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Group contributions to enthalpies of solvation in octan-1-ol and di-*n*-butyl ether[☆]

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Abstract

The standard enthalpies of solvation of selected *n*-alkanes (hexane, heptane, nonane, decane, dodecane, hexadecane) and aromatic hydrocarbons (benzene, toluene, ethylbenzene) in 1-octanol and di-*n*-butyl ether (DBE) have been determined at 298.15 K from experimental heats of solution. The values obtained, together with the data collected from literature, form a dataset of 89 and 59 enthalpies of solvation in 1-octanol and di-*n*-butyl ether, respectively. The data have been employed for setting up a group contributions scheme to the enthalpies of solvation of organic compounds in the two solvents. Two different methods, the first based on a multiple regression analysis, the second consisting by a step procedure which takes the *n*-alkanes as reference compounds, have been used to calculate the values of the contributions. The different results obtained with these approaches have been compared and discussed.

Keywords: Group contributions; Enthalpies of solution; Enthalpies of solvation; 1-Octanol; Di-*n*-butyl ether

1. Introduction

Group contributions schemes have been extensively employed as a practical method for predicting a plethora of thermodynamic and related properties such as free energies and enthalpies of formation [1], enthalpies of vaporisation [2], critical properties and boiling points [3], vapour pressure of pure liquids [4], and so on. The basic idea underlying these approaches is that a solute molecule acts as a number of fragments independently contributing to the investigated property. These fragments can be constituted by individual atoms or simple atomic groups and usually coincide with portion of alkyl chains or with the functional groups characterising the different classes of organic compounds.

In particular, several schemes of group additivity have been developed in order to rationalise and predict thermodynamic functions of solvation and partial molar properties at infinite dilution of a wide variety of compounds in different solvents [5,6]. Although some efforts have been made in order to assess the molecular basis of these approaches [7], the group contribution schemes basically remain empirical procedures. The general form of a group contributions equation to the thermodynamic functions of solvation is

$$\Delta_{\mathrm{solv}} X^{\circ} = A + \sum_{j} n_j B_j \tag{1}$$

where X is the thermodynamic function of interest, B_j the contribution to the property of the jth group present n_j times in the solute structure and A is a constant term whose meaning has been widely discussed [5,8]. Some authors also added in Eq. (1) correction terms to account for peculiar features of the compounds like cyclic structures, conformational isomerism or polysubstitution [5,9].

The usual procedure employed for determining the values of the group contributions is based on a linear multiparameter regression in which the experimental values of the solvation property are fitted to Eq. (1). The group contributions A and B_j are then obtained as the regression parameters while the correction terms are later deduced as a difference between the experimental values and those calculated using the A and B_j contributions. This approach is reliable when the dataset of experimental values is large enough with respect to the number of parameters to be determined and adequately distributed among the different classes of compounds.

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Anyway, even in case these conditions are not matched, it is still possible to obtain the values of the group contributions using different procedures. In most of these simplified approaches the hydrocarbons are taken as the reference compounds.

In a previous paper [10], we worked out a group contributions scheme to the free energies and enthalpies of solvation of organic non-electrolytes in di-*n*-butyl ether (DBE) and in octan-1-ol (1-OCT) where the contributions of the alkyl groups (CH_3, CH_2, CH and C) were assumed to be proportional to their van der Waals surface area. The CH_2 group contribution was first calculated as the average increment of the thermodynamic property in homologous series of compounds and the contributions of the other alkyl groups were estimated by a proportionality criterion. The constant A term and the contributions B_j for the polar groups were then determined by difference from the *n*-alkanes and from the homologous series of monofunctional compounds. This procedure demonstrates very useful when a limited number of data is available. Its reliability in view of the prediction of the examined property critically depends on the accuracy of the experimental values of *n*-alkanes which determine the value of the constant A.

