Dioxane	7.57	5.3[79]	−8.3	−11.7[59]
Dipropyl ether	0.7	5.9[13]	−12.8	
Dimethylformamide	8.62	−0.6[34]	−13.8	−15.1[59]
Dimethyl sulfoxide	13.87	−1.4[27]	−13.3	−15.4[60]
Ethyl acetate	5.98	5.7[10]	−8.6	−10.2[59]
Hexametapol	4.45	−7.1[18]	−22.2	

Continues

Table 4. Continued

Solvent (S)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}$(sp) (kJ mol^{-1})	$\Delta_c H^{A\cdots S}$ (kJ mol^{-1})
3-Methylsulfolane	9.87	5.7[34]	−7.2	
Nitrobenzene	4.99	11.0[13]	−3.8	
Nitromethane	13.74	9.3[38]	−2.6	
Propylene carbonate	10.14	6.3[36]	−6.5	
Pyridine	6.66	−1.9[10]	−15.9	−17.6;[62] −16.0[59]
Tetrahydrofuran	3.28	3.1	−12.8	
Triethylamine	0.43	−4.8[80]	−24.1	−25.1;[59] −17.6[59]
Solute (A): methyl propiolate; $\Delta_{soln}H^{A/C_6H_{12}} = 14.4$;[81] $\Delta_{soln}H^{A/CCl_4} = 7.8$;[66] $V_x^A = 0.6019$				
Acetone	7.65	−2.9[66]	−7.0	
Acetonitrile	10.66	−0.5[81]	−4.4	
Benzene	5.02	3.0[81]	−1.8	
Dibutyl ether	0.53	2.4[81]	−6.1	
1,4-Dioxane	7.57	−2.3[81]	−6.4	
Dimethylformamide	8.62	−5.5[81]	−9.5	
Dimethyl sulfoxide	13.87	−3.5[81]	−7.3	
Ethyl acetate	5.98	−2.4[66]	−6.9	
Tetrahydrofuran	3.28	−4.6[81]	−10.1	
Solute (A): 2-methyl-2-butanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.5$;[28] $\Delta_{soln}H^{A/CCl_4} = 19.2$;[28] $V_x^A = 0.8718$				
Benzene	5.02	16.6[28]	−1.3	
Dibutyl ether	0.53	11.2[28]	−8.1	
1,2-Dichloroethane	8.56	15.0[28]	−3.5	
Dimethylformamide	8.62	3.5[28]	−15.1	
Dimethyl sulfoxide	13.87	5.4[28]	−15.0	
Ethyl acetate	5.98	8.7[28]	−9.3	
Mesitylene	1.10	14.9[28]	−3.7	
Toluene	2.65	16.3[28]	−1.7	
Triethylamine	0.43	−0.3[28]	−19.7	
Solute (A): *N*-methylaniline; $\Delta_{soln}H^{A/C_6H_{12}} = 11.6$;[32] $\Delta_{soln}H^{A/CCl_4} = 5.6$;[32] $V_x^A = 0.9571$				
