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ENTHALPIES OF SOLUTION AND INTERMOLECULAR FORCES. *tert*-BUTYL HALIDES IN HYDROXYLIC SOLVENTS

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The application of cavity theories of solution and linear solvation energy relationships to the interpretation of enthalpy of solution values of *tert*-butyl halides in hydroxylic media, measured at 25 °C and infinite dilution, is deserted, in order to define the intermolecular forces acting between solutes and solvents. It is concluded that solvent dipolarity and solvent HBD acidity effects dominate the solution process. An empirical equation relating the enthalpies of solution with selected properties of both solvents and solutes is proposed. New experimental ΔH_s^∞ values for *tert*-butyl iodide in 13 alcohols are reported.

INTRODUCTION

A key problem in physical organic chemistry is the quantitative consideration of solvent effects on thermodynamic data concerning equilibrium, kinetics and thermochemical phenomena. Thermodynamic solution data can be treated by means of a cavity theory of solution. The model underlying the solution process can be envisaged as being composed of several stages: the creation of a cavity of suitable size to accommodate the solute molecules, the reorganization of the solvent molecules around the cavity and the introduction of the solute into the cavity to set up various solvent–solute interactions. In this context, several methods for calculating the energetics of cavity formation in liquids have been advanced which provide the possibility of obtaining solvent–solute interaction energies.[1,2]

Recently, we proposed an alternative method, based on a new formulation of the reference cavity formation process, which allows a consistent description of the dissolution process from a thermodynamic point of view.[3] Thermochemical results can also be treated in terms of linear solvation energy relationship analysis, which splits the solvent effect into separate contributions corresponding to different types of solute–solvent–solvent interaction mechanisms:[4] long-range intermolecular forces, specific solvation interactions and solvent–solvent interactions due to the cavity effect.[4–7] In a previous paper we discussed the enthalpies of solution, ΔH_s^∞, of 2-chloro-2-methylpropane (*t*-BuCl) in water and several alcohols by means of the application of cavity theories of solution.[8] Later, a linear solvation energy relationship was successfully applied to ΔH_s^∞ data for *t*-BuCl and *t*-BuBr in water and 13 monoalcohols.[9]

In this paper we present new experimentally obtained enthalpies of solution values for 2-iodo-2-methylpropane in 14 hydroxylic solvents at 25 °C and infinite dilution. We used our new method and the scaled particle theory (SPT) to estimate the cavity enthalpies, H_c, of *t*-BuX (X = halogen) in the different solvents and these values are compared and discussed. Moreover, H_c values were used to obtain the enthalpy of interaction, H_i, according to the equation

$$H_i = \Delta H_s^\infty - \Delta H_{vap} - H_c \qquad (1)$$

where ΔH_{vap} is the solute vaporization enthalpy at 25 °C. The H_i values from both models are also compared and discussed. Using appropriate solvent parameters, multiple regression analysis was applied to ΔH_s^∞ data, which reveals significant information about the dominant solute–solvent–solvent interaction mechanisms.

We obtained a common relationship to relate ΔH_s^∞

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and selected properties of both solvents and solutes, making use of a step by step procedure and least-squares multiple regression, similar to that performed by Glikberg and Marcus.[10] The ultimate aim of such a treatment is to permit the prediction of enthalpies of solution from known solvent and solute properties.

EXPERIMENTAL

The general calorimetric technique and instrumentation for obtaining ΔH_s^∞ values were described previously in detail.[8,11] The rate of the heat evolution was linear during the electrical calibration and exponential during the solution process. The corrected temperature change was obtained by the graphical extrapolation method of Dickinson.[12] The concentration of the solute ranged from 0·01 to about 0·04 mol dm^{-3}. The ΔH_s^∞ values obtained are effectively partial molar heats of solution at infinite dilution, as shown by our ability to break three to five ampoules of the solute into the same solution without producing any change in the measurements outside experimental error. At least two independent runs were performed and the results are the mean values of the calorimetric experiments.