We report here the results of a calorimetric investigation on the enthalpies of solvation, $\Delta_{\text{solv}}H^{\circ}$, of some selected *n*-alkanes and aromatic hydrocarbons in DBE and 1-OCT obtained from the heats of solution experimentally determined and from the literature enthalpies of vaporisation. These values, together with the data collected through an exhaustive literature investigation, allowed us to build up two datasets including enthalpies of solvation of 89 and 59 compounds in 1-OCT and DBE, respectively. The group contributions values to $\Delta_{\text{solv}}H^{\circ}$ in both solvents have been determined by applying either the multiple linear regression analysis or the simplified procedure based on the *n*-alkanes as reference compounds. The two approaches have been compared and discussed.

2. Experimental

2.1. Materials

All chemicals were Fluka or Aldrich products of the best grade available. Their declared mass fraction purities were as follows: octan-1-ol > 0.995; di-*n*-butyl ether > 0.995; hexane > 0.99; heptane > 0.99; nonane > 0.98; decane > 0.99; dodecane > 0.995; hexadecane > 0.995; benzene > 0.99; toluene > 0.98; ethylbenzene > 0.99. The purity of all samples was checked by GLC and was in all cases better than 99.3%. The samples showed a water content $<0.01\%$ (determined by Karl Fischer titration) and were used without further purification.

2.2. Apparatus and procedure

The calorimetric measurements of the heats of solution in 1-OCT and DBE were performed with an isoperibol calorimeter built for this purpose and already described [11]. For each compound and for each solvent at least 20 measurements were carried out in the range 0.001–0.045 of the solute mole fraction, X_S. Only for hexane in 1-OCT and aromatic hydrocarbons in DBE the measurements were

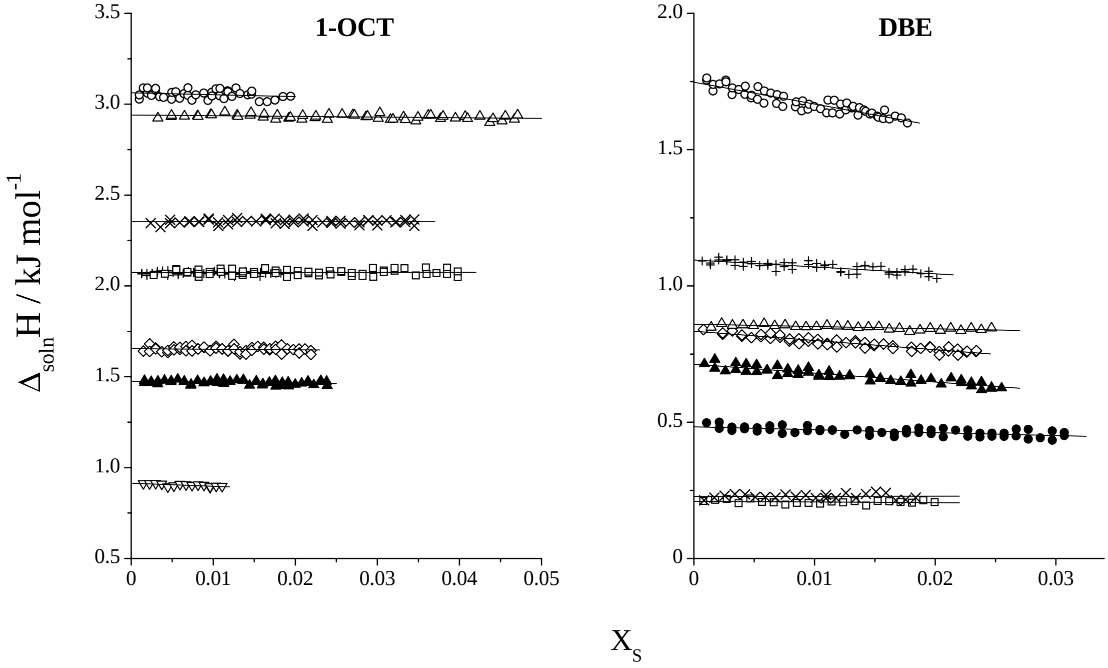

Fig. 1. Experimental $\Delta_{\text{soln}}H$ vs. the solute mole fraction X_S in 1-octanol and di-*n*-butyl ether. Solutes: (▽) hexane; (●) heptane; (▲) nonane; (◇) decane; (+) dodecane; (○) hexadecane; (△) benzene; (□) toluene; (×) ethylbenzene.