Acetonitrile	10.66	2.1[66]	−3.2	
Chloroform	3.47	−1.5[32]	−5.5	
Dibutyl ether	0.53	1.2[66]	−4.4	
1,4-Dioxane	7.57	−2.1[66]	−6.5	
Dimethylformamide	8.62	−5.3[57]	−9.9	−20.9[59]
Dimethyl sulfoxide	13.87	−3.4[57]	−9.9	
Ethyl acetate	5.98	−1.4[66]	−5.4	−14.6[59]
Pyridine	6.66	−4.3[32]	−8.5	−15.9[59]
Toluene	2.65	2.6[66]	−1.5	
Solute (A): *N*-methylpyrrole; $\Delta_{soln}H^{A/C_6H_{12}} = 7.9$;[5] $\Delta_{soln}H^{A/CCl_4} = 1.6$;[32] $V_x^A = 0.7183$				
Chloroform	3.47	−6.2[3]	−5.6	
Solute (A): naphthalene; $\Delta_{soln}H^{A/C_6H_{12}} = 23.0$;[13] $\Delta_{soln}H^{A/CCl_4} = 18.8$;[12] $V_x^A = 1.0854$				
Chloroform	3.47	15.4[10]	−2.8	
Solute (A): 1-octanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.6$;[13] $\Delta_{soln}H^{A/CCl_4} = 19.9$;[8] $V_x^A = 1.295$				
Acetophenone	5.31	9.1[13]	−11.2	
Benzene	5.02	18.2[8]	−1.9	
Benzonitrile	4.01	10.6[13]	−9.0	
Benzylamine	7.85	−1.9[13]	−23.9	
Dibutyl ether	0.53	8.1[8]	−11.1	−12.6[8]
1,2-Dichloroethane	8.56	18.8[8]	−3.6	
Dimethylformamide	8.62	7.2[8]	−15.3	−14.6[8]
Dimethyl sulfoxide	13.87	10.7[8]	−16.0	−15.9[8]
Ethyl acetate	5.98	11.3[8]	−9.4	−10.0[8]
Mesitylene	1.10	16.9[8]	−2.0	
Nitrobenzene	4.99	14.2[13]	−5.9	
Toluene	2.65	16.8[8]	−2.2	
1.1,1-Trichloroethane	2.57	17.7[8]	−1.3	
Triethylamine	0.43	−5.1[8]	−24.4	−26.4[8]
Solute (A): 1-pentanol; $\Delta_{soln}H^{A/C_6H_{12}} = 24.1$;[38] $\Delta_{soln}H^{A/CCl_4} = 19.1$;[28] $V_x^A = 0.8718$				
Acetonitrile	10.66	11.6[34]	−7.9	
Benzene	5.02	17.7[28]	−0.3	
Dibutyl ether	0.53	8.3[28]	−10.7	
1,2-Dichloroethane	8.56	16.6[28]	−2.1	
N,*N*-Dimethylacetamide	7.66	1.9[34]	−16.6	