The alcohols were obtained from BDH and Merck. They were dried over molecular sieves and their purity was established by gas chromatography and infrared spectrometry. The water content was kept lower than 0·02%; however, traces of water do not cause significant errors in the measurements. *t*-BuI was obtained from BDH and Fluka. It was distilled under reduced pressure and copper wire was added to stabilize the material during storage in dark flasks at temperatures below 5 °C.

RESULTS AND DISCUSSION

The experimental ΔH_s^∞ values are summarized in Table 1 together with previously obtained data. The solution enthalpy of *t*-BuCl in water, extrapolated from Arnett *et al.*'s data for water–ethanol mixtures,[14] is also included, together with the corresponding solution enthalpies of *t*-BuBr and *t*-BuI estimated from the following good linear correlations using the alcoholic solvents (Figure 1):

$$\Delta H_s^\infty(t\text{-BuBr}) = 0{\cdot}23397 + 1{\cdot}0361\Delta H_s^\infty(t\text{-BuCl}) \qquad (r = 0{\cdot}994;\ \sigma = 0{\cdot}19;\ N = 13) \tag{2}$$

and

$$\Delta H_s^\infty(t\text{-BuI}) = 0{\cdot}26825 + 1{\cdot}0766\Delta H_s^\infty(t\text{-BuCl}) \qquad (r = 0{\cdot}987;\ \sigma = 0{\cdot}29;\ N = 13) \tag{3}$$

where σ is the standard deviation of the fit and N is the number of pairs of ΔH_s^∞ values.

The solvation enthalpies at 25 °C, $\Delta H_{\text{solv}}^\infty$, are also listed in Table 1 and were obtained by subtracting the enthalpies of vaporization of the solutes (Table 2) from the solution enthalpies.

Application of cavity theories of solution

In the study of solvent effects, the calculation of the energetics of cavity formation makes it possible to obtain the solute–solvent interaction energy.[20] This enables us to separate the different contributions to the thermodynamic solution parameters and to interpret the observed solvent effects in terms of the molecular characteristics of the species involved. It has been

Table 1. ΔH_s^∞ and $\Delta H_{\text{solv}}^\infty$ values (kJ mol^{-1}) of *tert*-butyl halides in water and alcohols at 25 °C

		t-BuCl[a]		*t*-BuBr[a]		*t*-BuI	
No.	Solvent	ΔH_s^∞	$-\Delta H_{\text{solv}}^\infty$	ΔH_s^∞	$-\Delta H_{\text{solv}}^\infty$	ΔH_s^∞	$-\Delta H_{\text{solv}}^\infty$
1	Water	1·05[b]	27·93	1·32	30·49	1·40	34·15
2	Methanol	1·56	27·42	2·20	29·61	2·61	32·80
3	Ethanol	1·50	27·48	1·75	30·06	1·80	33·61
4	Propan-1-ol	1·62	27·36	2·00	29·81	2·04	33·37
5	Propan-2-ol	3·57	25·41	4·12	27·69	4·37	31·04
6	Butan-1-ol	2·10	26·88	2·37	29·44	2·52	32·89
7	Butan-2-ol	5·11	23·87	5·57	26·24	5·80	29·61
8	2-Methylpropan-1-ol	3·09	25·89	3·36	28·45	3·39	32·02
9	2-Methylpropan-2-ol	6·32[c]	22·66[c]	7·26[c]	24·55[c]	7·53[c]	27·88[c]
10	Pentan-1-ol	2·56	26·42	2·62	29·19	2·60	32·81
11	Pentan-2-ol	5·26	23·72	5·43	26·38	5·77	29·64
12	2-Methylbutan-1-ol	3·78	25·20	4·12	27·69	4·06	31·35
13	2-Methylbutan-2-ol	4·78	24·20	5·19	26·62	5·59	29·82
14	3-Methylbutan-1-ol	2·80	26·18	2·95	28·86	3·09	32·32

[a] ΔH_s^∞ values are from Refs 8, 9, 11 and 13.
[b] Extrapolated from Ref. 14.
[c] Values at 27 °C.