performed by a TAM 2277 isothermal calorimeter equipped with a 20 ml titration cell. In these cases the X_S composition range explored was 0.001–0.02. A linear trend of the heats of solution versus X_S was observed for all studied solutes, so that it was always possible to linearly extrapolate in order to obtain the limiting solution enthalpies. Depending on the way the measurements are carried out, it is only possible to estimate the maximum uncertainty affecting either the experimental heats of solution or the corresponding X_S values. By evaluating all the sources of error these uncertainties can be estimated as large as 0.05 kJ mol^{-1} for the values of the heat of solution and 0.5% for X_S. However, the uncertainty on the limiting enthalpies of solution was always lower than 0.01 kJ mol^{-1}.

In Fig. 1 the experimental $\Delta_{\text{soln}}H$ values are plotted against the mole fraction X_S for all investigated organic solutes in 1-OCT and DBE. The figure also reports the fitting straight lines obtained by a least squares procedure.

3. Results and discussion

In Table 1 the values of the enthalpy of solution at infinite dilution, $\Delta_{\text{soln}}H^\circ$, for the investigated solutes in 1-OCT and DBE are summarised with the values of the *b* slopes of the fitting straight lines. Direct measurements of the heats of solution of linear hydrocarbons, benzene and toluene in both solvents have been reported some years ago by Fuchs and Stephenson [12,13]. Moreover, for most of the investigated binary mixtures values of the excess enthalpies, H^E, are also known in the whole composition range and the $\Delta_{\text{soln}}H^\circ$ values can be calculated from the parameters of the equation (usually the Redlich–Kister one) describing the curves of H^E versus mixtures composition. Our data are in good agreement with those reported by Fuchs and Stephenson [12,13], the differences usually not exceeding 0.15 kJ mol^{-1} in 1-OCT whereas in DBE are less than 0.07 kJ mol^{-1}. Only in the case of hexane the differences are larger, being our data lower by 0.3 and 0.15 kJ mol^{-1} in 1-OCT and in DBE, respectively. However, the hexane $\Delta_{\text{soln}}H^\circ$ values here determined agree well with the values deduced from H^E data by Christensen et al. [14] (1-OCT, 0.84 kJ mol^{-1}) and by Marsh et al. [15] (DBE, 0.33 kJ mol^{-1}). For decane in DBE and ethylbenzene in 1-OCT our $\Delta_{\text{soln}}H^\circ$ experimental values can only be compared with those deduced from H^E data by Segade et al. [16] (0.86 kJ mol^{-1}) and by Lien et al. [17] (2.50 kJ mol^{-1}), respectively. For ethylbenzene in DBE no literature data are available.

The standard enthalpies of solvation at 298.15, $\Delta_{\text{solv}}H^\circ$, i.e. the enthalpy changes related to the isothermal transfer of the solute from the ideal gas state to infinitely dilute solution in the considered solvents, have been calculated by the relationship:

$$\Delta_{\text{solv}}H^\circ = \Delta_{\text{soln}}H^\circ - \Delta_{\text{vap}}H^\circ \tag{2}$$

$\Delta_{\text{vap}}H^\circ$ being the standard enthalpy of vaporisation.

The standard solvation enthalpies in 1-OCT and DBE for the examined compounds, calculated by Eq. (2) using known $\Delta_{\text{vap}}H^\circ$ values, are given in Table 2. The table also reports the results of an accurate literature investigation on the enthalpies of solution of hydrocarbons and monofunctional compounds in the considered solvents obtained by either direct calorimetric measurements or H^E versus composition data. When several literature values were found for the same system a critical evaluation of the data sources was made and the direct measurements of $\Delta_{\text{soln}}H^\circ$ were usually preferred. Alternatively, we took care to select the sources whose reported H^E values were adequately distributed over the whole composition range. Since the values of $\Delta_{\text{soln}}H^\circ$ deduced from H^E data critically depend on the form of the fitting equation, in some cases we performed a new fitting of the literature data by employing the number of parameters more suitable to obtain reliable limiting enthalpies of solution.