Continues

Table 4. Continued

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}$(sp) (kJ mol^{-1})	$\Delta_c H^{A\cdots S}$ (kJ mol^{-1})
Dimethylformamide	8.62	3.8[34]	−15.0	
Dimethyl sulfoxide	13.87	5.4[36]	−15.3	
Ethyl acetate	5.98	9.5[28]	−8.6	
Mesitylene	1.10	16.3[28]	−2.2	
3-Methylsulfolane	9.87	10.7[34]	−8.5	
Nitromethane	13.74	17.0[34]	−3.7	
Propylene carbonate	10.14	11.6[36]	−7.7	
Toluene	2.65	16.8[39]	−1.1	
Triethylamine	0.43	−4.4[28]	−23.6	
Solute (A): phenol; $\Delta_{soln}H^{A/C_6H_{12}} = 31.9$;[24] $\Delta_{soln}H^{A/CCl_4} = 26.2$;[35] $V_x^A = 0.7751$				
Acetone	7.65	2.1[10]	−22.3	−20.1;[59] −21.3[82]
Acetonitrile	10.66	9.3[10]	−15.5	−14.2;[82] −19.5[59]
Anisole	5.69	11.8[10]	−12.5	−13.0[59]
Benzene	5.02	19.7[35]	−4.6	−4.9;[59] −3.8[83]
Chloroform	3.47	18.7[24]	−5.8	
1,2-Dichloroethane	8.56	18.9	−5.6	
N,*N*-Dimethylacetamide	7.66	−7.0[10]	−31.4	−28.5[59]
1,4-Dioxane	7.57	3.8[35]	−20.6	−21.3;[59] −20.9[35]
Dipropyl ether	0.70	3.0[13]	−23.2	
Dimethylformamide	8.62	−4.6[35]	−29.1	−26.3;[59] −28.7;[62] −25.5[84]
Dimethyl sulfoxide	13.87	−3.0[35]	−28.6	−30.1;[59] −28.9[84]
Ethyl acetate	5.98	4.1[35]	−20.2	−20.2;[59] −18.6[85]
Mesitylene	1.10	19.3[39]	−6.3	
Pyridine	6.66	−5.9[35]	−30.2	−30.5;[59] −28.5[62]
Tetrahydrofuran	3.28	−1.7[35]	−26.2	−24.0;[59] −23.0[35]
Toluene	2.65	19.4[86]	−5.3	−5.5;[59] −10.3[35]
1,1,1-Trichloroethane	2.57	19.7[64]	−5.0	
p-Xylene	1.31	20.2[86]	−5.3	−6.6;[59]
Solute (A): phenylacetylene; $\Delta_{soln}H^{A/C_6H_{12}} = 6$;[10] $\Delta_{soln}H^{A/CCl_4} = 1.6$;[10] $V_x^A = 0.9122$				
Dipropyl ether	0.70	−1.6[13]	−2.8	
Solute (A): 2-Propanol; $\Delta_{soln}H^{A/C_6H_{12}} = 22.8$;[87] $\Delta_{soln}H^{A/CCl_4} = 18.8$; $V_x^A = 0.59$				
Dimethyl sulfoxide	13.87	3.6[36]	−15.1	
Propylene carbonate	10.14	9.9[36]	−8.1	
Solute (A): *N*-propylaniline; $\Delta_{soln}H^{A/C_6H_{12}} = 8.6$;[32] $\Delta_{soln}H^{A/CCl_4} = 3.2$;[32] $V_x^A = 1.2389$				
Chloroform	3.47	−3.1[32]	−5.4	
Pyridine	6.66	−5.6[32]	−9.1	
Solute (A): pyrrole; $\Delta_{soln}H^{A/C_6H_{12}} = 15.7$;[3] $\Delta_{soln}H^{A/CCl_4} = 9.3$;[3] $V_x^A = 0.577$				
Acetonitrile	10.66	−1.3[88]	−6.7	−8.2;[62] −7.9[88]
Anisole	5.69	1.4[3]	−4.7	
Benzene	5.02	3.3[3]	−3.1	
Benzonitrile	4.01	−2.2[3]	−8.9	
Chlorobenzene	2.56	5.0[3]	−2.5	
Chloroform	3.47	1.4[3]	−5.6	
Cyclohexanone	4.66	−5.8[3]	−12.2	
1,2-Dichlorobenzene	3.47	5.1[3]	−1.9	
1,4-Dioxane	7.57	−5.1[88]	−10.8	
Dipropyl ether	0.70	−3.6[13]	−13.1	
Dimethylformamide	8.62	−9.1[88]	−14.7	
Dimethyl sulfoxide	13.87	−9.3[3]	−14.7	−17.6;[59] −12.5[59]
Ethyl acetate	5.98	−4.2[3]	−10.2	
Hexametapol	4.45	−18.5[3]	−25.1	
Nitrobenzene	4.99	0.3[3]	−6.1	
Nitromethane	13.74	1.5[3]	−3.9	
Pyridine	6.66	−8.4[3]	−14.3	−18.0;[59] −13.4;[88]
Tetrahydrofuran	3.28	−7.9[3]	−15.0	
Toluene	2.65	3.9[3]	−3.6	
Triethylamine	0.43	−11.1[3]	−21.2	−24.9;[59] −18.0[59]
Solute (A): toluene; $\Delta_{soln}H^{A/C_6H_{12}} = 2.9$;[38] $\Delta_{soln}H^{A/CCl_4} = -0.1$;[39] $V_x^A = 0.8573$				
Chloroform	3.47	−3.1[3]	−2.6	
Solute (A): trichloroethene; $\Delta_{soln}H^{A/C_6H_{12}} = 2.5$;[13] $\Delta_{soln}H^{A/CCl_4} = 0.3$;[10] $V_x^A = 0.7146$				
Acetone	7.65	−0.9[65]	−2.6	
Acetonitrile	10.66	1.6[65]	−1.5	

