

LINEAR ENERGY RELATIONSHIPS AND SOLVENT EFFECTS  
FOR THE SOLUTION OF tert-BUTYL CHLORIDE AND BROMIDE  
IN WATER AND ALCOHOLS

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SUMMARY

Solvent effects on the enthalpies of solution of t-BuCl and t-BuBr in water and 13 monoalcohols, from 1 to 5 carbon atoms, are analysed in terms of linear solvation energy relationships. The experimental data, at 25 °C and infinite dilution, are well correlated through equations of the type,

$$\Delta_s H^\infty = a_0 + a_1 f(\epsilon) + a_2 E_T^N + a_3 C$$

where  $f(\epsilon)$  is the Kirkwood function of the dielectric constant,  $E_T^N$  is the normalized Dimroth and Reichardt parameter and  $C$  is the solvent cohesive energy. Pertinent information on the dominant solvent-solvent-solute interactions is obtained.

KEY WORDS : Linear energy relationships; enthalpies of solution; t-BuCl and t-BuBr; water and alcohols; Kirkwood function,  $E_T$  and cohesive energy parameters.

## INTRODUCTION

The study of solvent effects may receive a fundamental support by the knowledge of thermodynamic functions of solution and the nature of the various solvent-solvent-solute interaction mechanisms acting in a solution process can be revealed by constructing physico-chemical models.<sup>1</sup> In essence, there are two types of interaction between solvent and solute, arising from nonspecific and specific intermolecular forces. The concept of nonspecific, long-range, solvent-solute interactions includes various types of electrostatic, induction, or dispersion interactions, which depend on the static or induced distribution of charges of the solute molecule and on the polarity and polarizability of the solvent. The short-range, specific, solvent-solute interactions are mainly the formation of donor-acceptor bonds between molecules, the most important manifestation being connected with the behaviour of protic acids as Lewis acids, when hydrogen-bonded structures are involved,<sup>2,3</sup> as it is the case when water and alcohols are used as solvents. The more sophisticated models take also into consideration the solvent-solvent interactions, due to the cavity effect.<sup>4</sup> A general way of treating solvent effects on chemical phenomena makes use of empirical solvent parameters and multiple linear solvation energy relationships.<sup>2-5</sup>

In this work we applied linear solvation energy relationships to the enthalpies of solution values, at 25 °C and infinite dilution, of tert-butyl halides, t-BuCl and

t-BuBr, in hydroxylic media using water and straight and branched chain monoalcohols as solvents. The results are interpreted according to the chosen empirical parameters (dielectric constant, refractive index, and Dimroth and Reichardt and cohesive energy parameters) to perform this analysis.

## EXPERIMENTAL

The enthalpies of solution at infinite dilution and at 25 °C of both 2-halogen-2-methylpropane (t-BuCl and t-BuBr) in 2-methyl-1-butanol and 3-methyl-1-butanol were obtained by a calorimetric technique as previously described.<sup>6,7</sup> The rate of the heat evolution was linear during the electrical calibration and exponential during the solution process. The corrected temperature change was obtained using the Dickinson's method.

The alcohols were from BDH and Merck (min. 99.5%) and the tert-butyl halides from BDH (min. 99%).

The regression coefficients,  $a_0$  and  $a_j$ , standard deviations,  $\sigma$ , and correlation coefficients,  $r$ , of the regression analysis were calculated using a program run in a IBM compatible computer. The equations used for  $\sigma$  and  $r$  are as follows:<sup>8</sup>

$$\sigma = (N-n-1)^{-1} \sum_{i=1}^N (y_i - a_0 - \sum_{j=1}^n a_j x_{ij})^2$$

$$r^2 = \frac{\sum_{j=1}^n (a_j s_j r_{jY} / s_Y)}{\sum_{j=1}^n (a_j s_j r_{jY} / s_Y)}$$

where  $r_{jY} = s_{jY}^2 / s_j s_Y$ .