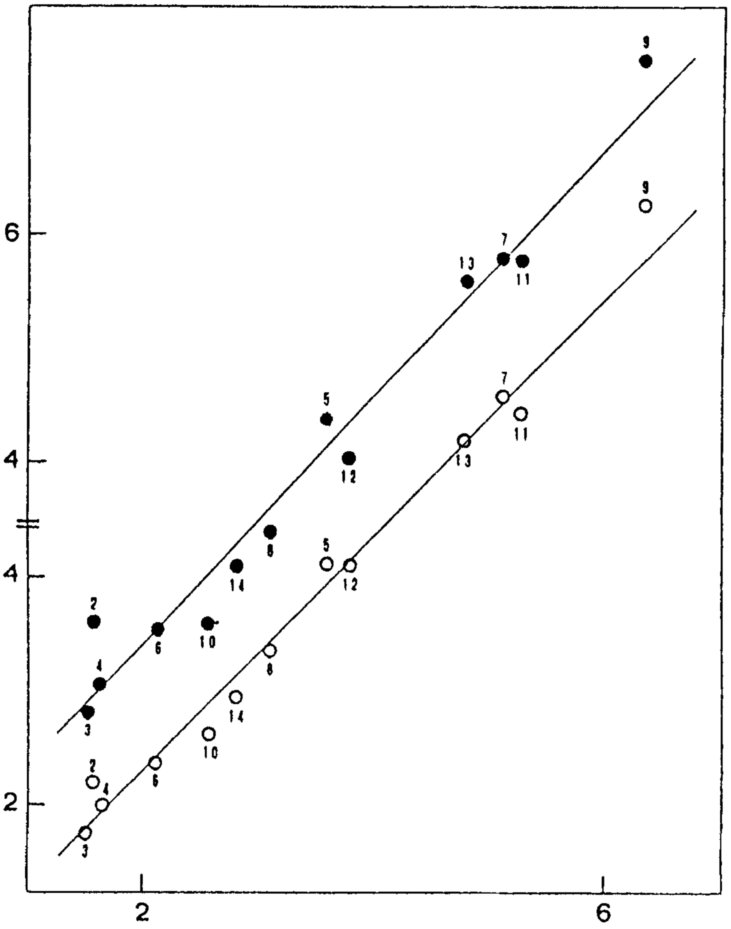

Figure 1. Plot of (○) ΔH_{s}^{∞} (*t*-BuBr) and (•) ΔH_{s}^{∞} (*t*-BuI) against ΔH_{s}^{∞} (*t*-BuCl) (kJ mol^{-1}). The numbers refer to the solvents listed in Table 1

Table 2. Selected properties and molecular parameters of *tert*-butyl halides at 25 °C

Solute	ΔH_{vap} (kJ mol^{-1})	Ref.	V_2 (cm^{3}mol^{-1})	Ref.	σ_2 (Å)[a]	μ (D)	Ref.
t-BuCl	28·98	15	109·9	16	5·67	2·14	17
t-BuBr	31·81	15	112·2	16	5·71	2·21	18
t-BuI	35·41	15	119·1	16	5·83	2·20	18

[a] Calculated from Stearn and Eyring's expression.[19]

emphasized by many workers[8,20–22] that the different models available in the literature for calculating the energetics of cavity formation in liquids lead to results which differ considerably and may even lead to opposite interpretations. Recently we reinvestigated this problem and proposed a new method for calculating the cavitation energetics.[3] This method was checked by applying it to different problems, namely, to the interpretation of the solution enthalpies and Gibbs energies in binary mixtures of alkanes at infinite dilution,[3] to the analysis of the solvent effect on the solvolysis of *tert*-butyl chloride[3] and to the study of the interactions of rare gas solutes with *n*-alkane solvents.[23]

