An Extension of the Kamlet–Taft Basicity Scale of Solvents

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A critical analysis is given of currently popular scales of solvent Lewis basicity (Koppel–Palm, Paju–Koppel, and Gutmann) with particular consideration to and extension of the Kamlet–Taft scale, B_{KT}. Measurements for 22 new solvents were carried out and B_{KT} values for 70 solvents are reported. A rough agreement between B_{KT} and other parameters for solvent basicity has been found. A linear dependence of the Koppel–Palm E values with E_T was shown for solvents of higher polarity (E_T > 42).

RECENTLY there has been increasing interest in applying empirical models of solute–solvent interactions or solvent effects. Katritzky *et al.*[1] surveyed the use of multiparameter regression to describe solvent effects. Exhaustive reviews by Koppel and Palm,[2] including detailed analysis of specific and nonspecific contributions according to equation (1), led to many applications and modifications.[3-12] In equation (1) $f(n^2)$ is a function of

$$\delta Q = p\mathrm{f}(n^2) + y\mathrm{f}(\varepsilon) + eE + bB \qquad (1)$$

the refractive index and describes the polarizability, $\mathrm{f}(\varepsilon)$ describes the ' polarity ' in terms of a nonspecific interaction model where ε is the dielectric constant, and E and B are parameters of solvent electrophilicity and basicity, respectively.[2]

Usually the results obtained were fairly satisfactory and the regression coefficients p, y, e, and b indicated which particular interaction contributed significantly to the overall solvent effect δQ. The application of models such as equation (1) needs parameters which are well defined for a wide range of solvents. There is a large number of solvent parameter scales in the literature [13-24] often called Lewis acidity or basicity scales.

Recently it was found [25] by the use of an independent method, characteristic vector analysis, that in many cases equation (1) may be reduced to a planar regression with parameters describing solvent Lewis acidity and basicity sufficient to account for up to 90—95% of the variation in δQ. The Lewis acidity parameter E_T introduced to Dimroth and Reichardt *et al.*[15] is at present available for more than 150 solvents [26] and its application has been tested successfully by many authors,[4-7,18,27,28] so it seems that it is of considerable merit. The situation is more complex when basicity parameters are concerned. At present there are in use at least four scales of basicity parameters: DN introduced by Gutmann,[29] the B parameter introduced by Gordy and Stanford [19] and applied widely by Koppel and Palm,[2] and two very recently introduced scales, B_1 of Koppel and Paju [30] and B_{KT} of Kamlet and Taft.[11]

The aim of this paper is (i) to analyse critically the above mentioned scales, (ii) to extend the Kamlet–Taft scale [11] of basicity parameters, and (iii) to discuss how far equivalent are various scales of solvent parameters.

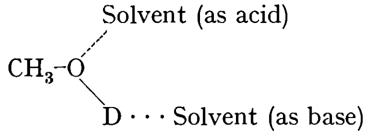
Basicity Scales.—In measuring the Lewis basicity of solvent molecules one has to choose a suitable detecting substance (molecule). It must have Lewis acid properties and be soluble in a wide range of solvents, retaining the mechanism of solvent–solute interactions qualitatively unchanged. If the parameters are to be used in models similar to equation (1) they should be measured with very high accuracy because errors will be propagated in the least squares procedure usually applied to equation (1).

Gordy–Kagiya–Koppel–Palm Basicity Scale.—These authors [2,19,20] suggested basicity parameters which are essentially the shift of the OD stretching vibration of MeOD in a series of solvents, various reference media being used. Gordy and Stanford [19] showed a correlation

$$\Delta\tilde{\nu}_{\mathrm{OD}} = \tilde{\nu}_{\mathrm{OD}}^{\mathrm{ref}} - \tilde{\nu}_{\mathrm{OD}}^{\mathrm{solvent}} = B_{\mathrm{G(K-K-P)}} \qquad (2)$$

between these B_G values and the pK_b values of solvents, thus establishing a relationship between B_G and Brønsted basicity. However for detecting-substances whose molecules are very weak Brønsted bases the interactions with solvents are chiefly of the Lewis acid–base type, including hydrogen-bond formation.

