Linear Solvation Energy Relationships: Charge Transfer Band Maxima of N-Alkylpyridinium Iodides in Pure Solvents

Krishna Medda, Prasanta Chatterjee, Asit Kumar Chandra and Sanjib Bagchi *
Department of Chemistry, Burdwan University, Burdwan-713 104, India

Linear solvation energy relationships have been used to explain the solvatochromic behaviour of the charge transfer energy of N-alkylpyridinium iodides. It has been observed that a three parameter correlation involving dipolarity, hydrogen bond donating ability and hydrogen bond accepting ability of the solvent explains the observed solvent effect. From the correlation equation the relative contribution of different modes of solute–solvent interaction in determining the overall transition energy is also discussed.

The vast literature on solvent effects on kinetic, equilibrium and spectroscopic properties of a solute indicates that the interaction between solute and solvents can be described by a relatively small number of general effects.[1] In general three modes of interactions can be distinguished *viz.*, (i) non-specific long-range interactions, (ii) specific short-range interactions and (iii) cavity effects. It has been found by several authors that linear solvation energy relationships provide a suitable generalised treatment of solvent effects.[2] Thus multiparameter correlations using only a few solvent parameters have been found to work well in explaining solvent effects.[3,4]

Charge transfer (CT) transitions involving major electron density shifts between the ground and excited states are very sensitive towards the state of solvation of the solute. Thus solvatochromic CT bands have gained practical importance as colour indicators and empirical solvent polarity scales.[5] The solute acts here as a micropolarity reporter and the polarity parameter supposedly reflects solute–solvent interactions at the microscopic level.[7,8] The Z value of Kosower[6] and the $E_T(30)$ scale of Dimroth *et al.*[7] based on the CT transition in 1-ethyl-4-methoxycarbonylpyridinium iodide and pyridinium betaine respectively, are two such polarity parameters which find wide application in physical organic chemistry. The two parameters are linearly correlated[8] indicating that the basic 'model process'[9] involved is the same in both cases. It has been found that Z or $E_T(30)$, however, cannot in general be correlated with a single polarity parameter,[1,10] except for a selected set of solvents.[11]

The present work addresses the problem of solvent effects on the CT transition energy of N-alkylpyridinium iodides. Multiple linear regression analysis of Kosower's Z values with various solvent parameters indicating different modes of solute–solvent interaction have been presented. Similar studies have also been made using the CT transition energy, $Z(4CN)$, of 4-cyano-N-ethylpyridinium iodide taken as the indicator solute.

Equations and Parameters.—In dilute solution only solute–solvent interactions are important and eqn. (1) below summarises

$A = A_0 + \text{non-specific interaction term} +$
$\qquad \text{specific interaction term} + \text{cavity term}$ (1)

marises the generalised expression for any physicochemical property (A) in the presence of a solvent. A_0 represents the value of A in a reference solvent where solute–solvent interactions are assumed to be absent. It has been observed[12] that the solvent effect is best understood if one assumes that there are linear solvation energy relationships for each of the contributing

terms to the observed total solvation parameter A. Thus it is customary to express the solvent dependent parameter A as a multiparameter equation. Two main approaches in the field of multiple linear regression analysis may be distinguished *viz.*, the approach suggested by Koppel and Palm[1] and that by Abraham, Kamlet and Taft.[2,12] In Koppel and Palm's approach functions of relative permittivity (ε) and refractive index (n) were used to describe non-specific interactions. Thus the Onsager reaction field parameter ($\varepsilon - 1$)/($2\varepsilon + 1$) was used to describe the non-specific dipolar interaction while ($n^2 - 1$)/($n^2 + 2$) was used to describe the polarisability term. In Abraham, Kamlet and Taft's approach the dipolarity and polarisability were described by the experimentally determined parameter π^*. The specific interactions were described by the parameters E (electrophilic solvation ability) and B (nucleophilic solvation ability) in the Koppel and Palm procedure. But Abraham, Kamlet and Taft preferred the use of hydrogen bond donating (HBD) or hydrogen bond accepting (HBA) ability of the solvent, represented by the empirical Kamlet–Taft parameters α and β respectively.[13] The endothermic cavity formation term was taken, in Abraham, Kamlet and Taft's approach, as equal to the solute molar volume times the Hildebrand cohesive energy density (δ_H^2), defined as the enthalpy of vaporisation per unit volume. Koppel and Palm's original approach did not take this factor into account, although this term was introduced later by Makitra and Pirig.[14] In this present work the reaction field model has been used for non-specific dipolarity and polarisability terms. It has been shown that a dielectrically saturable Block–Walker reaction field model[15] or an individual solvent molecule dipole reaction field approach[16] provides a suitable description for the non-specific interactions.[11,16,17] The parameter $\theta(\varepsilon)$ given by eqn. (2) describes the dipolar interaction part in the former case,