Continues

Table 4. Continued

Solvent (*S*)	$\delta_{cav}h^S$ (kJ cm^{-3} × 10^2)	$\Delta_{soln}H^{A/S}$ (kJ mol^{-1})	$\Delta_{int}H^{A/S}$(sp) (kJ mol^{-1})	$\Delta_c H^{A\cdots S}$ (kJ mol^{-1})
Benzene	5.02	0.3[65]	−0.4	
Chlorobenzene	2.56	−0.3[65]	−0.2	
1,2-Dichlorobenzene	3.47	−1.2[65]	−1.4	
1,4-Dioxane	7.57	−1.6[65]	−3.3	
Dimethylformamide	8.62	−3.5[65]	−5.6	
Dimethyl sulfoxide	13.87	−0.9[65]	−5.6	
Ethyl acetate	5.98	−2.2[65]	−3.3	
Pyridine	6.66	−0.9[65]	−2.2	
Tetrahydrofuran	3.28	−5.2[65]	−5.3	
Solute (A): Tri-*n*-butylamine; $\Delta_{soln}H^{A/C_6H_{12}} = 2.1$;[25] $\Delta_{soln}H^{A/CCl_4} = 0.9$;[56] $V_x^A = 1.8992$				
Chloroform	3.47	−11.1[25]	−13.9	

METHODOLOGY

The data on solution enthalpies used in this paper were mainly taken from papers listed in the tables. Some solution enthalpy data were measured using a differential quasi-adiabatic calorimeter. The detailed technique for the determination of the solution enthalpies can be found elsewhere.[12,90] The volume of the calorimetric cell was 100 ml. The final solute concentration did not exceed 0.03 mol l^{-1}. The absence of a concentration dependence of the heat effect was controlled by successive dissolution of weighed samples. The results were obtained as the average of 4–6 measurements. All calorimetric data, our own and obtained from the literature, were measured at 298 K.

For calculation of q values by Eqn (8), the latter were converted to the form

$$Y^S = qY^{CCl_4} \tag{11}$$

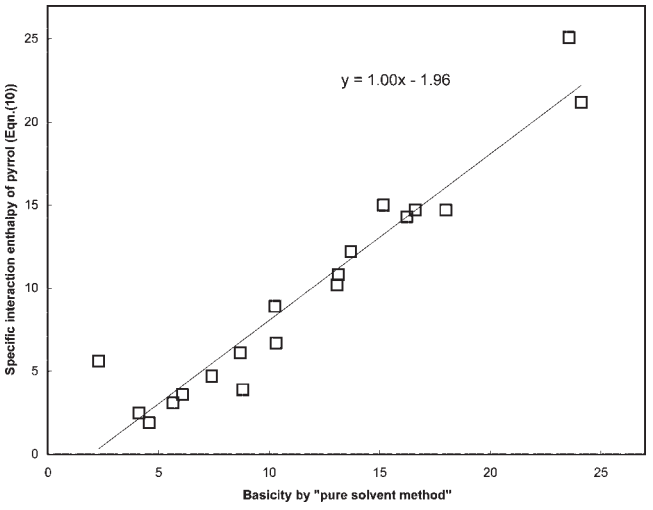

Figure 2. Correlation of specific interation enthalpy for pyrrole with the solvents [$-\Delta_{int(sp)}H^{Pyrrol/S}$] and data for 'pure solvent method' ($\delta\Delta H^0_{solv}$)