The whole set of data reported in Table 2 has been treated in order to obtain a pattern of group contributions to solvation enthalpy in 1-OCT and DBE. As above mentioned two distinct methodologies have been applied.

Table 1
Standard enthalpies of solution, $\Delta_{\text{soln}}H^\circ$, in octan-1-ol and di-*n*-butyl ether and slopes of the fitting lines, *b*, at 298.15 K[a]

Compound	1-OCT		DBE	
	$\Delta_{\text{soln}}H^{\circ\,b}$	b^b	$\Delta_{\text{soln}}H^{\circ\,b}$	b^b
Hexane	0.91 ± 0.003	−1.7 ± 0.4	–	–
Heptane	–	–	0.48 ± 0.003	−1.1 ± 0.2
Nonane	1.48 ± 0.003	−0.5 ± 0.2	0.71 ± 0.003	−3.3 ± 0.2
Decane	1.66 ± 0.004	−0.3 ± 0.3	0.83 ± 0.003	−3.4 ± 0.2
Dodecane	2.07 ± 0.002	−0.2 ± 0.2	1.10 ± 0.003	−2.5 ± 0.3
Hexadecane	3.06 ± 0.007	−1.1 ± 0.7	1.75 ± 0.005	−8.0 ± 0.5
Benzene	2.94 ± 0.004	−0.4 ± 0.1	0.86 ± 0.002	−0.84 ± 0.1
Toluene	2.07 ± 0.004	0.0 ± 0.2	0.21 ± 0.003	−0.2 ± 0.2
Ethylbenzene	2.35 ± 0.004	0.0 ± 0.2	0.23 ± 0.004	0.1 ± 0.3

[a] Data in kJ mol^{-1}.

[b] Limiting enthalpies of solution obtained by $\Delta_{\text{soln}}H = \Delta_{\text{soln}}H^\circ + b\,X_S$, where $\Delta_{\text{soln}}H$ is the measured heat of solution at mole fraction X_S of the solute.

Table 2
Standard enthalpy of solvation of organic compounds in 1-octanol and di-*n*-butyl ether at 298.15 K[a]