## RESULTS AND DISCUSSION

Correlations of the solution enthalpies at infinite dilution,  $\Delta_s H^\infty$ , of *t*-BuCl and *t*-BuBr in water and straight and branched monoalcohols, from 1 to 5 carbon atoms, with specific and nonspecific solvent parameters, chosen according to the set of studied solvents and a suitable physico-chemical model of the solution process, were attempted using the general equation:

$$[1] \quad \Delta_s H^\infty = a_0 + a_1 f(\epsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 C$$

In this equation,  $f(\epsilon)$  is the dielectric Kirkwood function  $(\epsilon-1)/(2\epsilon+1)$  which, following the classical dielectric theories, measures the solvent polarization and  $g(\eta)$  is the refractive index function  $(\eta^2-1)/(\eta^2+2)$  representing the polarizability of the solvent.  $E_T^N$  is the normalized  $E_T(30)$  parameter, first proposed by Dimroth, Reichardt *et al.*,<sup>9</sup> using water and tetramethylsilane as references. The inclusion of  $E_T^N$  in equation [1] is in agreement with the assumption that this parameter is a measure of the solvent hydrogen-bond acidity of protic solvents.<sup>3</sup> Finally,  $C$  is the cohesive energy,<sup>10</sup> originally defined in terms of the molecular cohesive energy ( $-E$ ) per unit volume,  $C = -E/V$ . At temperatures below the normal boiling point  $-E \approx \Delta_v U$ , and assuming ideal gas behaviour  $-E \approx \Delta_v H - RT$ . Thus,  $C$  may be evaluated from the molar vaporization energy,  $\Delta_v H$ , at the temperature required (usually 25 °C):

$$[2] \quad C = (\Delta_v H - RT)/V = \delta_H^2$$

where  $\delta_H$  is the solubility parameter of Hildebrand and Scott.<sup>11</sup>  $C$  is a solvent property which measures the work necessary to separate the solvent molecules to create a suitable sized cavity, large enough to accommodate the solute. Therefore, highly ordered self-associated solvents, as the water and the lower carbon chain alcohols, exhibit relatively large  $C$  values.

The physico-chemical model underlying the proposed procedure, and used to connect the macroscopic solvent parameters and the microscopic details of the solution process, is identical to that used before to correlate rate constants of *tert*-butyl halides solvolysis.<sup>12,13</sup>

Table I gives the solution enthalpies of *tert*-butyl halides in water and alcohols, at 25 °C and infinite dilution, previously obtained,<sup>6,7,14-16</sup> together with the new results in 2-methyl-1-butanol and 3-methyl-1-butanol, using the same experimental conditions. An estimated value for the enthalpy of solution of *t*-BuBr in water (Table I) was included in the expectation that comparisons amongst the two sets of enthalpies of solution would be statistically more valid if they involved the same solvent set.

A compilation of self-consistent sets of  $f(\epsilon)$ ,  $g(\eta)$ ,  $E_T^N$  and  $C$  values used in this work are in Table II.

One of the most important features that a multiparameter equation must obey is the noncollinearity of the chosen parameters. In order to prove this assumption for equation [1], a critical comparison between any two parameters was performed. The results are shown in Table III.

Table I. Enthalpies of solution at infinite dilution of tert-butyl halides in water and alcohols, at 25°C

SOLVENT	$\Delta_s H^\infty / \text{kJ mol}^{-1}$			
	<u>t</u> -BuCl	Ref.	<u>t</u> -BuBr	Ref.
water	1.05 <sup>a</sup>	14	1.32 <sup>b</sup>	—
methanol	1.56	6	2.20	7
ethanol	1.50	6	1.75	7
1-propanol	1.62	6	2.00	7
2-propanol	3.57	6	4.12	7
1-butanol	2.10	6	2.37	7
2-butanol	5.11	16	5.57	16
2-methyl-1-propanol	3.09	16	3.36	16
2-methyl-2-propanol	6.56 <sup>c</sup>	6	7.25	7
1-pentanol	2.56	6	2.62	7
2-pentanol	5.26	16	5.43	16
2-methyl-1-butanol	3.78		4.12	
2-methyl-2-butanol	4.78	16	5.19	16
3-methyl-1-butanol	2.80		2.95	

<sup>a</sup>Extrapolated value from water-ethanol mixtures. <sup>b</sup>Value obtained from the good linear regression in alcoholic solvents,  $\Delta_s H^\infty(\text{t-BuBr}) = 0.23397 + 1.0361 \Delta_s H^\infty(\text{t-BuCl})$  ( $r=0.994$ ;  $\sigma=0.19$ ). <sup>c</sup>Extrapolated value from higher temperatures (27-40°C).