The main shortcoming of this scale is due to the possibility of dual [7] interactions (3) and hence in hydrogen-



(3)

bond donor solvents the measured shift is affected by both interactions and does not measure basicity alone. A dual mechanism of interaction can also occur for weaker interacting solvents as in the case of anisole for which $\tilde{\nu}_{\mathrm{OD}} = 2\,630$ cm^{-1} for the MeOD · · · n electrons of the methoxy-group and 2 659 cm^{-1} for the MeOD · · · π electrons of the ring.[31,32] Thus it is difficult to decide which values to apply as basicity parameters. Moreover, if measurements of i.r. spectra are carried out in concentrated solutions (>0.1M) of alcohol there are important disturbances due to autoassociation.[31] Hence it seems to be not too advantageous to use this scale of basicity.

Due to the possibility of interactions such as (3) B_G cannot be measured with reasonable accuracy for solvents which are both hydrogen-bond donors and acceptors (alcohols, amides, and water). Thus the B_G parameter does not seem to be convenient or reliable as a basicity parameter.

The Paju–Koppel Scale.[23]—This is based on values of $\tilde{\nu}_{OH}$ of phenol interacting with molecules of solvents dissolved and measured in CCl_4. An objection to this scale in spite of the better precision of measurements and higher sensitivity (about three times that of B_G [23]) is that both solvents and detecting molecules (phenol) are solutes in the hydrophobic (aprotic) CCl_4. Moreover the Koppel–Paju scale is based upon spectral measurements of varying accuracy carried out in various laboratories and the final values of the parameters are obtained by averaging. According to the authors [23] B_G and B_{K-P} are mutually related by a regression line with a correlation coefficient r of 0.987.

Gutmann DN (Donor Number) Scale.[22]—The process applied to obtained the DN values is the formation of the adduct of $SbCl_5$ (Lewis acid) with the solvent molecule (Lewis base) as a solute in 1,2-dichloroethane [reaction (4)]. The higher DN the more basic is the solvent.

$$SbCl_5 + Solv \longrightarrow SbCl_5{\cdot}Solv \quad DN = -\Delta H^\circ_{form} \quad (4)$$

These parameters are, however, hardly measurable for solvents with active hydrogen (hydroxylic, amides) and the resulting data for these solvents seem to be too low. Usually DN values for these solvents are obtained from indirect measurements (*e.g.* $^{23}Na^+$ n.m.r. measurements [21]) and the parameters are obtained by extrapolation from a graph giving so-called bulk donor numbers. Obviously these difficulties as well as an evident shortcoming due to measurements being made in a third medium do not encourage too wide a use of this basicity scale.

Each of these basicity scales was successfully used in various ways but the above mentioned criticisms suggest looking for another scale more free of serious shortcomings.

Recently Kamlet and Taft [11] presented a scale of Lewis basicity of solvents based upon the idea of homomorphy [33] which seems to be free of many of the restrictions mentioned above.

Kamlet–Taft Basicity Scale [11] and its Extension.—The Kamlet–Taft parameters are based on differences of the longest wavelength band in the u.v.–visible spectra measured for a hydrogen-bond donor (1) relative to its homomorph (2), *i.e.* a molecule without this hydrogen-bonding ability. Examples are for (i), *p*-nitroaniline and *p*-nitrophenol and for (ii), *NN*-diethyl-*p*-nitroaniline and *p*-nitroanisole. The authors [11] calculated the regression line $\tilde{\nu}_{max.}(1)$ *versus* $\tilde{\nu}_{max.}(2)$ for solvents ' of varying polarity but wherein hydrogen bonding is excluded '. They used for this purpose the following solvents: heptane, hexane, cyclohexane, CCl_4, toluene, $Cl_2C{=}CHCl$, benzene, chlorobenzene, CH_2Cl_2, and $ClCH_2$-CH_2Cl.