$$\theta(\varepsilon) = 3\varepsilon \ln \varepsilon/(\varepsilon \ln \varepsilon - \varepsilon + 1) - 6/\ln \varepsilon - 2 \qquad (2)$$

while in the latter case the correlation should be sought with the parameter $\mu/\bar{V}$, where μ and $\bar{V}$ are respectively the dipole moment and the molar volume of the solvent.

The polarisability term arising through induction of dipoles in the solvent *via* electronic polarisation is best described by the Onsager reaction field model.[17] Thus the parameter $\varphi(n^2) = 2(n^2 - 1)/(2n^2 + 1)$ has been used in the present work to describe this mode of interaction. The α and β parameters have been used to describe the specific interaction term as in Abraham, Kamlet and Taft's approach. In the present work, considering the different mechanisms of solute–solvent interaction, we have attempted a multiple linear regression analysis

Table 1 Z, $Z(4CN)$ (kcal mol^{-1}) and other solvent parameters of pure solvents. $Z(4CN)$ value calculated in this work.

Solvent	Z	$Z(4CN)$[1,2]	α	β	$\mu/\bar{V}$	$\theta(\varepsilon)$	δ_H^2	$\varphi(n^2)$
Methanol	83.6	79.4	0.93	0.66	0.041	0.434	205.2	0.338
Ethanol	79.6	76.0	0.83	0.75	0.028	0.408	162.1	0.362
Propan-1-ol	78.3	73.7	0.78	0.80	0.023	0.391	143.2	0.379
Propan-2-ol	76.3	72.4	0.76	0.84	0.022	0.380	133.1	0.371
Butan-1-ol	77.7	73.5	0.79	0.82	0.019	0.376	129.5	0.390
tert-Butyl alcohol	71.3	68.1	0.68	0.93	0.018	0.324	111.9	0.380
Pentan-1-ol	77.6	72.9	0.70	0.92	0.016	0.354	119.8	0.397
Isoamyl alcohol	77.6	73.3	0.78	0.90	0.017	0.360	116.3	0.394
Glycol	85.1	—	0.90	0.58	0.041	0.445	274.0	0.411
Acetic acid	79.2	—	1.12	0.45	0.029	0.264	203.5	0.370
Acetonitrile	71.3	67.8	0.19	0.40	0.066	0.443	137.8	0.350
Benzonitrile	65.0	60.6	0.00	0.41	0.040	0.412	122.9	0.471
Acetone	65.7	61.6	0.08	0.48	0.037	0.394	90.6	0.361
Butan-2-one	64.0	60.4	0.06	0.48	0.031	0.383	86.0	0.375
Ethyl acetate	64.0	58.7	0.00	0.45	0.019	0.260	79.2	0.370
Dioxane	64.6	61.1	0.00	0.37	0.005	0.125	100.0	0.406
Tetrahydrofuran	58.8	55.0	0.00	0.55	0.022	0.288	86.4	0.394
Dibutyl ether	64.0	—	0.00	0.46	0.007	0.173	59.6	0.390
Dimethoxyethane	61.2		0.00	0.41	0.017	0.496	67.2	0.376
DMSO[a]	70.2	66.9	0.00	0.76	0.061	0.467	168.8	0.441
Formamide	83.3	—	0.71	0.60	0.100	0.524	361.7	0.422
DMF[b]	68.5	65.3	0.00	0.69	0.050	0.444	138.9	0.411
Dimethylacetamide	66.9	—	0.00	0.76	0.040	0.446	116.6	0.416
HMPA[c]	62.8	—	0.00	1.05	0.032	0.426	73.4	0.429
Chloroform	63.2	57.8	0.44	0.00	0.014	0.232	88.7	0.421
Dichloromethane	64.2	59.3	0.30	0.00	0.024	0.308	97.7	0.407
Dichloroethane	63.4	58.4	0.00	0.00	0.022	0.326	98.3	0.420
Chlorobenzene	64.0	—	0.00	0.07	0.015	0.253	93.6	0.469
Pyridine	64.0	60.4	0.00	0.64	0.028	0.342	111.3	0.460
(*Z*)-Dichloroethene	63.9	—	0.00	0.00	0.023	0.310	44.0	0.423
Benzene	54.0	54.0	0.00	0.10	0.000	0.129	83.8	0.455
1,1,2,2-Tetrachloroethane	64.3	—	0.00	0.00	0.016	0.297	97.8	0.451
Cyclohexane	60.1	—	0.00	0.00	0.000	0.110	67.2	0.408
Nitromethane	71.2	68.2	0.22	0.25	0.066	0.442	158.5	0.378