The only observed significant correlation is  $r=0.857$  between  $E_T^N$  and C parameters. However, smaller  $r$  values were found for other sets of solvents,<sup>12</sup> which demonstrates the non-existence of a close relationship from a physico-chemical point of view.<sup>18</sup>

The results of the regression analysis by the complete and truncated versions of equation [1] are given in

Table II. Selected parameters of water and alcohols, at 25°C<sup>a</sup>

SOLVENT	$f(\epsilon)$	$g(\eta)$	$E_T^N$	$10^{-3}C/\text{MPa}$
water	0.49048	0.20569	1.000	2.307
methanol	0.47738	0.20311	0.762	0.887
ethanol	0.47006	0.22147	0.654	0.703
1-propanol	0.46420	0.23467	0.617	0.590
2-propanol	0.46327	0.23011	0.546	0.552
1-butanol	0.45836	0.24210	0.602	0.485
2-butanol	0.45604	0.24087	0.506	0.488
2-methyl-1-propanol	0.45931	0.24023	0.552	0.516
2-methyl-2-propanol	0.44219 <sup>b</sup>	0.23581	0.389	0.467
1-pentanol	0.44792	0.24776	0.568	0.497
2-pentanol	0.44722	0.24584	0.488	0.465 <sup>c</sup>
2-methyl-1-butanol	0.45350	0.24712	0.534 <sup>d</sup>	0.482
2-methyl-2-butanol	0.35669	0.24510	0.321	0.443
3-methyl-1-butanol	0.45220	0.24627	0.565 <sup>d</sup>	0.497

<sup>a</sup>Values of  $\epsilon$ ,  $\eta$  and  $E_T^N$  from ref. (2) and values of C from ref. (10), except when indicated. <sup>b</sup>Value at 30°C. <sup>c</sup>Value obtained from  $\Delta_s H^\infty$  (25°C) in ref. (17). <sup>d</sup>Value from ref. (18).

Table IV as well as the correlation coefficients,  $r$ , and the standard deviations,  $\sigma$ , of the goodness of the fits.

No single macroscopic physical parameter can account for the multitude of solvent-solvent-solute interactions on the molecular microscopic level as verified by the poor correlations shown by equations A to D for both solutes (Table IV). Also multiple regression analysis only including nonspecific (equations E) or specific intermolecular forces (equations J) are inadequate to describe solvent effects. On the other hand, the multiple

Table III. Results of the single linear correlations of the solvent parameters shown in Table II

$$Y = a_0 + a_1x$$

Y	x	a <sub>0</sub>	a <sub>1</sub>	r <sup>a</sup>	σ <sup>b</sup>
f(ε)	g(η)	0.71495	-1.1170	0.543	0.03
f(ε)	E <sub>T</sub> <sup>N</sup>	0.36937	0.14408	0.764	0.02
f(ε)	10 <sup>-3</sup> C	0.43340	0.028915	0.461	0.03
g(η)	E <sub>T</sub> <sup>N</sup>	0.27580	-0.070958	0.773	0.01
g(η)	10 <sup>-3</sup> C	0.24980	-0.022496	0.738	0.01
E <sub>T</sub> <sup>N</sup>	10 <sup>-3</sup> C	0.38810	0.28475	0.857	0.09

<sup>a</sup>Linear correlation coefficient. <sup>b</sup>Standard deviation.

dependencies involving simultaneously f(ε), E<sub>T</sub><sup>N</sup> and C or the complete set of solvent parameters are meaningful for both solutes - equations M and O in Table IV. Ehrenson's criterion<sup>20</sup> for relative fitting to a more restricted equation form was used in order to distinguish between each pair of equations. To do so, the value of the statistical parameter, f,

$$[3] \quad f = \left\{ \frac{\sum_{i=1}^n (\Delta_s H_{\text{obs}}^{\infty} - \Delta_s H_{\text{calc}}^{\infty})^2}{\sum_{i=1}^n (\Delta_s H_{\text{obs}}^{\infty})^2} \right\}^{1/2}$$

was calculated for all cases: f<sub>1</sub>(t-BuCl;p=4) = 0.145 ;

f<sub>2</sub>(t-BuCl;p=5) = 0.145 ; f<sub>1</sub>(t-BuBr;p=4) = 0.142 ;