It seems that among the ' inactive solvents ', used by Kamlet and Taft [11] in order to get the standard line described by equation (6), there are two solvents benzene and toluene which are known as good π-donors in charge transfer complex formation.*[34] Therefore in our extension the B_{KT} scale to other solvents, solvents of the above mentioned type have been excluded. Instead, in order to have more points for the standard line we have chosen some other solvents as well as alkanes, which are known to be very weak (if at all) σ- or π-donors: n-pentane, n-hexane, n-heptane, cyclohexane, carbon tetrachloride, fluorobenzene, chlorobenzene, bromobenzene, *m*-dichlorobenzene, ethylene chloride, and chloroform. The line obtained has the form (5) with r

$$\tilde{\nu}_{max.}(1) = 1.127\,9\,\tilde{\nu}_{max.}(2) + 0.319\,2\ \text{kK} \qquad (5)$$

0.998 9 for 11 points. This equation does not differ too much from that, (6), of Kamlet and Taft [11] with r 0.987

$$\tilde{\nu}_{max.}(1) = 1.035\,\tilde{\nu}_{max.}(2) + 2.64\ \text{kK} \qquad (6)$$

for nine points. However, it is apparent that regression (5) has a slightly higher precision, probably due to the exclusion of solvents which can act as weak π-electron donors. Figure 1 shows a plot of $\tilde{\nu}_{max.}(1)$ *versus* $\tilde{\nu}_{max.}(2)$ and it is immediately clear that all the solvents whose molecules are known as good π-donors, *e.g.* mesitylene, or xylenes, are systematically red-shifted by *ca.* 0.2 kK from the standard line (5). This seems to be good support for the choice of solvents used to obtain equation (5).

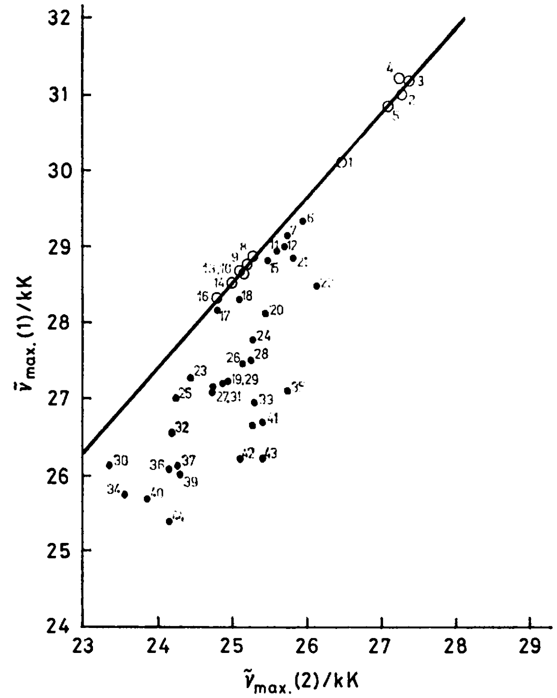


FIGURE 1 Plot of $\tilde{\nu}_{max.}(1)$ *versus* $\tilde{\nu}_{max.}(2)$. Empty circles are for solvents chosen for standard line as ' inactive solvents.' For key see Table 1

In order to obtain B_{KT} values, normalized in a similar way as in the paper by Kamlet and Taft,[11] the B_{KT} for

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* This point has been recently recognized by Kamlet and Taft, *cf.* ref. 12.

HMPA is assumed to be equal to 1.00, *i.e.* the B_{KT} values are calculated by means of formula (7). In the denominator $\Delta\tilde{\nu}$ for HMPA taken from ref. 11 was recalculated by applying equation (5). Table 1 presents all the data with assignments of solvents as in Figure 1. By definition solvents applied as standards have B_{KT} 0.00 and this definition is fulfilled within the range of experimental error. Some results in Table 1 need commentary. Cyclohexane has B_{KT} 0.18 whereas that of benzene is 0.09. This result is in agreement with a much higher polarizability (and mobility) of the π-electrons in the unsaturated compound which is also reflected in its much greater reactivity. On the other hand halogenobenzenes are blue-shifted from benzene and toluene, indicating almost the same properties as alkanes (hence taken as standard solvents). This can be explained by means of the electron-withdrawing action of the substituents decreasing the π-electron mobility of the ring. Even though the molecules are dipolar, their interaction as bases is not observable.