[a] Dimethyl sulfoxide. [b] Dimethyl formamide. [c] Hexamethylphosphoramide.

Table 2 Correlation coefficient R (X,Y) for single linear intercorrelation of solvent parameters X and Y

	X				
Y	α	β	$\mu/\bar{V}$	δ_H^2	$\varphi(n^2)$
α	1.000	0.440	0.134	0.619	0.468
β		1.000	0.229	0.294	0.311
$\mu/\bar{V}$			1.000	0.718	0.095
δ_H^2				1.000	0.113
$\varphi(n^2)$					1.000

using eqn. (3). The dipolarity parameter P may be either $\theta(\varepsilon)$ or $\mu/\bar{V}$.

$$Z\,[\text{or } Z(4CN)] = A_0 + pP + a\alpha + b\beta + f\varphi(n^2) + d\delta_H^2 \quad (3)$$

Experimental

The Z values, $Z(4CN)$ values and various solvent parameters have been listed in Table 1. Z values for pure and mixed solvents have been taken from the works of Kosower[6] and Griffiths and Pugh.[18] The values of $Z(4CN)$ have been collected from our previous works[19] and the work of Mackay and Poziomeck.[20] The $Z(4CN)$ value for some of the solvents were determined in the present work using a Shimadzu UV 160A spectrophotometer provided with a peak detecting algorithm. Solvents were purified by standard procedures and distilled from calcium hydride prior to the work. This ensured the absence of peroxides. Care was taken to minimise contamination of air and moisture during the

preparation of solutions. Multiple linear regression analysis was performed on a IBM PC-AT/386 using a program developed by us.

Results and Discussion

Table 2 gives the matrix of the correlation coefficients for a linear intercorrelation of solvent parameters. It appears that highly significant linear correlations are not observed. The results of multiple linear regression analyses for the Z values using complete and truncated versions of eqn. (3) are given in Table 3. From the table it appears that the single parameter regression analyses have no relevant statistical meaning except where the Kamlet–Taft α-parameter is concerned. A comparison of the application of multiple linear regression analysis shows that the best two, three and four-parameter versions of the general eqn. (3) are the eqns. (3.7), (3.19) and (3.26). The best fit was determined with reference to Ehrenson's criterion.[21] To achieve this, the function, f defined as in eqn. (4), was calculated

$$f = \left[\sum_{i=1}^{n} (Z_{calc} - Z_{obs})^2 \bigg/ \sum_{i=1}^{n} (Z_{obs})^2 \right]^2 \quad (4)$$

for the complete and best truncated versions of eqn. (3). To test the hypothesis that a set of variables provides as good a fit as another set obtained by the removal of one variable from the previous set, the ratio f_i/f_{i+1}, where i is the number of variables, was compared with R_1, $n - (i + 1)$ and α, where α represents the confidence level. The f values for eqns. (3.3), (3.7), (3.19), (3.26) and (3.31) are 0.0553, 0.0388, 0.0359, 0.0350 and 0.0340 respectively. The ratios for f_2/f_3, f_3/f_4, f_4/f_5 and f_5/f_6 are 1.42, 1.08, 1.025 and 1.029 respectively. The values over 1.05 mean

