Tetrahedron Vol 37, pp 119 to 125
Pergamon Press Ltd. 1981. Printed in Great Britain

0040-4020/81/0101-0119 $02.00/0

AN EMPIRICAL RELATIONSHIP BETWEEN THE ELUANT STRENGTH PARAMETER ε° AND SOLVENT LEWIS ACIDITY AND BASICITY

TADEUSZ M. KRYGOWSKI*, JAN P. RADOMSKI, ANNA RZESZOWIAK and PIOTR K. WRONA
Institute of Fundamental Problems of Chemistry, Department of Chemistry, University of Warsaw, Pasteura 1, PL-02093 Warsaw, Poland

and

CHRISTIAN REICHARDT*
Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-3550 Marburg, Fed. Rep. Germany

(*Received in Germany* 16 *April* 1980)

Abstract—It has been found that Snyder's eluant strength parameter ε°, used in liquid–solid adsorption chromatography, can be well described by a complementary Lewis acid-base model for solute–solvent interactions: $\varepsilon^{\circ} = 0.152 + 0.859 \cdot E_T^N + 0.332 \cdot B_{KT}$ (*cf* Eq. 9), with a correlation coefficient of $r = 0.949$ for 28 solvents. This result is in agreement with the theoretical interpretation of ε°. The correct statistical procedure for estimating the significance of added explanatory parameters in the sequential multiparameter regression analysis is shown (*cf* Appendix). A comprehensive list of improved Kamlet-Taft solvent basicity parameters, B_{KT}, is given.

Liquid–solid adsorption chromatography (LSC) which is often used to separate mixtures of reaction products requires a knowledge of the eluotropic properties of the solvents used. This solvent property is usually characterized quantitatively by Snyder's eluant strength parameter ε°[1,2] which is related to the ratio, K°, of sample concentration in adsorbed and unadsorbed phases by eqn (1),

$$\lg K^{\circ} = \lg V_a + \alpha(S^{\circ} - A_s \cdot \varepsilon^{\circ}) \qquad (1)$$

where V_a stands for the adsorbent surface volume (i.e. the volume of an adsorbed solvent monolayer, per unit weight of adsorbent), α stands for some function of the adsorbent activity, S° is the energy of adsorption of a sample compound on an adsorbent of unit activity ($\alpha = 1$) from n-pentane as solvent, and A_s is the area required by an adsorbed sample molecule on the adsorbent surface. Then, ε° stands for the adsorption energy of solvent per unit area of adsorbent with unit activity, defined as $\varepsilon^{\circ} = 0$ for n-pentane on alumina. The arrangement of solvents in order of increasing ε°-values, which are known for 46 solvents,[2] is referred to as an eluotropic series.

For a given mixture of samples and for adsorbents of the same type, the K°-value depends only on ε°: the larger its value, the smaller the K°-value, i.e. the smaller the concentration of adsorbed sample molecules. In order to arrive at eqn (1) Snyder assumed that the most important contributions to the net energy of adsorption are due to adsorption of the sample and eluant molecules onto the initially bare adsorbent surface. The solvation of the sample (adsorbate) and solvent molecules in the liquid phase has been neglected. Since in reality, however, the adsorbent surface is not bare, the total adsorption energy of the eluant which displaces the sample upon adsorption has to be subtracted from the adsorption energy of the sample in order to get the net adsorption energy.

Therefore, one can expect a kind of relation between some chemical properties of a solvent, namely, its Lewis acidity and basicity, and its ability to elute sample molecules adsorbed on a given chromatographic bed. Depending on the particular kind of adsorbent used, Lewis and/or Bronsted acidic and basic centres can be found on its surface. In practice, however, the possibilities of interaction between a given sample and a given kind of adsorbent are rather limited. With the exception of completely nonpolar molecules all other molecules can interact either as a Lewis acid or Lewis base. Thus, the solvent interacting with adsorbate and adsorbent has to apply to both possible interactions: solvents as Lewis acids or Lewis bases. The combination of Lewis acidic and basic properties of a solvent depends on its chemical constitution. Some solvents are mainly basic (e.g. pyridine), others are chiefly acidic (e.g. acetic acid), whereas some are amphoteric (e.g. water).