$$B_{KT} = (\tilde{\nu}^{exp.}_{max} - \tilde{\nu}^{calc}_{max})/2.78 \qquad (7)$$

TABLE 1

Spectral data for *p*-nitroaniline and *NN*-diethyl-*p*-nitroaniline. $\tilde{\nu}_{max.}(1)$ and $\tilde{\nu}_{max.}(2)$ were calculated according to equation (5), and B_{KT} was calculated according to equation (7)

	Solvent	$\tilde{\nu}_{max.}(2)$/kK	$\tilde{\nu}_{max.}(1)$(obs.)/kK	$\tilde{\nu}_{max.}(1)$(calc.)/kK	$\Delta\tilde{\nu}$/kK	B_{KT}
1	Carbon tetrachloride	26.48	30.12	30.18	0.06	0.00
2	n-Heptane	27.28	31.00	31.09	0.09	0.00
3	n-Pentane	27.36	31.24	31.18	−0.06	0.00
4	n-Hexane	27.28	31.20	31.09	−0.11	0.00
5	Cyclohexane	27.09	30.83	30.87	0.04	0.00
6	Mesitylene	25.94	29.32	29.57	0.25	0.09
7	*p*-Xylene	25.72	29.13	29.33	0.20	0.07
8	*m*-Dichlorobenzene	25.26	28.84	28.80	−0.04	0.00
9	Fluorobenzene	25.22	28.78	28.76	−0.02	0.00
10	Chloroform	25.16	28.68	28.70	0.02	0.00
11	*o*-Xylene	25.58	28.94	29.17	0.23	0.08
12	*m*-Xylene	25.69	29.00	29.29	0.29	0.10
13	Chlorobenzene	25.15	28.64	28.69	0.05	0.00
14	Bromobenzene	25.00	28.52	28.52	0.00	0.00
15	Benzene	25.48	28.80	29.06	0.26	0.09
16	Ethylene chloride	24.80	28.32	28.29	−0.03	0.00
17	Anisole	24.80	28.18	28.29	0.11	0.04
18	Ethoxybenzene	25.08	28.30	28.61	0.31	0.11
19	Methyl n-butyl ketone	24.94	27.22	28.45	1.23	0.44
20	Dioxan	25.44	28.12	29.01	0.89	0.32
21	Cyclohexene	25.72	28.84	29.33	0.49	0.18
22	Diethyl ether	26.16	28.48	29.83	1.35	0.49
23	Acetonitrile	24.47	27.28	27.92	0.64	0.23
24	Ethyl acetate	25.28	27.78	28.83	1.06	0.38
25	Propylene carbonate	24.24	27.00	27.66	0.66	0.24
26	Methyl t-butyl ketone	25.16	27.44	28.70	1.26	0.45
27	Acetone	24.72	27.16	28.20	1.04	0.37
28	Tetrahydrofuran	25.24	27.48	28.79	1.31	0.47
29	Cyclohexanone	24.89	27.24	28.39	1.15	0.41
30	Water	23.36	26.16	26.67	0.51	0.18
31	Ethyl n-butyl ketone	24.76	27.12	28.25	1.13	0.41
32	Nitromethane	24.18	26.54	27.59	1.05	0.38
33	Methanol	25.30	26.92	28.86	1.96	0.71
34	Formamide	23.54	25.75	26.87	1.12	0.40
35	t-Butylamine	25.72	27.08	29.01	1.93	0.69
36	*NN*-Dimethylformamide	24.16	26.08	27.57	1.49	0.54
37	*N*-Methylformamide	24.26	26.08	27.36	1.28	0.46
38	n-Propanol	25.27	26.66	27.68	1.02	0.37
39	Ethylene glycol	24.30	26.04	27.73	1.69	0.61
40	Dimethyl sulphoxide	23.84	25.70	27.21	1.51	0.54
41	n-Pentanol	25.40	26.66	28.65	1.99	0.72
42	α-Picoline	25.09	26.20	28.62	2.42	0.87
43	s-Butyl alcohol	25.40	26.20	28.97	2.77	0.99
44	Ethylenediamine	24.14	25.40	27.55	2.15	0.77

In Table 2 our B_{KT} values and those from Kamlet and Taft [11] are compared (column 2). Also given are other popular basicity parameters.