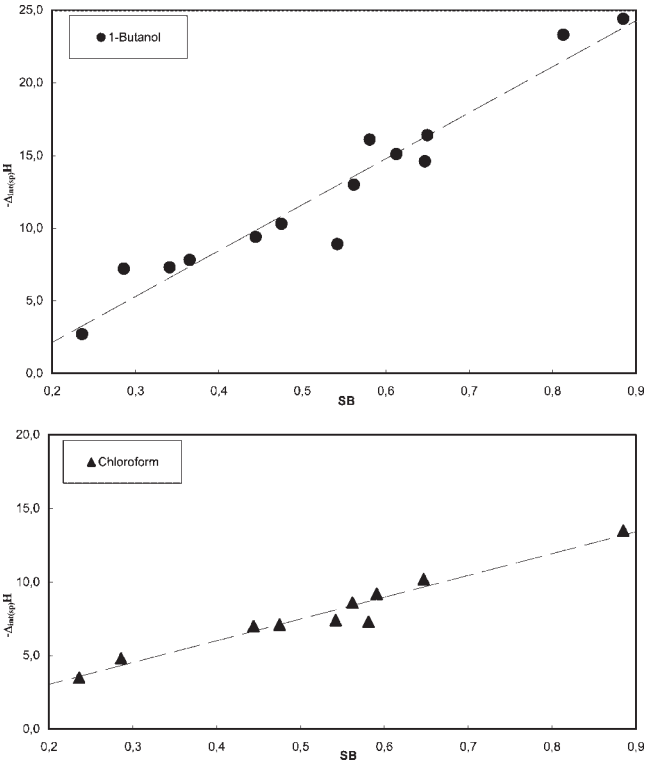

Figure 3. Correlations of specific interation enthalpies for 1-butanol and chloroform ($-\Delta_{int(sp)}H^{A/S}$) with SB scale of the solvents

where

$$Y^S = \Delta_{solv}H^{A/S} - \Delta_{solv}H^{A/C_6H_{12}} - \left(\delta_{cav}h^S - \delta_{cav}h^{C_6H_{12}}\right)V_x^A$$

and

$$Y^{CCl_4} = \Delta_{solv}H^{A/CCl_4} - \Delta_{solv}H^{A/C_6H_{12}} - \left(\delta_{cav}h^{CCl_4} - \delta_{cav}h^{C_6H_{12}}\right)V_x^A$$

The values of q were obtained from Eqn (11) by linear regression analysis for each solvent.

CONCLUSION

We have proposed a simple and very general method for the extraction of specific interaction enthalpy from the solvation enthalpy. It will give opportunities for obtaining new data on hydrogen bonding enthalpies for those systems where spectral methods can hardly be applied. This method may be especially useful for the determination of the specific interaction enthalpy with the solvents associated owing to intermolecular hydrogen bonding (such as water, alcohols, carbonic acids, aniline and formamide). It can also be used for the determination of the enthalpy of the hydrophobic effect for non-polar solutes.