The aim of this paper is to analyse how the Lewis acidity and basicity of solvents may be used both to describe and predict their eluotropic properties. It should be mentioned that some correlation between ε° and the empirical parameter of Lewis acidity, $E_T(30)$,[3] has been found already by Rohrschneider.[4] Other solvent parameters have also been used to describe variations of the eluant strengths of solvents.[5-7]

The model

It has been suggested many times in the literature (for reviews see [8-10]), that solvent-dependent physicochemical properties, Q, such as rate and equilibrium constants, absorption maxima etc can be analysed in terms of regression analysis using various complementary solvent parameters as "explanatory variables". Pal'm and Koppel[11] summarised these ideas suggesting a four-parameter equation which includes, apart from Lewis acidity and basicity parameters, contributions due also to nonspecific interactions using functions of dielectric constant and refraction index. It was found recently,[12] that in many cases already a two-parameter regression analysis fits the solvent-dependent experimental data quite well, and a third or fourth nonspecific solvent parameter is not statistically significant. On the other hand, summarising a recently developed point of view,[13] a proper regression analysis of solvent effects should be carried out using a sequential regression analysis with careful estimation of the significance of subsequently added further solvent parameters (*cf* Appendix).

In our regression analysis of the eluant strength parameter ε we use a two-parameter approach as presented in eqn (2),

$$\varepsilon = \alpha \cdot A + \beta \cdot B + \gamma \qquad (2)$$

where A and B are empirical Lewis acidity and basicity parameters, resp., and α and β describe the sensitivity of ε to changes of solvent acidity and basicity. The choice of eqn (2) is justified since in LSC the adsorbed sample molecules are eluted due to competitive Lewis acid-base equilibria between sample and solvent molecules being adsorbed with a basic (acidic) part onto acidic (basic) centres of the adsorbent surface. Elution takes place when the Lewis acid-base interactions of eluant molecules with the adsorbent provide greater adsorption energy than the corresponding interaction of sample molecules with the adsorbent. Thus, for this part of interaction the solvent basicity and acidity is responsible for the progress of the elution. Furthermore, the adsorbed sample molecules are often dipoles with both positively charged (acidic) and negatively charged (basic) ends and hence their solvation by dipole–dipole and dipole-induced dipole interaction has to be taken into account. Thus, Lewis acidity as well as Lewis basicity parameters of the solvent are required in order to describe its eluotropic abilities.

The solvent acidity and basicity parameters

Of the various Lewis acidity parameters of solvents (for reviews see [8–10]) the most popular are the empirical parameters introduced by Winstein and Grunwald (Y-scale),[14] by Kosower (Z-scale),[15] and the $E_T(30)$-values of Dimroth and Reichardt,[3,8] modified recently by Pal'm and Koppel.[11,16] This modification was done in order to eliminate non-specific contributions to the $E_T(30)$-values, but a recent study of Krygowski *et al.*[21] has shown clearly, that for solvents with $E_T(30) > 42$ kcal/mol there is an excellent linear correlation (correlation coefficient $r = 0.983$ for 23 solvents) between the modified Koppel-Pal'm parameters and the original $E_T(30)$-values. Lewis basicity parameters of solvents are less popular in spite of being introduced as early as 1940 by Gordy and Stanford.[17] Recently, Pal'm and Koppel established a basicity scale based on this early approach,[11,16] but the low accuracy of these parameters for alcohols limits the application of their scale. Further parameters of Lewis basicity have been introduced by Koppel and Paju[18] and by Gutmann *et al.*,[19] but the recently published basicity parameter of Kamlet and Taft[20] has proven the most useful and easily measurable. For application of eqn (2) we have chosen a slightly modified form of the basicity parameter of Kamlet and Taft which gives more proper values for alcohols and water.[21] The $E_T(30)$-values[3,8] have been chosen as Lewis acidity parameters since not only are they known for more than 200 solvents but they have been also well tested.