Compound	1-OCT				DBE			
	$\Delta_{\mathrm{solv}}H^\circ$	Reference	Δ[b]		$\Delta_{\mathrm{solv}}H^\circ$	Reference	Δ[b]	
			M1[c]	M2[c]			M1[c]	M2[c]
Pentane	−26.02	[14]	0.40	−0.06	−26.42	[12]	0.04	0.27
Hexane	−30.82	t.w.	0.16	−0.08	−31.45	[10]	−0.25	0.01
Heptane	−35.54	[19]	0.00	−0.04	−36.18	t.w.	−0.24	0.05
Octane	−40.23	[19]	−0.13	0.04	−41.02	[10]	−0.34	−0.02
Nonane	−44.95	t.w.	−0.30	0.08	−45.72	t.w.	−0.30	0.05
Decane	−49.74	t.w.	−0.52	0.07	−50.56	t.w.	−0.40	−0.02
Dodecane	−59.44	t.w.	−1.10	−0.10	−60.41	t.w.	−0.78	−0.33
Hexadecane	−78.32	t.w.	−1.73	0.09	−79.63	t.w.	−1.04	−0.46
3-Ethylpentane	−34.23	[20]	−0.77	−0.78	−34.90	[20]	0.32	1.29
2,2,4-Trimethylpentane	–				−34.80	[21]	−0.11	6.83
Cyclohexane	−31.62	[19]	0.85	0.66	−32.38	[10]	0.29	0.28
Methylcyclohexane	−34.33	[14]	0.63	2.69	–			
1-Octene	–				−40.40	[14]	0.00	0.00
1-Octyne	–				−43.22	[22]	0.00	0.00
2-Octyne	–				−44.85	[22]	−0.90	−0.90
4-Octyne	–				−43.05	[22]	0.90	0.90
Benzene	−30.98	t.w.	0.36	0.00	−33.06	t.w.	1.31	0.00
Toluene	−35.99	t.w.	0.23	−1.52	−37.85	t.w.	1.08	−1.46
ethylbenzene	−39.91	t.w.	0.87	−0.67	−42.03	t.w.	1.63	−0.87
1,2-Dimethylbenzene	−41.53	[23]	−0.43	−3.58	–			
1,3-Dimethylbenzene	−41.00	[23]	0.10	−3.05	–			
1,4-Dimethylbenzene	−40.59	[23]	0.51	−2.64	–			
1,3,5-Trimethylbenzene	−45.88	[13]	0.10	−4.44	−47.38	[13]	0.65	−4.33
Methanol	−37.08	[14]	1.25	0.49	−31.24	[10]	−1.51	−0.79
Ethanol	−41.79	[14]	1.10	0.55	−35.32	[24]	−0.85	−0.10
1-Propanol	−46.96	[14]	0.49	0.15	−39.45	[10]	−0.23	0.55
2-Propanol	–				−39.64	[25]	−1.14	0.32
1-Butanol	−51.96	[19]	0.05	−0.08	−44.94	[10]	−0.99	−0.18
2-Butanol	−49.38	[19]	0.56	2.46	−40.65	[10]	2.59	4.08
2-Methyl-1-propanol	–				−44.58	[26]	−1.34	0.15
2-Methyl-2-propanol	−47.12	[19]	0.89	5.43	−37.13	[26]	1.55	8.31
1-Pentanol	−56.74	[27]	−0.17	−0.09	−48.71	[27]	−0.02	0.82
2,2-Dimethyl-1-propanol	−53.64[d]	[27]	−1.07	3.68	−40.63[d]	[27]	2.79	9.58
1-Hexanol	−61.49	[14]	−0.36	−0.08	–			
1-Heptanol	–				−59.02	[24]	−0.85	0.06
1-Octanol	−70.98		−0.73	−0.03	–			
1-Decanol	−81.40	[14]	−2.03	−0.91	–			
Diethyl ether	−25.08	[19]	0.29	−0.77	−27.16	[10]	0.46	−0.29
Butyl methyl ether	−29.64	[13]	0.28	−0.56	−32.32	[13]	0.04	−0.67
Tert-butyl methyl ether	−28.03	[27]	−2.11	1.72	−29.68	[29]	−2.59	2.64
Dipropyl ether	−33.29	[19]	1.20	0.56	–			
Diisopropyl ether	−31.04	[30]	−0.70	2.74	–			
Dibutyl ether	−42.61	[19]	1.00	0.77	−45.00		1.58	0.96
Tetrahydrofuran	−28.07	[19]	1.27	0.49	−31.03	[10]	0.20	−0.44
Tetrahydropiran	−31.03	[19]	0.39	−0.40	–			
Propanone	−22.36	[19]	0.05	−0.42	−26.02	[10]	−0.42	−0.25
Butanone	−27.39	[19]	−0.42	−0.68	−30.74	[31]	−0.39	−0.19
2-Pentanone	−31.25	[19]	0.28	0.23	−35.12	[32]	−0.04	0.20
3-Pentanone	−31.76	[19]	−0.23	−0.28	−35.87	[10]	−0.78	−0.55
2-Hexanone	−36.38	[19]	−0.29	−0.13	−40.01	[32]	−0.19	0.08
2-Heptanone	−40.55	[31]	0.11	0.47	−44.31	[31]	0.25	0.55
4-Heptanone	−40.47	[19]	0.18	0.55	−44.44	[31]	0.12	0.42
2-Octanone	–				−49.33	[32]	−0.03	0.30
2-Nonanone	−50.29	[31]	−0.52	0.26	−53.97	[31]	0.07	0.43
5-Nonanone	−47.19	[31]	2.58	3.36	−51.33	[31]	2.71	3.07
2,2,4,4-Tetramethyl-3-pentanone	−40.63	[31]	1.14	11.26	−44.31	[31]	−0.82	11.43
Cyclopentanone	−34.39	[33]	1.13	1.34	−38.88	[10]	−0.20	0.15
Cycloesanone	−37.27	[31]	0.32	0.53	−41.58	[31]	−0.29	−0.28
1-Propylamine	−40.18	[19]	−0.51	0.23	−28.23	[10]	2.50	−0.01