REFERENCES

1. Solomonov BN, Antipin IS, Gorbatchuk VV, Konovalov AI. *Dokl. Akad. Nauk SSSR* 1978; **243**: 1499–1502; *Chem. Abst.* **90**: 120847.
2. Solomonov BN, Antipin IS, Gorbachuk VV, Konovalov AI. *J. Gen. Chem. USSR (Engl. Transl.)* 1982; **52**: 1917–1922; *Chem. Abst.* **98**: 41683.
3. Catalan J, Gomez J, Couto A, Laynez J. *J. Am. Chem. Soc.* 1990; **112**: 1678–1681.
4. Abraham MH, Taft RW. *J. Chem. Soc., Perkin Trans. 2* 1993; 305–306.
5. Catalan J, Gomez J, Saiz JL, Couto A, Ferraris M, Laynez J. *J. Chem. Soc., Perkin Trans. 2* 1995; 2301–2305.
6. Catalan J, Palomar J, Diaz C, Depaz JLG. *J. Phys. Chem. A* 1997; **101**: 5183–5189.
7. Arnett EM, Murty TSSR, Schleyer PVR, Joris L. *J. Am. Chem. Soc.* 1967; **89**: 5955–5957.
8. Stephenson WK, Fuchs R. *Can. J. Chem.* 1985; **63**: 342–348.
9. Solomonov BN, Novikov VB, Gorbachuk VV, Konovalov AI. *Dokl. Akad. Nauk SSSR* 1982; **265**: 1441–1445; *Chem. Abst.* **97**: 203921.
10. Solomonov BN, Konovalov AI, Novikov VB, Gorbachuk VV, Neklyudov SA. *J. Gen. Chem. USSR (Engl. Transl.)* 1985; **55**: 1681–1695; *Chem. Abst.* **104**: 25088.
11. Solomonov BN, Novikov VB, Solomonov AB. *Russ. J. Phys. Chem. (Engl. Transl.)* 2000; **74**: 1102–1108; *Chem. Abst.* **133**: 355856.
12. Solomonov BN, Konovalov AI, Novikov VB, Vedernikov AN, Borisover MD, Gorbachuk VV, Antipin IS. *J. Gen. Chem. USSR (Engl. Transl.)* 1984; **54**: 1444–1453; *Chem. Abst.* **101**: 210479.
13. Solomonov BN, Konovalov AI. *Russ. Chem. Rev.* 1991; **60**: 25–38; *Chem. Abst.* **104**: 246461, and references cited therein.
14. Solomonov BN, Chumakov FV, Borisover MD. *Russ. J. Phys. Chem. (Engl. Transl.)* 1993; **67**: 1158–1159; *Chem. Abst.* **120**: 16577.
15. Solomonov BN, Antipin IS, Gorbatchuk VV, Konovalov AI. *Dokl. Akad. Nauk SSSR* 1979; **247**: 405–408; *Chem. Abst.* **91**: 174635.
16. Abraham MH, McGowan JC. *Chromatographia* 1987; **23**: 243–246.
17. Drago RS, Parr LB, Chamberlain CS. *J. Am. Chem. Soc.* 1977; **99**: 3203–3210.
18. Borisover MD, Stolov AA, Cherkasov AR, Izosimova SV, Solomonov BN. *Russ. J. Phys. Chem. (Engl. Transl.)* 1994; **68**: 48–53; *Chem. Abst.* **120**: 308617.
19. Stolov AA, Izosimova SV, Breus VA, Neklyudov SA, Solomonov BN. *Russ. J. Phys. Chem. (Engl. Transl.)* 1993; **67**: 2112–2113; *Chem. Abst.* **120**: 163332.
20. Solomonov BN, Borisover MD, Konovalov AI. *J. Gen. Chem. USSR (Engl. Transl.)* 1986; **56**: 1–11; *Chem. Abst.* **104**: 224509).
21. Vandyshev VN, Korolev VP, Krestov GA. *Thermochim. Acta* 1990; **169**: 57.
22. Gerber JN, Sawyer DN. *Anal. Chem.* 1972; **44**: 1199–1203.
23. Spencer JN, Holmboe ES, Kirshenbaum MR, Firth DW, Pinto PB. *Can. J. Chem.* 1982; **60**: 1178–1182.
24. Spencer JN, Sweigart JR, Brown ME, Bensing RL, Hassinger TL, Kelly W, Housel DL, Reisinger GW, Gleim JE, Peiper JC. *J. Phys. Chem.* 1977; **81**: 2237–2240.
25. Ochkin AV, Vinetskaja TN, Frolov J. *Izv. Vissh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 1974; **17**: 677–680; *Chem. Abst.* **81**: 141815.
26. Drago RS, Nozari MS, Vogel GC. *J. Am. Chem. Soc.* 1972; **94**: 90–94.
27. Arnett EM, McKelvey DR. *J. Am. Chem. Soc.* 1966; **88**: 2598–2599.