Modification of Kamlet and Taft's solvent basicity parameter

Kamlet and Taft[20] introduced an empirical solvent scale of Lewis basicity applying the solvent-dependent UV/Vis absorption of five nitroaromatics in which the standard molecules used to determine the solvent basicity were assumed to interact with different solvents by the same solvation mechanisms. Then, using statistical procedures, Kamlet and Taft smoothed the normalized parameters (all values are in the range of 0–1) to get the best agreement for all five absorption processes. In this way they obtained an average solvent basicity parameter β_{1-5}. In our opinion, however, such a procedure is not an advantageous way for obtaining empirical solvent parameters since (i) there are large discrepancies between the parameters of some solvents obtained from different standard compounds, and (ii) when using statistical procedures in calculating these parameters their strict physical meaning is lost. For example, a large discrepancy is found for water as solvent, where $\beta_1 = 0.14$ and $\beta_2 = 0.47$, compared with e.g. $\beta_1 = 0.507$ for acetone.

In order to eliminate these shortcomings, we have modified the Kamlet–Taft procedure in the following manner:[21] we have chosen only one standard process in determining solvent basicity parameters, using the long-wavelength UV/Vis absorption of *p*-nitroaniline (p-NA) and of its homomorph, N,N-diethyl-*p*-nitroaniline (DEpNA). Both molecules are H-bond acceptors (HBA), but only *p*-nitroaniline can also act as H-bond donor (HBD). Then, following Kamlet–Taft's procedure, we plotted ν_{max}(pNA) vs ν_{max}(DEpNA) but using only solvents which are known to be very weak (if at all) σ- or π-donors in EPD/EPA interactions, thus excluding strong π-donor solvents such as benzene or its alkyl derivatives, in order to get a standard regression line free of any influence of specific interactions.

RESULTS AND DISCUSSION

Using solvents selected as mentioned above: n-pentane, n-hexane, n-heptane, cyclohexane, carbon tetrachloride, chloroform, 1,2-dichloroethane, fluorobenzene, chlorobenzene, bromobenzene, and *m*-dichlorobenzene, we obtained the regression line shown in eqn (3) with a correlation

$$\nu_{max}(\text{pNA}) = 1.128 \cdot \nu_{max}(\text{DEpNA}) + 0.319\,\text{kK} \quad (3)$$

coefficient of $r = 0.9989$. Kamlet and Taft obtained eqn. (4) for solvents such as n-hexane, n-heptane, cyclohexane, carbon tetrachloride, benzene, toluene, chlorobenzene, dichloromethane, 1,2-dichloroethane, and trichloroethylene with a correlation

$$\nu_{max}(\text{pNA}) = 1.035 \cdot \nu_{max}(\text{DEpNA}) + 2.64\,\text{kK} \quad (4)$$

coefficient of $r = 0.987$.

As a result of taking π-donor solvents into account, Kamlet and Taft's line (4) is slightly different from our line (3) and hence the estimated solvent basicities, measured as the bathochromic deviations of pNA absorptions from the line, are also slightly different. According to Kamlet and Taft, the solvent basicity parameters were determined as the enhanced bathochromic shifts of ν_{max}(pNA) obtained in HBA-solvents, compared to the corresponding ν_{max}-value predicted by eqn (3), i.e. for a situation without H-bond formation between *p*-nitroaniline and the basic solvent under study. Then, the basicity parameters were normalised in order to get zero values for solvents on line (3) and a value of 1.0 for the most basic solvent. Following Kamlet and Taft,[20] hexamethylphosphoric triamide was chosen as the most basic solvent for which the bathochromic deviation from line (3) is 2.78 kK. The equation for the modified Kamlet–Taft solvent basicity parameters, B_{KT}, is then as follows

$$B_{KT} = \frac{\Delta\nu}{2.78\,\mathrm{kK}}, \qquad (5)$$

Table 1. Solvent parameters: Snyder's eluotropic solvent strength parameters ε°,[1,2] normalized Lewis acidity parameters E_T^N according to Reichardt and Dimroth,[3,8] modified Kamlet and Taft B_{KT} parameters,[20,21] the ionizing power parameter IPP according to eqn (10), and reciprocal dielectric constants 1/ε (at 25°C)[9,23]