Table 2 (*Continued*)

Compound	1-OCT				DBE			
	$\Delta_{solv}H^\circ$	Reference	Δ[b]		$\Delta_{solv}H^\circ$	Reference	Δ[b]	
			M1[c]	M2[c]			M1[c]	M2[c]
1-Butylamine	−45.26	[19]	−1.03	−0.08	−32.99	[10]	2.48	0.01
1-Pentylamine	−50.10	[19]	−1.31	−0.15	–			
Diethylamine	−43.24	[34]	−0.49	−1.37	–			
Dipropylamine	−50.88	[19]	0.99	0.52	–			
Dibutylamine	−60.09	[19]	0.90	0.85	−49.24	[35]	0.00	0.00
Triethylamine	−43.60	[19]	−3.87	−1.55	−35.55	[20]	−1.54	−1.64
Tripropylamine	−49.41	[19]	4.00	6.94	–			
Tributylamine	−64.02	[19]	3.07	6.64	−60.90	[36]	1.54	1.64
Pyrrolidine	−47.94	[19]	−1.21	−1.83	–			
Piperidine	−48.99	[19]	−0.18	−0.80	–			
1-Methylpyrrolidine	−40.33	[19]	−1.19	1.19	–			
1-Methylpiperidine	−43.24	[19]	−2.01	0.36	–			
Ethanenitrile	–				−26.78	[10]	0.00	0.00
Butanenitrile	−31.39	[37]	0.00	0.00	–			
Methanoic acid	−46.90	[38]	0.01	0.02	–			
Ethanoic acid	−49.80	[38]	−0.86	−0.96	–			
Propanoic acid	−52.65	[38]	0.85	0.96	–			
Methyl methanoate	−21.40	[39]	−0.14	−0.49	–			
Propyl methanoate	−30.39	[40]	−0.01	0.06	–			
Butyl methanoate	−34.80	[41]	0.14	0.41	–			
Methyl ethanoate	−24.62	[42]	−1.33	−1.79	–			
Ethyl ethanoate	−27.78	[43]	0.07	−0.18	–			
Propyl ethanoate	−33.00	[44]	−0.58	−0.63	–			
Butyl ethanoate	−37.13	[45]	−0.15	0.01	–			
Pentyl ethanoate	−41.31[e]	[47]	0.23	0.60	–			
Methyl propanoate	−26.67	[48]	1.18	0.93	–			
Ethyl propanoate	−32.54	[32]	−0.12	−0.17	–			
Methyl butanoate	−33.04	[32]	−0.62	−0.67	–			
Methyl pentanoate	−37.02	[48]	−0.04	0.12	–			
1-Chloropropane	−26.02	[49]	0.57	0.16	–			
1-Chlorobutane	−31.00	[49]	0.16	−0.05	–			
2-Chlorobutane	−28.87	[14]	0.21	2.04	–			
1-Chloropentane	−35.92	[50]	−0.21	−0.21	−38.14	[51]	0.00	0.00
1-Chlorohexane	−40.43	[52]	−0.16	0.05	–			
1-Chlorooctane	−49.97	[53]	−0.58	0.05	–			
1-Bromobutane	–				−36.36	[54]	0.00	0.00
Nitrobenzene	−47.14	[13]	0.00	0.00	−50.95	[13]	0.00	0.00
Methyl phenyl ether	−41.35	[13]	−1.62	−3.76	−44.53	[13]	0.30	−3.17
Benzenamine	−51.19	[20]	2.85	2.50	−52.90	[20]	−4.97	−10.20
Ethyl benzoate	−54.52[e]	[17]	1.38	0.66	–			
1-Phenylethanone	−50.23[f]	[17]	−4.34	−5.48	–			