The differences between Kamlet and Taft's B_{KT} and that of ours are not very big except for a few cases, *e.g.* anisole, methanol, and ethylene glycol. It is difficult to explain these differences which are greater than the experimental error, but they may be due to the sum of the following factors: the experimental error and the difference in slope between equations (5) and (6). In Table 2 there are also given B_{KT} values calculated from Kamlet and Taft's measurements by means of equation (5). It can be seen that the change in slope from (6) to (5) does not considerably affect the B_{KT} values.

Comparison of B_{KT} *with Other Basicity Parameters.*—Comparison of B_{KT} with other basicity parameters shows only a partial equivalence. In Figure 2 a plot of B_G *versus* B_{KT} for which the regression line has form (8)

TABLE 2

Comparison of B_{KT} values and other basicity scales

	Solvent	B_{KT} [a]	B_{KT} [b]	B_{KT} [c]	B_G [d]/cm^{-1}	B_{KP} [e]/cm^{-1}	DN [f]/kcal mol^{-1}
1	Carbon tetrachloride	0.00	0.00		31	0	
2	n-Pentane	0.00	0.00				
3	n-Hexane	0.00	0.00			0	
4	n-Heptane	0.00	0.00				
5	Cyclohexane	0.00	0.00			0	
6	Trichloroethylene		0.00				
7	Toluene			0.03	54		
8	Mesitylene	0.09				77	
9	*p*-Xylene	0.07				68	
10	*m*-Dichlorobenzene	0.00			42		
11	Methylene chloride		0.00			23	
12	Fluorobenzene	0.00				38	
13	Chloroform	0.00			35	14	
14	*o*-Xylene	0.08				68	
15	*m*-Xylene	0.10				68	
16	Chlorobenzene	0.00	0.00			38	
17	Bromobenzene	0.00			49	40	
18	Benzene	0.09	0.00		52	48	0.1
19	Ethylene chloride	0.00	0.00			40	
20	Anisole	0.04	0.24	0.25	75	155	
21	Phenetole	0.11			76	158	
22	Methyl n-butyl ketone	0.44			111		
23	Dibenzyl ether		0.41	0.41			
24	Dibutyl ether		0.50	0.56	129	285	
25	Dioxan	0.32	0.38	0.40	128	237	
26	Cyclohexene	0.18					
27	Nitromethane	0.38			59	65	2.7
28	Diethyl ether	0.49	0.51	0.57	129	280	19.2
29	Ethyl chloroacetate		0.33	0.40			
30	Acetonitrile	0.23			101	160	14.1
31	Tri-n-butylamine		0.67	0.75			
32	Ethyl acetate	0.45	0.48	0.51	91		17.1
33	Propylene carbonate	0.24					15.1
34	Ethyl benzoate		0.44	0.44			
35	Triethylamine		0.70	0.78	314	650	
36	Tetrahydropyran		0.52	0.55			
37	Methyl t-butyl ketone	0.45			97		
38	Acetone	0.37	0.51	0.52	116	224	17.0
39	Tetrahydrofuran	0.47	0.55	0.58	142	287	20.0
40	Cyclohexanone	0.41			132	242	
41	Chloroethanol		0.31	0.28			
42	Dimethylbenzylamine		0.59	0.63			
43	Butan-2-one		0.51	0.52	109	209	
44	Water	0.18	0.14	0.08	123	156	18.0
45	Ethyl n-butyl ketone	0.41					
46	Butyrolactone		0.46	0.45			
47	Cyclopentanone		0.54	0.54	124		
48	Methanol	0.71	0.62	0.63		218	19.0
49	Phenylethanol		0.64	0.64			
50	Benzyl alconol		0.56	0.54		208	
51	Formamide	0.40				270	24.7
52	t-Butylamine	0.69					57.0
53	*NN*-Dimethylformamide	0.54	0.73	0.70	159	291	26.6
54	Pyridine		0.67	0.66	260	472	33.1
55	Ethanol		0.77	0.80		235	
56	*N*-Methylformamide	0.46				287	
57	n-Propanol	0.37				236	
58	Ethylene glycol	0.61	0.51	0.49		224	
59	Dimethyl sulphoxide	0.54	0.74	0.73	193	362	29.8
60	n-Pentanol	0.72					
61	Triethyl phosphate		0.79	0.80		331	
62	Dimethylacetamide		0.73	0.73	178		27.8
63	n-Butyl alcohol		0.85	0.87		231	
64	*N*-Methylpyrrolidone		0.75	0.74			27.3
65	α-Picoline	0.87			265	495	
66	Isopropyl alcohol		0.92	0.95		236	
67	t-Butyl alcohol		0.95	0.98		247	
68	s-Butyl alcohol	0.90				240	
69	Ethylenediamine	0.77					55.0
70	Hexamethylphosphoramide	1.00	1.00	1.00			38.8