No.	Solvent	ε° a) (Al_2O_3)	E_T^N	B_{KT}	IPP	$1/\varepsilon$
1.	Cyclohexane	0.04	0.01	0.00	0.01	0.500
2.	Carbon tetrachloride	0.18	0.05	0.00	0.05	0.454
3.	Xylene (mixture of isomers)	0.26	0.07	0.20	0.27	0.435
4.	Diisopropyl ether	0.28	0.10	0.41	0.51	0.256
5.	Toluene	0.29	0.09	0.03	0.12	0.417
6.	Chlorobenzene	0.30	0.21	0.00	0.21	0.179
7.	Benzene	0.32	0.11	0.09	0.20	0.435
8.	Bromoethane	0.37	0.21	0.23	0.44	0.106
9.	Diethyl ether	0.38	0.12	0.41	0.53	0.233
10.	Chloroform	0.40	0.26	0.00	0.26	0.208
11.	Dichloromethane	0.42	0.32	0.00	0.32	0.112
12.	4-Methyl-2-pentanone	0.43	0.26	0.57	0.83	0.076
13.	1,2-Dichloroethane	0.44	0.34	0.23	0.57	0.096
14.	2-Butanone	0.51	0.32	0.41	0.73	0.054
15.	Acetone	0.56	0.35	0.37	0.72	0.048
16.	1,4-Dioxane	0.56	0.16	0.32	0.48	0.454
17.	Tetrahydrofuran	0.57	0.20	0.47	0.67	0.132
18.	Ethyl acetate	0.58	0.22	0.45	0.67	0.167
19.	Methyl acetate	0.60	0.28	0.45	0.73	0.149
20.	1,2-Diaminoethane	0.63	0.34	0.77	1.11	0.078
21.	Nitromethane	0.64	0.48	0.38	0.86	0.028
22.	Acetonitrile	0.65	0.47	0.23	0.70	0.027
23.	Pyridine	0.71	0.29	0.67	0.96	0.081
24.	Dimethyl sulfoxide	0.75	0.44	0.54	0.98	0.021
25.	1-Propanol	0.82	0.61	0.37	0.98	0.049
26.	Ethanol	0.88	0.65	0.77	1.42	0.041
27.	Methanol	0.95	0.76	0.71	1.47	0.031
28.	1,2-Ethanediol	1.11	0.71	0.61	1.32	0.027

[a] Values of ε° for silica and other polar adsorbents are similar to the values in this table. ε° = 0 for n-pentane on alumina by definition.

where the difference $\Delta\nu$ between the experimental values of ν_{max}(pNA) and those calculated from eqn (3) are given in kK.

In order to normalise the Lewis acidity parameter in the same way, we have transformed the original $E_T(30)$-values of Dimroth and Reichardt[3,8] into E_T^N-values according to eqn (6)

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{n-hexane})}{E_T(\text{water}) - E_T(\text{n-hexane})}. \qquad (6)$$

All solvent parameters used in our calculations, especially the modified B_{KT}-values which we have determined and the normalised E_T^N-values are compiled in Table 1.

The greatest advantage of solvent parameter normalisation is that in regression equations such as (2) the contribution of the acidic and basic solvent properties, expressed by the regression coefficients α and β, are approximately in the same scale of magnitude. Their ratio describes more correctly the proportion in which solvent acidity and basicity contribute to the solvent effect under study.

Relationships between ε°, B_{KT}, and E_T^N

The ε°-values of Table 1 are subject to linear and planar regression analysis. It was found that for all twenty-eight ε°-values the linear regression against E_T^N has the form of eqn (7),

$$\varepsilon^\circ = 1.099 \cdot E_T^N + 0.192 \qquad (7)$$

with a correlation coefficient of $r = 0.910$ (*cf* Fig. 1). When the most deviating points were excluded, the regression becomes more reliable according to eqn (8),