The method of calculation of the enthalpy of cavity formation has been described elsewhere:[3]

$$H_c(\mathrm{J\ mol^{-1}}) = 40\cdot 84\ \gamma_0 A_0 (V^{2/3} - V_0^{2/3}) + H_{c_0} \quad (4)$$

where γ_0 is the solvent surface tension (dyn cm^{-1}), V and V_0 are the solute and the solvent molar volumes (cm^3 mol^{-1}), respectively, H_{c_0} is the enthalpy of the reference cavity (J mol^{-1}) and A_0 is an adimensional quantity given by

$$A_0 = 1 - T\left(\frac{1}{\gamma_0}\frac{d\gamma_0}{dT} + \frac{2}{3}\alpha_0\right) \quad (4a)$$

where α_0 is the isobaric thermal expansion coefficient of the solvent. In equation (4) it is implicitly considered that the surface tension at the surface of the microscopic spherical cavities depends on the surface curvature.[24] According to our model, the enthalpy of the reference cavity, H_{c_0}, can be calculated by the following equation:

$$H_{c_0} = 5\cdot 365(1 + \omega)RT_c \quad (5)$$

where ω is the Pitzer acentric factor and T_c is the critical temperature (K).

Tables 2 and 3 present the solute and solvent properties needed for the calculations. In order to obtain a consistent set of data, the hard sphere diameters of the solvents, σ_1, were deduced from de Ligny's equation:[27]

$$\frac{1}{6}\pi N\sigma_1^3 = -10 + 1\cdot 13V_\omega \quad (6)$$

where V_ω is Bondi's van der Waals volume[28] according to Treiner's proposal.[29] For this reason, some of the values listed in Table 3 are slightly different from those presented previously.[7]

Table 4 shows the enthalpies of cavitation, H_c, for *t*-BuX solutes in alcohols and water. The H_c values were calculated from equations (4) and (5) (top row in each instance) and from the SPT (bottom row). Qualitatively we expect that, for a given solute, it will be more difficult (more endothermic) to create the cavity in a primary than in a tertiary alcohol since the cohesive energy density is higher in the former. The H_c value for a secondary alcohol is expected to have an intermediate value. This behaviour is observed for H_c values calculated by our method (top rows) but an opposite behaviour is found for H_c values calculated by the SPT method (bottom rows). Water has a very high cohesive energy density, so we expect high H_c values in this solvent, particularly if we remember that the solute size (*ca* 110 cm^3 mol^{-1}) is large compared with the water molar volume and with the dimensions of the holes which are present in the water open structure. The very low H_c values obtained from SPT in water seem not to be

Table 3. Selected properties and molecular parameters of water and alcohols at 25 °C

No.	Solvent	V_1 (cm^3 mol^{-1})[a]	σ_1 (Å)[b]	$10^3\alpha$ (K^{-1})[c]	γ (dyn cm^{-1})[d]	$-d\gamma/dT$ (dyn cm^{-1} K^{-1})[e]	A[f]	ω[g]	T_c (K)[h]
1	Water	18·07	2·77	0·257	71·97	0·155	1·5910	0·344	647·3
2	Methanol	40·74	3·59	1·195	22·20	0·086	1·9175	0·556	512·6
3	Ethanol	58·69	4·35	1·093	21·85	0·084	1·9290	0·644	513·9
4	Propan-1-ol	75·17	4·92	0·995	23·30	0·081	1·8387	0·623	536·8
5	Propan-2-ol	76·96	4·92	1·064	21·24	0·055	1·5606	0·665	508·3
6	Butan-1-ol	91·99	5·38	0·932	24·16	0·082	1·7500	0·593	563·1
7	Butan-2-ol	92·35	5·38	0·910	23·05	0·085	1·9186	0·577	536·1
8	2-Methylpropan-1-ol	92·88	5·38	0·950	22·55	0·087	1·9615	0·592	547·8
9	2-Methylpropan-2-ol	97·76	5·38	1·335	20·02	0·102	2·2537	0·612	506·2
10	Pentan-1-ol	108·72	5·78	0·893	25·16	0·088	1·8653	0·579	588·2
11	Pentan-2-ol	109·45	5·78	0·970	23·47	0·102	2·1029	0·602[i]	558·3[k]
12	2-Methylbutan-1-ol	108·16	5·78	1·000	25·1	0·09	1·8703	0·549[j]	571·0
13	2-Methylbutan-2-ol	109·50	5·78	1·330	22·31	0·093	1·9785	0·497[j]	545·0
14	3-Methylbutan-1-ol	109·22	5·78	0·920	23·88	0·089	1·9283	0·583[i]	579·4