28. Fuchs R, Chambers EJ, Stephenson WK. *Can. J. Chem.* 1987; **65**: 2624–2627, and references cited therein.
29. Novikov VB, Stolov AA, Gorbatchuk VV, Solomonov BN. *J. Phys. Org. Chem.* 1998; **11**: 283–289.
30. Borisover MD, Solomonov BN, Breus VA, Gorbachuk VV, Konovalov AI. *Zh. Obshch. Khim.* 1988; **58**: 249–261; *Chem. Abst.* **108**: 174623.
31. Spencer JN, Berger EM, Powell CR, Henning BD, Furman GS, Loffredo WM, Rydberg EM, Neubort RA, Shoop CE, Slauch DN. *J. Phys. Chem.* 1981; **85**: 1236–1241.
32. Spencer JN, Gleim JE, Blevins CH, Garret RC, Mayer FJ. *J. Phys. Chem.* 1979; **83**: 1249–1255.
33. Saluja PS, Peacock LA, Fuchs R. *J. Am. Chem. Soc.* 1979; **101**: 1958–1962.
34. Krishnan CV, Friedman HL. *J. Phys. Chem.* 1971; **75**: 3598–3606.
35. Arnett EM, Joris L, Mitchell E, Murty TSSR, Gorrie TM, Schleyer PVR. *J. Am. Chem. Soc.* 1970; **92**: 2365–2377.
36. Krishnan CV, Friedman HL. *J. Phys. Chem.* 1969; **73**: 1572–1580.
37. Saluja PS, Young TM, Rodewald RF, Fuchs FH, Kohli D, Fuchs R. *J. Am. Chem. Soc.* 1977; **99**: 2949–2953.
38. Trampe DM, Eckert CA. *J. Chem. Eng. Data* 1991; **36**: 112–118.
39. Fuchs R, Peacock LA, Stephenson WK. *Can. J. Chem.* 1982; **60**: 1953–1958.
40. Fuchs R, Young TM, Rodewald RF. *J. Am. Chem. Soc.* 1974; **96**: 4705–4706.
41. Fuchs R, Cole RR, Rodewald RF. *J. Am. Chem. Soc.* 1972; **94**: 8645.
42. Konovalov AI, Ovchinnikov VV. *Phosphorus Sulfur Silicon* 1996; **111**: 668.
43. Dellagatta G, Stradella L, Venturello P. *J. Solution Chem.* 1981; **10**: 209–220.
44. Sherman SR, Suleiman D, Hait MJ, Schiller M, Liotta CL, Eckert CA, Li JJ, Carr PW, Poe RB, Rutan SC. *J. Phys. Chem.* 1995; **99**: 11239–11247.
45. Kiselev VD, Mavrin GV, Konovalov AI. *J. Org. Chem. USSR (Engl. Transl.)* 1980; **16**: 1233–1238; *Chem. Abst.* **93**: 238515.
46. Cox JD, Pilcher G. *Thermochemistry of Organic and Organometallic Compounds.* Academic Press: London, 1973.
47. Fuchs R, Rodewald RF. *J. Am. Chem. Soc.* 1973; **95**: 5897–5900.
48. Lebedev JA, Miroshnichenko EA. *Termokhimiya Paroobrazovaniya Organicheskikh Veschestv (Thermochemistry of Vaporization of Organic Substances).* Nauka: Moscow, 1981 (in Russian).
49. Fuchs R, Peacock LA, Das K. *Can. J. Chem.* 1980; **58**: 2301–2304.
50. Arnett EM, Mitchell E, Murty TSSR. *J. Am. Chem. Soc.* 1974; **96**: 3875–3891.
51. Solomonov BN, Antipin IS, Novikov VB, Konovalov AI. *J. Gen. Chem. USSR (Engl. Transl.)* 1982; **52**: 2364–2370; *Chem. Abst.* **98**: 79058.
52. Guitry RM, Drago RS. *J. Phys. Chem.* 1974; **78**: 454–459.
53. Arnett EM, Larsen JW. *J. Am. Chem. Soc.* 1969; **91**: 1438–1442.
54. Hossenlopp JA, Scott DW. *J. Chem. Thermodyn.* 1981; **13**: 423–428.
55. Stephenson WK, Fuchs R. *Can. J. Chem.* 1985; **63**: 2540–2544.
56. Arnett EM, Quirk RP, Burke JJ. *J. Am. Chem. Soc.* 1970; **92**: 1260–1266.
57. Spencer JN, Gleim JE, Hackman ML, Blevins CH, Garret RC. *J. Phys. Chem.* 1978; **82**: 563–565.
58. Vorobjev NK, Kuritsin LV. *Izv. Vissh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 1968; **11**: 274–278.
59. Joesten M, Schaad L. *Hydrogen Bonding*. Marcel Dekker: New York, 1974.
60. Rao CNR. *J. Chem. Soc., Faraday Trans. 1* 1975; **71**: 980–983.
61. Duer WC, Bertrand GL. *J. Am. Chem. Soc.* 1974; **96**: 1300–1304.