$$\varepsilon^\circ = 1.073 \cdot E_T^N + 0.161 \qquad (8)$$

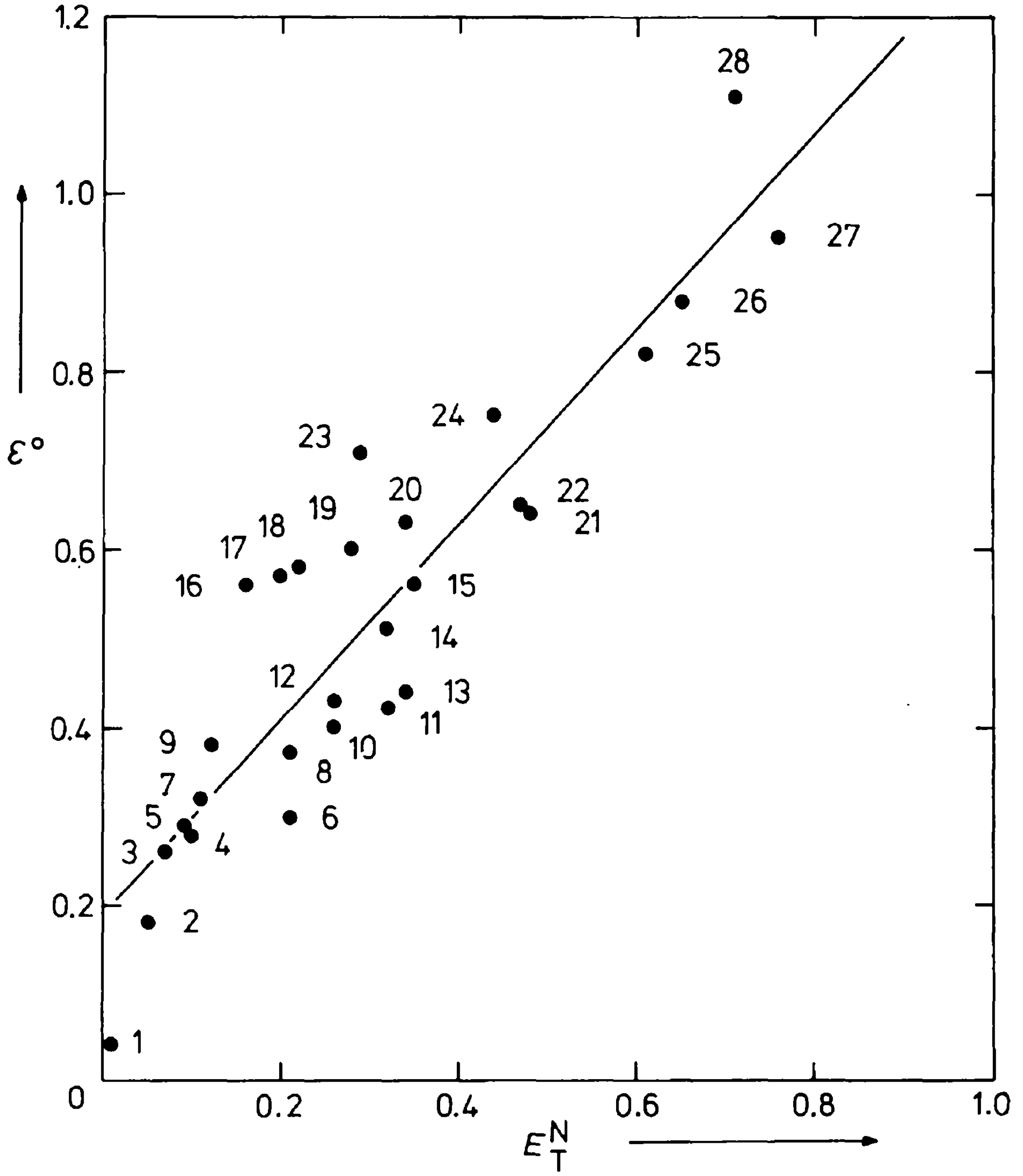

Fig. 1. Correlation between ε°-values[1,2] and E_T^N for twenty-eight solvents, according to eqn (7) (for solvent numbers *cf* Table 1).

with a correlation coefficient of $r = 0.951$. The following five solvents deviated most: 1,4-dioxane, tetrahydrofuran, pyridine, ethyl and methyl acetate. Some of these deviating solvents are either strongly basic or prone to chelating, or both. It can be assumed that the high basicity of some of these solvents increases their ε-values. In order to test this hypothesis, the planar regression, eqn (9), have been computed for the same set of 28 solvents:

$$\varepsilon = 0.152 + 0.859 \cdot E_T^N + 0.332 \cdot B_{KT} \qquad (9)$$

with a correlation coefficient of $r = 0.949$ (*cf* Fig. 2).