[a] All data in kJ mol^{-1}. $\Delta_{solv}H^\circ$ values calculated by Eq. (2) using the $\Delta_{solv}H^\circ$ values of the quoted references (t.w., this work) and the $\Delta_{vap}H^\circ$ values from [18] if not otherwise specified.

[b] $\Delta = \Delta_{solv}H^\circ$ (exp) − $\Delta_{solv}H^\circ$ (calc.).

[c] M1, M2 methods of calculation of the group contributions (see text).

[d] $\Delta_{vap}H^\circ$ from [28].

[e] $\Delta_{vap}H^\circ$ from [46].

[f] $\Delta_{vap}H^\circ$ from [55].

In the first procedure (M1), based on a least-squares method applied to Eq. (1), the values of the group contributions have been calculate as the coefficients of a multiple linear regression where the frequencies of each group in the solute molecule were taken as the independent variables. Obviously the contributions of the groups present in a single compound were evaluated a posteriori by difference.

In the second procedure (M2) the contribution of the CH_2 group was first calculated as an average value of the increments of the enthalpies of solvation in homologous series of *n*-alkanes, ethers, *n*-alkanols, ketones, amines and chloroalkanes. The contributions of the other alkyl groups (CH_3, CH and C) were then calculated by the surface area ratios with respect to CH_2 by referring to the intrinsic surface areas calculated according to Bondi [56]. The constant

Table 3
Group contributions to the standard enthalpies of solvation, B_j, of organic compounds in 1-octanol and di-*n*-butyl ether at 298.15 K[a]

Group	1-OCT (89 compounds)		DBE (59 compounds)	
	M1	M2	M1	M2
A	−2.89	3.32	2.58	2.62
CH_3	−7.81	−7.49	−7.41	−7.49
CH_2	−4.56	−4.77	−4.74	−4.77
CH	0.77	−2.01	−1.36	−2.01
C	5.95	0.00	5.88	0.00
Ch_{ar}	−5.71	−5.72	−6.16	−5.95
C_{ar}	−2.77	−1.71	−3.30	−1.78
OH	−33.41	−33.40	−24.90	−25.58
CO	−9.67	−10.28	−13.36	−13.41
O	−3.51	−3.12	−5.90	−4.97
NH_2	−25.63	−26.70	−16.41	−13.80
NH	−20.89	−20.67	−8.56	−8.24
N	−5.50	−8.60	−0.13	0.27
C≡N	−17.35	−17.68	−21.95	−21.91
H[b]	−5.78	−5.56		
COOH	−44.02	−44.67		
COO	−10.56	−11.17		
Cl	−12.55	−12.47	−14.35	−14.18
Br			−17.31	−17.17
NO_2	−18.74	−20.17	−19.44	−22.05
CH_2=CH			−11.87	−11.67
CH≡C			−14.69	−14.49
C≡C			−12.75	−12.50
5-Member ring[c]	−10.49	−9.68	−8.94	−9.16
6-Member ring[c]	−8.01	−6.99	−6.81	−6.65
σ[d]	1.37	2.96	1.59	3.78

[a] All data in kJ mol^{-1}. Group contributions calculated from data of Table 2 using the methods M1 and M2 (see text).

[b] Hydrogen atom of formic acid and formate esters.

[c] Correction term for cyclic structures.

[d] Standard deviation of the group contributions analysis.

term *A* was calculated from *n*-alkanes as the mean value of the difference between the experimental quantity and the sum of the contributions of alkyl groups. Finally, the contributions of polar groups were estimated by the differences between the values of the property and the contribution of alkyl chain including the constant *A*. Correction terms for five- and six-membered rings were also estimated by difference. The B_j value for CH_{ar} group was calculated as 1/6 of the solvation enthalpy for benzene diminished by the constant term *A*, whereas the C_{ar} group was evaluated by assuming a proportionality criterion based on the ratio of its surface area to that of the CH_{ar} group.