Table IV. Correlations of t-BuCl and t-BuBr enthalpies of solution at infinite dilution and 25°C

$$\Delta_s H^{\infty} = a_0 + a_1 f(\epsilon) + a_2 g(\eta) + a_3 E_T^N + a_4 C$$

	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	10 <sup>3</sup> a <sub>4</sub>	r <sup>a</sup>	σ <sup>b</sup>	
t-BuCl	A	16.789	-29.929	—	—	0.543	1.47	
	B	-11.199	—	61.507	—	0.543	1.47	
	C	8.0464	—	—	-8.3057	0.799	1.05	
	D	4.4103	—	—	—	-1.7490	0.506	1.51
	E	2.6717	-19.401	39.838	—	0.618	1.43	
	F	4.7532	8.9157	—	-9.5903	0.806	1.08	
	G	13.798	-21.661	—	—	-1.1226	0.615	1.44
	H	13.893	—	-21.199	-9.8100	0.808	1.08	
	I	-6.0997	—	42.074	—	-0.80247	0.565	1.51
	J	9.9582	—	—	-14.295	2.3217	0.871	0.90
	K	10.801	10.232	-23.689	-11.461	—	0.816	1.11
	L	6.1573	-18.513	25.127	—	-0.64841	0.631	1.49
	M	-3.1341	39.461	—	-24.628	4.1228	0.948	0.61
	N	11.930	—	-7.3395	-14.653	2.2583	0.872	0.94
	O	-1.5480	39.387	-5.8119	-24.892	4.0693	0.949	0.64
t-BuBr	A	17.239	-30.147	—	—	0.525	1.55	
	B	-9.6937	—	56.590	—	0.479	1.60	
	C	8.4971	—	—	-8.4785	0.783	1.13	
	D	4.7717	—	—	—	-1.7650	0.491	1.59
	E	5.7162	-21.554	32.515	—	0.574	1.56	
	F	4.7765	10.073	—	-9.9299	0.791	1.16	
	G	14.214	-21.787	—	—	-1.1351	0.595	1.53
	H	18.720	—	-37.066	-11.109	0.808	1.12	
	I	-2.8262	—	30.417	—	-1.0808	0.521	1.62
	J	10.512	—	—	-14.790	2.4465	0.858	0.98
	K	15.003	12.299	-40.059	-13.093	0.820	1.14	
	L	10.618	-20.306	11.828	—	-0.91181	0.598	1.60
	M	-3.6245	42.607	—	-25.947	4.3913	0.942	0.67
	N	16.768	—	-23.285	-15.924	2.2456	0.866	1.00
	O	2.2817	42.333	-21.643	-26.929	4.1920	0.949	0.66

<sup>a</sup>Linear or multiple correlation coefficient. <sup>b</sup>Standard deviation.

$f_2(\underline{t}\text{-BuBr}; p=5) = 0.134$ . The number of estimated parameters in equation [1] was represented by  $p$ . The ratio  $f_1/f_2$  gives 1.00 for  $\underline{t}\text{-BuCl}$  and 1.06 for  $\underline{t}\text{-BuBr}$ . These values were compared to the statistical function  $R_{b,n-p,\alpha}$ , where  $b=1$  (the difference in the number of parameters of alternative equations),  $n-p=7$  (the number of degrees of freedom) and  $\alpha$  is the significance level. The hypothesis that both equations (equations M and O, Table IV), for each solute, are indistinguishable from a statistical point of view should be accepted. Thus, the best equations fitting the data are:

$$[4] \quad \Delta_S H^\infty(\underline{t}\text{-BuCl}) = -3.1341 + 39.461 f(\epsilon) - 24.628 E_T^N + \\ + 4.1228 \times 10^{-3} C$$

and

$$[5] \quad \Delta_S H^\infty(\underline{t}\text{-BuBr}) = -3.6245 + 42.607 f(\epsilon) - 25.947 E_T^N + \\ + 4.3913 \times 10^{-3} C$$

As expected (see footnote b in Table I), identical solvent-solvent-solute interactions interpretation can be drawn for both solutes attending to the same order of magnitude of the coefficients affecting the empirical solvent parameters in equations [4] and [5].