Table 3 MLRA of Z values using complete and truncated versions of eqn. (3): $Z = A_0 + p(\mu/\bar{V}) + a\alpha + b\beta + f\varphi(n^2) + d\delta_H^2$

Eqn. no.	A_0	p	f	a	b	d	r
1	63.68	179.99	—	—	—	—	0.445
2	113.35	—	−110.33	—	—	—	0.463
3	63.23	—	—	18.81	—	—	0.878
4	61.99	—	—	—	14.18	—	0.557
5	56.31	—	—	—	—	0.101	0.781
6	104.82	164.16	−100.98	—	—	—	0.621
7	59.57	136.05	—	17.83	—	—	0.942
8	59.01	136.65	—	—	12.16	—	0.651
9	56.28	−85.88	—	—	—	0.121	0.795
10	69.83	—	−15.90	18.14	—	—	0.880
11	94.01	—	−76.41	—	11.64	—	0.635
12	93.43	—	−90.43	—	—	0.096	0.867
13	61.20	—	—	16.81	5.39	—	0.899
14	58.56	—	—	13.72	—	0.050	0.928
15	58.56	—	—	—	9.13	0.088	0.852
16	64.81	135.37	−12.56	17.30	—	—	0.943
17	90.23	133.66	−74.34	—	9.74	—	0.715
18	93.70	−89.98	−91.15	—	—	0.117	0.881
19	58.46	126.22	—	16.53	3.68	—	0.951
20	74.24	—	−39.09	11.45	—	0.056	0.939
21	84.06	—	−72.58	—	6.78	0.087	0.900
22	53.50	−91.22	—	—	9.24	0.109	0.867
23	59.11	133.27	—	16.81	—	0.012	0.943
24	65.09	—	−9.25	16.47	5.27	—	0.899
25	56.72	—	—	11.91	5.13	0.049	0.946
26	57.48	84.22	—	14.56	4.14	0.021	0.953
27	61.95	125.98	−8.29	16.22	3.57	—	0.951
28	69.89	—	−32.44	10.20	4.66	0.054	0.953
29	68.46	87.71	−23.63	14.74	—	0.024	0.946
30	84.20	−93.14	−73.05	—	6.87	0.108	0.915
31	66.47	60.06	−22.66	12.60	4.09	0.032	0.956

that the hypothesis must be rejected at a confidence level $> 90\%$ for $n = 34$ while values of ca. 1.02 mean that the hypothesis may be accepted in these cases. Thus a multiple linear regression analysis study indicates that a three parameter equation viz. α, $\mu/\bar{V}$ and β gives the best correlation of Z values from the statistical point of view. Similar studies using 4-cyano-N-ethylpyridinium iodide also point to statistically significant three parameter correlations. Thus we may write:

$$Z = 58.5 + 16.5\alpha + 3.7\beta + 126.1(\mu/\bar{V}):r = 0.951$$

$$Z(4CN) = 52.3 + 15.7\alpha + 6.4\beta + 155.2(\mu/\bar{V}):r = 0.964$$

Similar studies using the parameter $\theta(\varepsilon)$ in place of $\mu/\bar{V}$ to indicate dipolar interactions have also been carried out. The results are:

$$Z = 55.1 + 16.6\alpha + 1.6\beta + 23.1\theta(\varepsilon):r = 0.936$$

$$Z(4CN) = 48.7 + 13.3\alpha + 4.6\beta + 28.4\theta(\varepsilon):r = 0.949$$

Thus the Z [or $Z(4CN)$] value embodies the following modes of solute–solvent interaction: (i) non-specific interactions due to the dipolarity of the solvents, (ii) the specific HBD acidity interactions and (iii) the specific HBA basicity interactions.