Table 3 reports the results of the calculations of the group contributions to the enthalpies of solvation in 1-OCT and DBE performed by methods M1 and M2 and the overall standard deviations, σ, of the analysis. In both solvents the σ values obtained by applying the method M2 are more than twice those obtained by the method M1. Moreover, the standard deviations obtained by both methods in DBE are slightly larger than those in 1-OCT reflecting the different number of compounds in the dataset. The standard deviations on the contributions are usually lower than 6% of the value of the contribution itself and can be as low as 0.1 kJ mol^{-1} for the contribution of CH_2 group in both solvents. Only in case of contributions of the groups related to branched or cyclic structures the uncertainties can be significantly higher.

It can be observed that in each solvent the values of most parameters are quite similar independently of the method of calculation. Only the contributions of CH, C and C_{ar} groups significantly differ in the two cases. In particular the contribution of the tetrasubstituted carbon atom, whose value is null by definition in method M2,[1] becomes as large as 5.95 and 5.88 kJ mol^{-1} in 1-OCT and DBE, respectively, when calculated by regression analysis (method M1). In this regard we want to emphasize that the method M2 interprets the enthalpic effects of the alkyl chains only in terms of surface area exposed to the solvent. This hypothesis is reasonably founded when the interactions between the alkyl chains of the solutes and the solvent are prevailingly dispersive and no significant rearrangement of the solvent molecules induced by the apolar groups of the solute take place (hydrophobic interactions). However, also in these cases packing effects, not accounted for by method M2, can affect significantly the values of the solvation enthalpy. On the contrary, the method M1, not constraining the values of alkyl contributions to each other, includes these effects in the contributions of CH and C groups (as well as in the C_{ar} group in aromatic compounds). This observation can be supported by comparing the residuals between the experimental enthalpies of solvation and the corresponding values calculated by Eq. (1) using the B_j values determined by the methods M1 and M2 (see Δ values of Table 2). It can be noticed that the method M2 displays clearly lower Δ residuals than method M1 in case of linear compounds, while the contrary occurs when branched compounds are considered.

A further noteworthy observation emerging from the Δ values of Table 2 concerns the benzene derivative carrying a functional polar group. In these cases the residuals are quite large independent of the method of calculation. This suggests that distinct specific contributions should be defined for polar groups when attached to the aromatic ring. Other authors already suggested the use of different B_j values for polar groups according to whether they are bonded to aliphatic or aromatic structures [5].

As a general remark the choice of a specific group contributions model for the prediction of the enthalpies of solvation, or of any other thermodynamic property, should be directed by the following criteria. Method M1, i.e. a fully empirical determination of all group contributions through regression analysis, is to be recommended when the main goal is the minimum uncertainty in the property prediction. It requires, however, a very large set of experimental data in which both straight chain and branched

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[1] The null value of the C group contribution is due to the intrinsic van der Waals surface area of the tetrasubstituted carbon atom assumed null by Bondi [56].

molecules should be statistically represented. Method M2, which assumes surface-dependent interactions of hydrocarbon groups with the solvent, provides reliable predictions only in case of linear compounds, but can be successfully employed when one is interested in the analysis of the nature of the interactions between a given solvent and the different fragments of the solute molecules. To this purpose the contributions of Table 3, independently of the method of calculation, allow to recognise that the hydrocarbon portions of the solutes interact similarly with 1-OCT and DBE, whereas polar groups are involved in specific interactions with the two solvents. The solvent 1-OCT, due to its amphiphilic nature, shows the strongest ability to interact with hydrogen bond donor groups (OH, NH_2, NH) and exhibits a higher ability to stabilise cyclic structures with respect to DBE. The latter shows the highest affinity towards highly polarisable groups carrying π- and n-electron pairs (O, CN, Cl).

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