Comparison of the correlation coefficients for eqns (7) and (9) shows an improvement in accuracy of the planar regression. Application of the Fisher–Snedecor F-test[22] in a proper way (*cf* Appendix) indicates that addition of the second solvent parameter, B_{KT}, is significant at the 0.01 level. Thus, the value of $\beta = 0.33$ supports our suggestion that the eluotropic solvent strength depends on both, the Lewis acidic and basic properties of the eluants, with an approximate contribution of the latter equal to $[0.33/(0.33 + 0.86)] \cdot 100 = 28\%$. Inspection of Fig. 2 exhibits that the most deviating points belong to solvents the molecules of which are able to chelate the solute molecules.

Since both, the measured and the calculated solvent parameters, are subject to error (about 10–15%), it appears justified to introduce a scale of solvent parameters IPP (for "ionizing power parameter") as defined in eqn (10),

$$\mathrm{IPP} = E_T^N + B_{KT} \qquad (10)$$

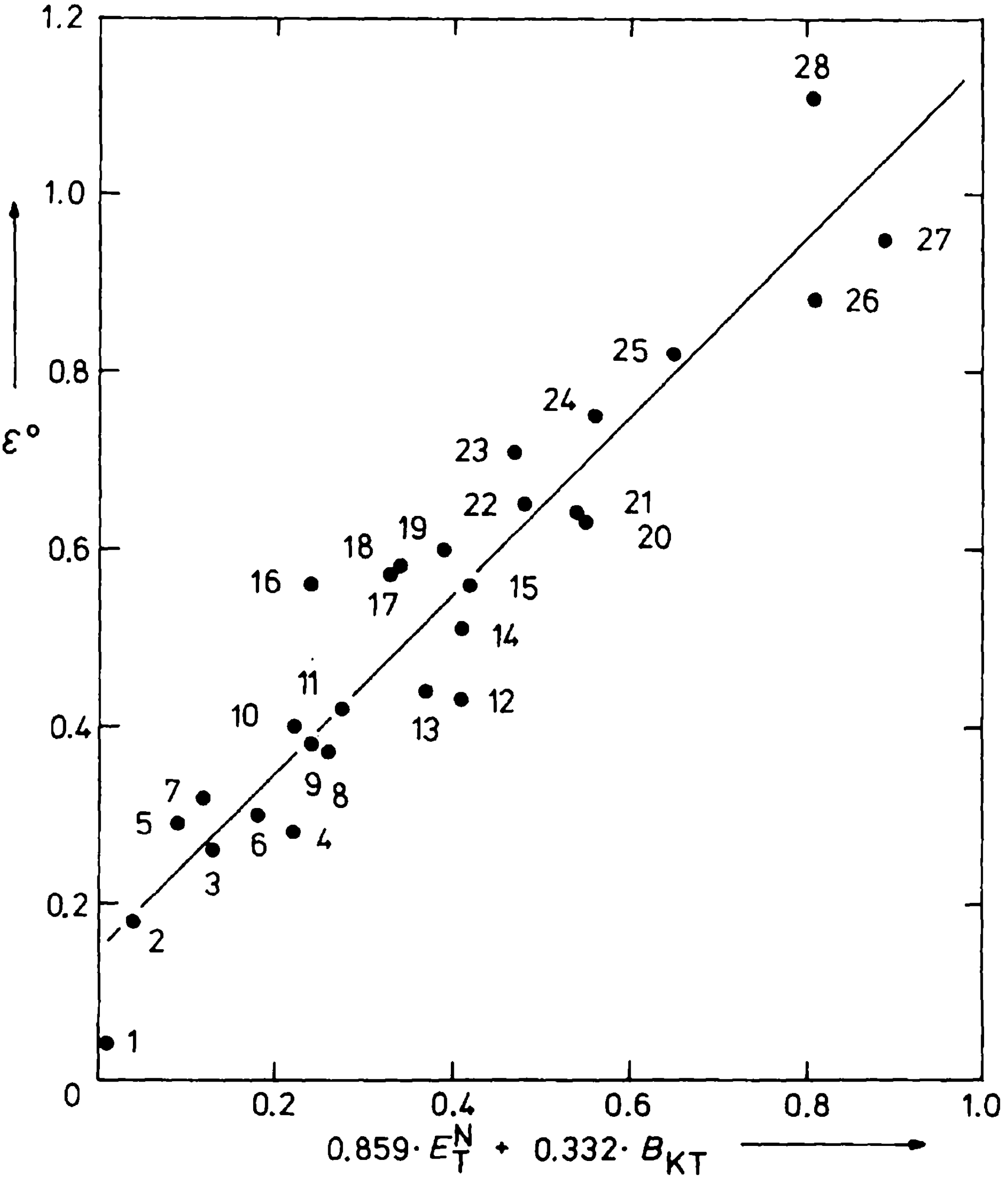

Fig. 2. Dependence of ε-values[1,2] on E_T^N and B_{KT} for twenty-eight solvents, according to eqn (9) (for solvent numbers *cf* Table 1).

assuming that $\alpha = \beta$ (*cf* eqn (2)). Using these IPP-values (Table 1) in the correlation with ε'-values, one obtaines eqn (11),

$$\varepsilon' = 0.562 \cdot \mathrm{IPP} + 0.159 \tag{11}$$

with a correlation coefficient of r = 0.922 for the same set of solvents used to calculate eqns (7) and (9). The small difference between the correlation coefficients of eqns (9) and (11) is not too significant, so that for simplicity the IPP-values can be used instead of E_T^N and B_{KT} for the description of the eluotropic properties of solvents.

The suggested parameter IPP can be understood as a solvent parameter describing the amphoteric Lewis acid-base properties of solvents and may be advantageous in the estimation of solute-amphoteric solvent interactions. It should be noted, however, that for a more quantitative analysis of solvent effects, eqn (2) should be applied—for the ε -values in form of eqn (9).

EXPERIMENTAL