[a] Molar volume from Refs 25 and 26.
[b] Hard sphere diameter calculated from values in Refs 27–29.
[c] Isobaric thermal expansion coefficient from Refs 25, 26 and 30.
[d] Surface tension from Ref. 26.
[e] From Ref. 26.
[f] Calculated from equation (4a).
[g] Pitzer acentric factor from Ref. 31 unless stated otherwise.
[h] Critical temperature from Ref. 31 unless stated otherwise.
[i] Predicted by the method proposed in Ref. 3.
[j] Calculated from the saturated vapour pressure given in Ref. 26.
[k] Predicted by the Ambrose method (see Ref. 31).

Table 4. H_c and H_i values (kJ mol^{-1}) of *tert*-butyl halides in water and alcohols at 25 °C calculated using equations (4) and (5) (top rows) and the SPT method (bottom rows)

		Solute					
		t-BuCl		*t*-BuBr		*t*-BuI	
No.	Solvent	H_c	$-H_i$	H_c	$-H_i$	H_c	$-H_i$
1	Water	113·90	139·54	115·39	143·70	119·81	151·67
		7·401	33·04	7·496	35·81	7·786	39·65
2	Methanol	54·88	80·70	55·44	83·45	57·08	88·28
		19·49	45·31	19·74	47·75	20·47	51·67
3	Ethanol	51·18	76·99	51·73	80·12	53·36	85·30
		24·91	50·72	25·23	53·62	26·17	58·11
4	Propan-1-ol	47·84	73·46	48·40	76·47	50·05	81·68
		29·17	54·79	29·54	57·61	30·65	62·28
5	Propan-2-ol	44·32	68·04	44·75	70·75	46·03	75·38
		28·32	52·04	28·68	54·68	29·75	59·10
6	Butan-1-ol	44·44	69·53	44·99	72·64	46·63	77·73
		31·15	56·24	31·54	59·19	32·73	63·83
7	Butan-2-ol	42·25	64·31	42·82	67·25	44·53	72·33
		29·87	51·93	30·25	54·68	31·39	59·19
8	2-Methylpropan-1-ol	43·29	67·40	43·87	70·54	45·57	75·81
		30·38	54·49	30·77	57·44	31·92	62·16
9	2-Methylpropan-2-ol	39·57	60·74	40·16	63·22	41·90	68·29
		34·18	55·35	34·60	57·66	35·89	62·28
10	Pentan-1-ol	41·74	66·34	42·35	69·72	44·16	75·15
		33·04	57·64	33·46	60·83	34·72	65·71
11	Pentan-2-ol	40·02	61·98	40·67	65·29	42·57	70·45
		34·73	56·69	35·16	59·78	36·49	64·37
12	2-Methylbutan-1-ol	39·92	63·38	40·53	66·48	42·34	71·95
		37·97	61·43	38·45	64·40	39·90	69·51
13	2-Methylbutan-2-ol	36·49	59·19	37·07	62·19	38·77	67·09
		47·51	70·21	48·11	73·23	49·92	78·24
14	3-Methylbutan-1-ol	41·09	65·47	41·66	68·72	43·47	73·99
		33·28	57·66	33·70	60·76	34·97	65·49

physically acceptable. On the other hand, when the dimensions of the solute cavity are not very different from the molecular dimensions of the solvent, the H_c values must be near the reference cavity enthalpy H_{c_0}, and this is not very far from the solvent vaporization enthalpy. In this context we can consider that the H_c values in Table 4 calculated by the SPT method are exceedingly low.