The parameter A_0 in eqn. (3) corresponds to the value of Z in an inert solvent. The value $A_0 = 58.3$ (or 55.1) obtained in our study may be compared with the Z value for a non-polar solvent. The Z value for benzene is 54.0 kcal mol^{-1} while that for cyclohexane has been reported to be 60.1 kcal mol^{-1}.* The two solvents mentioned above differ with respect to their polarisability, while the dipolarity and specificity parameters

are the same for both solvents. It appears from Table 3 that the sign of the coefficient of the polarisability parameter $\varphi(n^2)$ is always negative. This means that the stabilisation due to this factor is greater in the excited state, compared to the other factors for which the stabilisation of the ground state exceeds that of the excited state. In a non-polar solvent where other modes of interaction are absent the polarisability factor may be significant and this may explain why benzene, with a higher value of $\varphi(n^2)$, shows a lower Z value.

Regression coefficients also indicate the relative importance of the specific solute–solvent interaction term compared to the non-specific interaction term. To see this we should compare $a\Delta\alpha$ or $p\Delta P$ with ΔZ. Thus ca. 65% of the variation of the Z parameter in the change from methanol to cyclohexane is described by the HBD acidity, a specific interaction term, while the non-specific dipolar interaction corresponds to ca. 20%. Thus the specific interaction, probably through hydrogen bond donation of the solvent to the anion of the indicator solute (iodide ion), plays a more important part in the solvation of N-alkylpyridinium iodides. This result substantiates earlier observations by other workers working with fewer solvents.[1,10]

References
1 I. A. Koppel and V. A. Palm, in *Advances in Linear Free Energy Relationships*, eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972.
2 R. W. Taft, J. L. M. Abboud, M. J. Kamlet and M. H. Abraham, *J. Solution Chem.*, 1985, 14, 153.

* 1 cal = 4.184 J.

3 (a) R. M. C. Goncalves, A. M. N. Simoes and L. M. C. Albuquerque, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1379; (b) M. H. Abraham, R. J. Abraham, P. Leonard, N. S. True and C. Suarez, *J. Chem. Soc., Perkin Trans. 2*, 1991, 463.

4 W. J. Cheong and P. W. Carr, *Anal. Chem.*, 1989, **61**, 1524.

5 E. M. Itskovitch, J. Ulstrup and Vorotynstev, in *The Chemical Physics of Solvation, Part B*, eds. R. R. Dogonadze, E. Kalman, A. A. Kornyshev and J. Ulstrup, Elsevier, New York, 1986.

6 E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253.

7 K. Dimroth, C. Reichardt, T. Siepman and F. Bohlmann, *Justus Liebigs. Ann. Chem.*, 1963, **661**, 1.

8 J. G. Dawber, J. Ward and R. A. Willams, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 713.

9 E. M. Kosower, *An Introduction to Physical Organic Chemistry*, Wiley, New York, 1968.

10 M. J. Kamlet, J. L. M. Abboud and R. W. Taft, *Prog. Phys. Org. Chem.*, 1980, **13**, 485.

11 K. Medda, P. Chatterjee, M. Pal and S. Bagchi, *J. Solution Chem.*, 1990, **19**, 271.

12 M. H. Abraham, P. L. Grellier, J. L. M. Abboud, R. M. Doherty and R. W. Taft, *Can. J. Chem.*, 1988, **66**, 2673.

13 M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.

14 R. G. Makitra and Ya. N. Pirig, *Org. React. USSR*, 1979, **16**, 535.

15 H. Block and S. M. Walker, *Chem. Phys. Lett.*, 1973, **19**, 363.

16 (a) A. H. Reddoch and S. Konishi, *J. Chem. Phys.*, 1979, **70**, 2121; (b) S. Ehrenson, *J. Am. Chem. Soc.*, 1981, **103**, 6036.

17 J. E. Brady and P. W. Carr, *J. Phys. Chem.*, 1982, **86**, 3053.

18 T. R. Griffiths and D. C. Pugh, *Coordination Chem. Rev.*, 1979, **29**, 129.

19 M. Pal and S. Bagchi, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 961; *Indian J. Chem.*, 1984, **23A**, 800.

20 R. A. Mackay and E. J. Poziomek, *J. Am. Chem. Soc.*, 1970, **92**, 2432.

21 S. Ehrenson, *J. Org. Chem.*, 1979, **44**, 1793.