The ν_{max}-values for eqn (3) were measured with commercially available (Fluka) *p*-nitroaniline and with N,N-diethyl-*p*-nitroaniline, synthesised according to Vogel,[25] purified both by crystallisation from EtOH.

The solvents used were commercial products purified by standard procedures.[23] These involved thorough drying and fractional distillation (under reduced pressure if necessary).

The UV/Vis spectra were recorded with an UV/Vis Specord (GDR) spectrophotometer with an approximate precision of 40 cm^{-1}.

Acknowledgement—This work was supported in Poland by the grant of the Interdepartment Project MR I-11. The authors are grateful to Mr. Janusz Borodziński for his assistance in carrying out some measurements and calculations.

APPENDIX

An important problem in any application of multiparameter regression analysis is the estimation of the significance of the next added "explanatory" parameter. Hence, a sequential regression analysis is recommended consisting of successive steps of analysis, starting with a linear regression and then bringing in further variables in the order of decreasing relevance.

Assuming, we have to analyse the variation of a physicochemical property Q_i measured in n solvents. The multiparameter equation proposed is:

$$Q_i = \alpha \cdot E_T^N + \beta \cdot B_{KT} + \gamma \cdot \frac{1}{\varepsilon}. \tag{12}$$

We start off with three linear regressions,

$$Q_i = \alpha_{11} \cdot E_T^N + \delta_{11} \tag{13}$$

with correlation coefficient r_{11},

$$Q_i = \beta_{11} \cdot B_{KT} + \delta_{12} \tag{14}$$

with correlation coefficient r_{12}, and

$$Q_i = \gamma_{11} \cdot \frac{1}{\varepsilon} + \delta_{13} \tag{15}$$

with correlation coefficient r_{13}.

Then, if eqns (13)–(15) are tested for *the same number* of experimental points, n, we choose that equation with the highest correlation coefficient to the next step of analysis. Let us assume for example that $r_{11} > r_{12}$ or r_{13}. Thus, we try to analyse the solvent effect by planar regressions as shown below:

$$Q_i = \alpha_{21} \cdot E_T^N + \beta_{21} \cdot B_{KT} + \delta_{21} \tag{16}$$

with correlation coefficient r_{21}, and

$$Q_i = \alpha_{22} \cdot E_T^N + \gamma_{21} \cdot \frac{1}{\varepsilon} + \delta_{22} \tag{17}$$

with correlation coefficient r_{22}.