Table 4 also gives the solute–solvent interaction enthalpies, H_i, for the same systems. These halide solute molecules are able to interact with the solvent via dipolar interactions (Keesom and Debye) and specific interactions involving the hydroxylic protons of the alcohols and the lone electron pairs of the solute. In primary alcohols the hydroxylic group is free to participate in those interactions since it is not sterically hindered. In a tertiary alcohol such as 2-methylpropan-2-ol or 2-methylbutan-2-ol, in contrast, there is a steric hindrance which partially prevents those interactions. We therefore expect the interaction of a given solute with a primary alcohol to be more exothermic than that with a corresponding tertiary alcohol. A secondary alcohol is expected to show an intermediate behaviour. From Table 4 we may conclude that this is the observed behaviour of the H_i values calculated from our cavity model (top rows) but not of H_i values obtained from the SPT method. This discussion provides sufficient evidence to conclude that our cavity model is more reliable than that based on SPT. A similar conclusion was reached in previous work.[3,23]

Application of linear solvation energy relationships

One of the most important attempts to express solvent effects quantitatively involves different solvent parameter scales and multiparameter treatments. In spite of the criticisms about the additive contribution hypothesis of solvent effects and the choices of the best empirical parameters and the statistically preferred equation, there is no doubt that linear solvation energy relationships can provide a sound interpretation of the observed phenomena and can predict thermodynamic properties from solvent properties. A general formulation of this problem, however, should not avoid the simultaneous treatment of solvent and solute effects. Although it is not known how both effects are interrelated, some studies have been made on this aspect.[10,32,33]

Correlations of ΔH_s^∞ of *t*-BuX in the 14 hydroxylic solvents listed in Table 1 were attempted using the general equation[34]

$$\Delta H_s^\infty = a_0 + a_1 f(\varepsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 C \tag{7}$$

where $f(\varepsilon)$ is the dielectric Kirkwood function, $g(\eta)$ is the refractive index function $(\eta^2 - 1)/(\eta^2 + 2)$, E_T^N is the normalized parameter of Dimroth and Reichardt[35–37] and C is the cohesive energy density.[38,39]

The set of chosen parameters is in agreement with the physico-chemical model of the solution process already described and shows only moderate colinearity.* The values of the empirical parameters of solvent polarity used in this analysis are listed in Table 5. The application of equation (7) to the enthalpies of solution was performed as described in a previous paper.[9] The criterion for the inclusion of a solvent property in the regression was its correlation with the dependent variable, ΔH_s^∞, or with the residuals when some variables have already been included. Ehrenson's criterion[42] for relative fitting to a more restricted equation form was used to give the best statistical equations. Thus, the most meaningful dependences of ΔH_s^∞ for the three halides are

$$\Delta H_s^\infty(t\text{-BuCl}) = -3{\cdot}1341 + 39{\cdot}461\, f(\varepsilon) - 24{\cdot}6278\, E_T^N + 4{\cdot}1228 \times 10^{-3} C \tag{8}$$

$$(r = 0{\cdot}948;\ \sigma = 0{\cdot}61;\ N = 14)$$

$$\Delta H_s^\infty(t\text{-BuBr}) = -3{\cdot}6245 + 42{\cdot}607\, f(\varepsilon) - 25{\cdot}947\, E_T^N + 4{\cdot}3913 \times 10^{-3} C \tag{9}$$

$$(r = 0{\cdot}942;\ \sigma = 0{\cdot}67;\ N = 14)$$

$$\Delta H_s^\infty(t\text{-BuI}) = -2{\cdot}6796 + 41{\cdot}147\, f(\varepsilon) - 26{\cdot}261\, E_T^N + 4{\cdot}4864 \times 10^{-3} C \tag{10}$$

$$(r = 0{\cdot}925;\ \sigma = 0{\cdot}79;\ N = 14)$$

It should be pointed out that the optimum correlation for each halide is also the best correlation according to a common model for all the halides.