We may then conclude that in the solution process of  $\underline{t}\text{-BuCl}$  and  $\underline{t}\text{-BuBr}$  in water and alcohols: (i) the solvent dipolarity effect, of dipole-dipole type, is important; (ii) the polarizability is relatively unimportant; (iii) electrophilic assistance by protonic solvents is relevant and

(iv) the cavity solvent-solvent interaction has to be taken into consideration.

#### CONCLUSIONS

The past thirty years have seen enormous progress in the study of interactions of solvents with solute molecules using information obtained from the experimental functions of solution. A successful way to treat this problem makes use of linear solvation energy relationships. In spite of the fact that every empirical solvent scales based on a particular reference process is not expected to be universal and useful for all kinds of processes, we were able to show that the enthalpies of solution at infinite dilution of  $\underline{t}\text{-BuCl}$  and  $\underline{t}\text{-BuBr}$  correlate well with the three parameters  $f(\epsilon)$ ,  $E_T^N$  and  $C$  for 14 hydroxylic solvents. A critical examination of the best equations improved our knowledge on the dominant solvent-solvent-solute interactions. Finally, it should be pointed out that these relationships are very useful in the prediction of the solution enthalpies of the same substrates in other solvents and in the correlation of data between a new solution series and the old series in order to establish interaction mechanistic similarities.

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REFERENCES

1. S. Cabani, Portugaliae Electrochimica Acta, **3** (1985) 5.
2. Advances in Linear Free Energy Relationships, ed. N.B. Chapman and J. Shorter (1972) Plenum Press, London.
3. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry (1988) VCH, 2nd ed., Weinheim.
4. M.H. Abraham, P.L. Grellier, J.-L.M. Abboud, R.M. Doherty and R.W. Taft, Can. J. Chem., **66** (1988) 2673.
5. J.N. Spencer, A. Grushow, T.F. Ganunis, K.N. Allott, S.P. Kneizys, H. Willis, S. Puppala, C.M. Salata, A.I. Zafar, B.J. Stein and L.C. Hahn, J. Solution Chem., **18** (1988) 471.
6. R.M.C. Gonçalves and A.M.N. Simões, J. Solution Chem., **16** (1987) 39.
7. R.M.C. Gonçalves and A.M.N. Simões, Can. J. Chem., **65** (1987) 1474.
8. P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences (1969) McGraw-Hill, New York.
9. K. Dimroth, C. Reichardt, T. Siepman and F. Bohlmann, Liebigs Ann. Chem., **661** (1963) 1.
10. A.F.M. Barton, Chem. Rev., **75** (1975) 731.
11. J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, Regular and Related Solutions (1970) Van Nostrand-Reinhold, Princeton.
12. R.M.C. Gonçalves, A.M.N. Simões and L.M.P.C. Albuquerque, J. Chem. Soc., Perkin Trans. 2 (1990) 1379.
13. R.M.C. Gonçalves, A.M.N. Simões and L.M.P.C. Albuquerque, J. Chem. Soc., Perkin Trans. 2, in press.
14. E.M. Arnett, W.G. Bentrude, J.J. Burke and P.McC. Duggleby, J. Am. Chem. Soc., **87** (1965) 1541.
15. R.M.C. Gonçalves and A.M.N. Simões, communication to the "2nd Meeting of the Portuguese Electrochemical Society" (1986).
16. R.M.C. Gonçalves and A.M.N. Simões, J. Solution Chem., **19** (1990) 315.
17. J.A. Riddick and W.B. Bunger, Organic Solvents. Physical Properties and Methods of Purification (1970) Wiley, 3rd ed., New York.
18. C. Reichardt, M. Eschner and G. Schäfer, Liebigs Ann. Chem. (1990) 57.
19. S. Glikberg and Y. Marcus, J. Solution Chem., **12** (1983) 255.
20. S. Ehrenson, J. Org. Chem., **44** (1979) 1793.

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