[a] This paper. [b] Kamlet and Taft parameters.[11] [c] Kamlet and Taft measurements of $\Delta\nu_{max.}$ applied to obtain B_{KT} by use of equation (5). [d] Data from refs. 19, 20, and 32. [e] Data from ref. 23. [f] Data from ref. 22 and V. Gutmann, *Electrochim Acta*, 1976, **21**, 661.

is presented. The correlation coefficient is 0.88 for 22 points. The other basicity parameters show a worse dependence on B_{KT}. However, when characteristic

$$B_{\mathrm{G}} = 20.8 \quad B_{\mathrm{KT}} + 41.8 \qquad (8)$$

vector analysis [25] is applied to B_{G}, B_{KT}, DN, and B_{KP} values for 15 solvents a variance of 92.89% is common. Such a high value of common variance for these basicity parameters may be due to the low number of solvents taken into account. However, there are no more experimental data by which to check this problem more precisely.

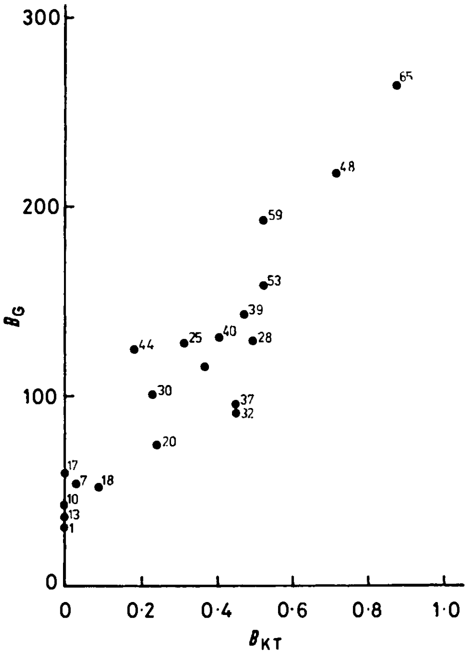

FIGURE 2 Plot of B_{G} *versus* B_{KT}. For key see Table 2

On Choosing Solvent Lewis Acidity and Basicity Parameters applied to Multiparameters Models [*as in Equation* (1)].—In conclusion it seems that B_{KT} can be recommended to replace B_{G} in the description of the solvent effect by one- or multi-parameter models. We should, however, be aware of their high sensitivity to the quality of the standard line [equations (5) and (6)] due in turn to the precision of measurement. Hence, measurements of the highest quality are required for this purpose.