We may than describe the solution process of *tert*-butyl halides in water and alcohols as being dominated by the non-specific interactions coming from the polarization of the solvent, the specific solvent hydrogen bond acidity interactions and the solvent–solvent interactions on account of the solute cavity effect.

In order to relate the experimental ΔH_s^∞ values to the properties of the solvents and of the solutes simultaneously, we decided to adopt a method similar to that described by Glikberg and Marcus.[10] First, the enthalpies of solution values are submitted to a multiple regression analysis in terms of solvent parameters to select the properties that are statistically relevant. This is exactly what we have done so far [equations (8) to

Table 5. Empirical parameters of solvent polarity[a]

No.	Solvent	$f(\varepsilon)$	$g(\eta)$	E_T^N	$10^{-3}C$(MPa)
1	Water	0·49048	0·20569	1·000	2·307
2	Methanol	0·47738	0·20311	0·762	0·887
3	Ethanol	0·47006	0·22147	0·654	0·703
4	Propan-1-ol	0·46420	0·23467	0·617	0·590
5	Propan-2-ol	0·46327	0·23011	0·546	0·552
6	Butan-1-ol	0·45836	0·24210	0·602	0·485
7	Butan-2-ol	0·45604	0·24087	0·506	0·488
8	2-Methylpropan-1-ol	0·45931	0·24023	0·552	0·516
9	2-Methylpropan-2-ol	0·44219	0·23581	0·389	0·467
10	Pentan-1-ol	0·44792	0·24776	0·568	0·497
11	Pentan-2-ol	0·44722	0·24584	0·488	0·465
12	2-Methylbutan-1-ol	0·45350[b]	0·24712[b]	0·534[c]	0·482[d]
13	2-Methylbutan-2-ol	0·35669	0·24510	0·321	0·443
14	3-Methylbutan-1-ol	0·45220[e]	0·24627[e]	0·565[e]	0·497[d]

[a] Values from Ref. 9 except where indicated otherwise.
[b] Value from Ref. 40.
[c] Value from $E_T(30)$ in Ref. 41.
[d] Value from ΔH_{vap} at 25 °C in Ref. 26.
[e] Value from Ref. 7.

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* A high correlation coefficient, $r = 0{\cdot}857$, was found for the E_T^N–C linear relationship. However, smaller r values were found for other sets of solvents,[34] which questions the existence of a close relationship from a physico-chemical point of view.[10]

(10)]. Second, the regression coefficients of that analysis are submitted to single regressions in terms of solute properties in order to identify the relevant interdependences. A common model is then obtained relating all studied solvents and solutes.

The explanatory variables selected in the first step are checked after the second step to see if their presence is statistically still warranted. The statistical criterion of Ehrenson[42] was used again to terminate this procedure.

The values of the considered solute properties, the molar volume V_2 and the dipole moment μ, are listed in Table 2. These two variables do not show any significant collinearity. The best dependence of ΔH_s^∞ on the properties of the solvents and of the solutes simultaneously is then

$$\begin{aligned}\Delta H_s^\infty = {} & -6{\cdot}4179 - 11{\cdot}380\,f(\varepsilon) + 1{\cdot}3995\,E_T^N \\ & + 2{\cdot}2516 \times 10^{-3} C \\ & + 3{\cdot}0320 \times 10^{-2} V_2 \\ & + [23{\cdot}709\,f(\varepsilon) - 12{\cdot}238\,E_T^N \\ & + 0{\cdot}92701 \times 10^{-3} C]\mu \qquad (12)\end{aligned}$$

$$(r = 0{\cdot}938;\ \sigma = 0{\cdot}65;\ N = 42)$$

The fit achieved with these final parameters is shown in Figure 2, where the calculated ΔH_s^∞ values from equation (12) are plotted against the experimental data from Table 1. The continuous straight line corresponds to a perfect fit. Only methanol shows a strong deviation from the perfect fit; we have no simple explanation for this behaviour.