62. Iogansen AV. *Spectrochim. Acta, Part A* 1999; **55**: 1585–1612.
63. Spencer JN, Andrefsky JA, Naghdi J, Patti L, Trader JF. *J. Phys. Chem.* 1987; **91**: 2959–2962.
64. Abraham MH, Duce PP, Prior DV, Schulz RA, Morris JJ, Taylor PJ. *J. Chem. Soc., Faraday Trans. 1* 1988; **84**: 865–869.
65. Borisover MD, Stolov AA, Izosimova SV, Baitalov FD, Breus VA, Solomonov BN. *Russ. J. Phys. Chem. (Engl. Transl.)* 1991; **65**: 315–318; *Chem. Abst.* **114**: 235918.
66. Neklyudov SA. PhD Dissertation, Kazan State University, 1984.
67. Borisover MD, Stolov AA, Kudryavtsev VY, Solomonov BN. *Russ. J. Phys. Chem. (Engl. Transl.)* 1991; **65**: 164–166; *Chem. Abst.* **114**: 206480.
68. Stokes RH, Burfitt C. *J. Chem. Thermodyn.* 1975; **7**: 803–804.
69. Khairetdinova AK, Perelygin IS. *Opt. Spektrosk.* 1969; **26**: 62–67; *Chem. Abst.* **70**: 86841.
70. Kiselev VD, Mavrin GV, Korshin EE, Konovalov AI. *J. Gen. Chem. USSR (Engl. Transl.)* 1980; **50**: 919–922; *Chem. Abst.* **93**: 32613.
71. Safin DH, Chmutova GA, Solomonov BN. *J. Org. Chem. USSR (Engl. Transl.)* 1985; **21**: 1712–1721; *Chem. Abst.* **104**: 108938.
72. Maria PC, Gal JF, De Franceschi J, Fargin E. *J. Am. Chem. Soc.* 1987; **109**: 483–492.
73. Laurence C, Gueheneuf G, Wojtokowiak B. *J. Am. Chem. Soc.* 1979; **101**: 4793–4800.
74. Guryanova EN, Goldshtein IP, Romm IP. *Donorno–Aktseptornaya Svyaz' (Donor–Acceptor Bonding).* Khimiya: Moscow, 1973 (in Russian).
75. Kiselev VD, Huzjasheva DG, Konovalov AI. *Zh. Obshch. Khim.* 1979; **49**: 2570–2573; *Chem. Abst.* **92**: 110378.
76. Hartley BK, Skinner HA. *Trans. Faraday Soc.* 1950; **46**: 621–625.
77. Huyskens PL, Mahillon P. *Bull. Soc. Chim. Belg.* 1980; **89**: 709–714.
78. Arnett EM, Carter JV. *J. Am. Chem. Soc.* 1971; **93**: 1516–1518.
79. Duer WC, Bertrand GL. *J. Am. Chem. Soc.* 1975; **97**: 3894–3897.
80. Spencer JN, Wolbach WS, Hovick JW, Ansel L, Modaress KJ. *J. Solution Chem.* 1985; **14**: 805–814.
81. Breus VA, Neklyudov SA, Solomonov BN, Konovalov AI. *J. Org. Chem. USSR (Engl. Transl.)* 1983; **19**: 1426–1429; *Chem. Abst.* **99**: 211879.
82. Perelygin IS, Ahunov TF. *Opt. Spektrosk.* 1971; **30**: 679–683; *Chem. Abst.* **75**: 27627.
83. Seidal H, Bayer C, Fruwert J, Geiseler G. *Z. Phys. Chem. (Leipzig)* 1978; **259**: 625–634.
84. Kroeger MK, Drago RS. *J. Am. Chem. Soc.* 1981; **103**: 3250–3262.
85. Singh BS, Murthy ASN, Rao CNR. *Trans. Faraday Soc.* 1966; **62**: 1056–1066.
86. Goralski P, Tkaczyk M. *J. Chem. Soc., Faraday Trans. 1* 1987; **83**: 3083–3092.
87. Abraham MH, Whiting GS, Fuchs R, Chambers EJ. *J. Chem. Soc., Perkin Trans. 2* 1990; 291–300.
88. Spencer JN, Gleim JE, Blevins CH, Garret RC, Mayer FJ, Merkle JH, Smith SL, Hackman ML. *J. Phys. Chem.* 1979; **83**: 2615–2621.
89. Abboud JLM, Notario R. *Pure Appl. Chem.* 1999; **71**: 645–718.
90. Borisover MD, Stolov AA, Baitalov FD, Morozov AI, Solomonov BN. *Thermochim. Acta* 1996; **285**: 199–209.