A few more problems arise in using Lewis acidity parameters. Koppel and Palm [2] claimed that their E parameters are free of non-specific contribution due to the procedure described by equation (9) [2] where non-

$$E = E_{\mathrm{T}} - E25.57 - 14.39\,\frac{\varepsilon - 1}{\varepsilon + 2} - 9.08\,\frac{n^2 - 1}{n_2 + 2} \qquad (9)$$

specific contributions are subtracted from E_{T} values. These contributions were estimated for some non-acidic solvents by a plot of E_{T} *versus* $(\varepsilon - 1)/(\varepsilon + 2)$ and $(n^2 - 1)/(n^2 + 2)$. However, this idea does not prove to be as good as it might: the E values when plotted against E_{T} give a very good straight line, as shown in Figure 3 and equation (10) with r 0.983 for 23 solvents.

$$E = -38.95 + 0.964E_{\mathrm{T}} \qquad (10)$$

This equation works for solvents with $E_{\mathrm{T}} > 42$ (except for acetic acid, aniline, and t-butyl alcohol).

Thus it seems that it is not advantageous to use E in equations such as (1) since it is not only prone to experimental error as is E_{T}, but in addition it is biased by errors in estimation [equation (9)] which are quite considerable. The standard deviations for the regression coefficient of equation (9) are as big as 1.11 and 4.08 for the first and second slopes, respectively.

In conclusion it seems to be more appropriate to use E_{T} instead of E values as a solvent parameter.

Moreover, it should also be pointed out that for solvent effects for solvents with $\varepsilon > 10$—20 it is hopeless to expect any considerable contribution from non-specific interactions since for ε 10 and 20 the $(\varepsilon - 1)/(2\varepsilon + 1)$ values are 0.474 and 0.478, respectively, *i.e.* they are equal to 95 and 97% of the overall variation of this function. Thus for $\varepsilon > 10$ there remains not more than 5% of the total variation in $(\varepsilon - 1)/(2\varepsilon + 1)$. Hence, it seems that equations such as (1) may be applied successfully as a general equation whereas equations such as (11)

$$\delta Q = \alpha A + \beta B + \gamma \qquad (11)$$

are quite sufficient to account for solvent effects for solvents with $\varepsilon > 10$. A and B are Lewis acidity and basicity solvent parameters, preferably E_{T} and B_{KT} values. For convenience it is better to use normalized [36] values of these parameters, since they allow a direct comparison of α and β and even express them as the percentage contributions of Lewis acidity and basicity to the total solvent effect.

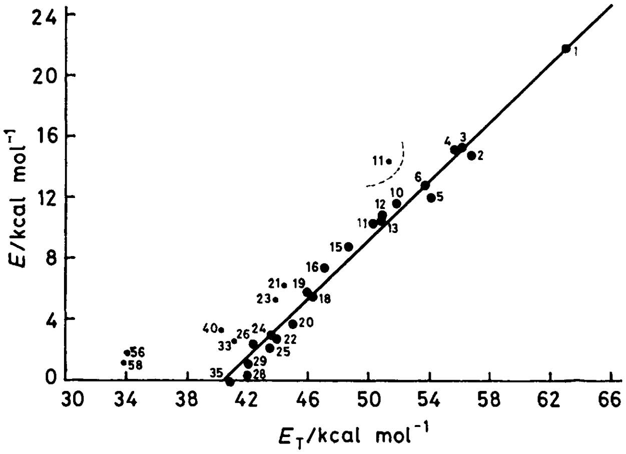

FIGURE 3 Plot of E [2] *versus* E_{T}.[19] 1, Water; 2, formamide; 3, ethylene glycol; 4, methanol; 5, *N*-methylformamide; 6, ethylene glycol; 10, ethanol; 11, acetic acid; 12, benzyl alcohol; 13, n-propyl alcohol; 14, n-butyl alcohol; 15, isopropyl alcohol; 16, isoamyl alcohol; 18, nitromethane; 19, acetonitrile; 20, dimethyl sulphoxide; 21, aniline; 22, sulpholan; 23, t-butyl alcohol; 24, *NN*-dimethylformamide; 25, dimethylacetamide; 26, acetone; 28, nitrobenzene; 29 benzonitrile; 33, dichloromethane; 35, hexamethylphosphoramide; 40, chloroform; 56, benzene; 58, toluene

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