CONCLUSIONS

In the study of solvent effects on chemical processes, two different semi-empirical approaches are of great value, the cavity theories of solution and the linear solvation energy relationships. The correct utilization of a cavity model in the study of binary mixtures at infinite dilution gives information about the energetics of cavity formation and allows the interaction term to be obtained, which enables us to interpret the observed solvent effect in terms of the molecular characteristics of the species involved. Thus, the H_i values for *t*-BuX in hydroxylic solvents were discussed on the basis of dipolar solute–solvent interactions and specific interactions involving the hydroxylic protons of water and alcohols and the lone electron pairs of the solutes. The application of correlation analysis to the solution enthalpies of *t*-BuX also reveals important information on the solvent–solvent–solute interactions which dominate the solution process. The experimental ΔH_s^∞ values reflect not only the direct interactions of solute and solvent, but also the accompanying changes in solvent–solvent interactions. The solvent properties chosen to perform the multiparameter procedure lead us to conclude that the solution enthalpies are sensitive to the solute–solvent and solvent–solvent polarity effects and to the ability of the solvents to act as Lewis acids, in a close agreement with the conclusions drawn from the physical approach.[7,34]

It is relevant that we were able to reach similar inter-

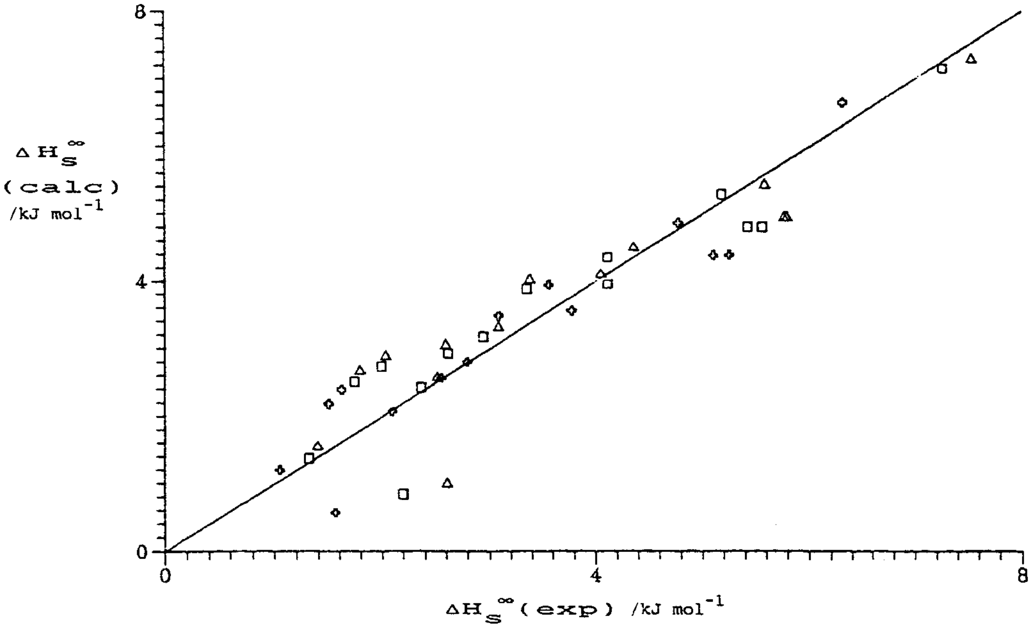

Figure 2. Plot of ΔH_s^∞ calculated according to equation (12) against the experimental ΔH_s^∞ values. (+) *t*-BuCl; (□) *t*-BuBr; (△) *t*-BuI

pretations of the solution enthalpy values of *tert*-butyl halides in hydroxylic solvents using two different methods, one based on the application of the cavity theories of solution and the other based on linear solvation energy relationships.

Finally, a statistical treatment of data was made in terms of the properties of the solvents and the solutes simultaneously.[10,43] The proposed empirical equation permits the prediction of new ΔH_s^{∞} values from known solvent and solute properties, provided that the interaction mechanisms are similar in nature.

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