Now we proceed to the planar regression with the higher correlation coefficient, e.g. $r_{21} > r_{22}$. The planar regression (16) is now analysed considering the significance of addition of the second term to the linear regression (13).

We calculate the Snedecor F-value[22] for the situation in which we compare differences between residual variances for regressions (13) and (16), resp., with the residual variance of regression (16), according to

$$F_{\alpha,f_1,f_2} = \frac{\sum_{i=1}^{n} (Q_i - \hat{Q}_i(13))^2 - \sum_{i=1}^{n} (Q_i - \hat{Q}_i(16))^2}{\sum_{i=1}^{n} (Q_i - \hat{Q}_i(16))^2/(n-2)}, \tag{18}$$

where $\hat{Q}_i(13)$ and $\hat{Q}_i(16)$ stand for values of Q_i estimated by regressions (13) and (16), resp., α is the significance level chosen for testing the hypothesis, and f_1 and f_2 stand for the degrees of freedom for the expressions in numerator and denominator, resp.: $f_1 = (n - 1) - (n - 2)$; $f_2 = n - 2$.

Eq (18) can be easily transferred into an expression (19) containing the correlation coefficients instead of residual variances, in our case r_{11} and r_{21}, resp.

$$F_{\alpha,f_1,f_2} = \frac{(r_{21}^2 - r_{11}^2) \cdot (n - 2)}{(1 - r_{21}^2)}. \tag{19}$$

Now, with eqn (19) F-values can be easily calculated using the appropriate correlation coefficients.

In order to decide whether the improvement due to addition of the second parameter is significant, we have to compare the calculated F-value of eqn (19) with the value of F_{α,f_1,f_2} taken from Statistical Tables.[24] If $F_{calc} > F_{\alpha,f_1,f_2}$, it means that we are allowed to assume that the improvement of correlation (16) relative to (13) is significant at the level α. In other words, we are in error in $\alpha \cdot 100$ cases when we accept this improvement.

If an investigator feels that the addition of a further solvent parameter, e.g. $1/\varepsilon$, can improve the regression, this procedure can be repeated with r_{21} and r of eqn (12), applied to eqn (19)

In this work we have to analyse the relation between ε' and E_T^N, B_{KT}, and $1/\varepsilon$. The three equations of linear regression for 28 solvents (n = 28) are as follows:

$$\varepsilon = 1.099 \cdot E_T^N + 0.192 \qquad r = 0.910 \qquad (20$$

$$\varepsilon = 0.744 \cdot B_{KT} + 0.265 \qquad r = 0.753 \qquad (21$$

$$\varepsilon' = -1.108 \cdot \frac{1}{\varepsilon} + 0.716 \qquad r = -0.727. \qquad (22$$

For further analysis we have chosen the ε' vs E_T^N dependence The corresponding equations of the two-paramete regression with (E_T^N, B_{KT}) and $(E_T^N, 1/\varepsilon)$ are as follows (fo n = 28):

$$\varepsilon = (0.859 \pm 0.087) \cdot E_T^N + (0.332 \pm 0.059) \cdot B_{KT} + (0.152 \pm 0.018) \qquad (23$$

$$r_{21} = 0.942; \; F_{imp} = 13.69$$

and

$$\varepsilon = (1.064 \pm 0.026)\cdot E_T^N - (0.057 \pm 0.041)\cdot\frac{1}{\varepsilon} + (0.213 \pm 0.047) \tag{24}$$

$$r_{22} = 0.911;\ F_{imp} = 0.27.$$

The addition of the second parameter, B_{K1} or $1/\varepsilon$, is statistically significant if the F_{imp}-value is greater than $F_{(0.01,26,1)} = 7.64$. It follows from these calculations that only eqn (23) is statistically significant. The third possible two-parameter regression with B_{Kr} and $1/\varepsilon$ as solvent parameters has the form:

$$\varepsilon = (0.487 \pm 0.198)\cdot B_{K1} - (0.651 \pm 0.047)\cdot\frac{1}{\varepsilon} + (0.468 \pm 0.067) \tag{25}$$

$$r_{23} = 0.825;\ F_{imp} = 9.30.$$

The improvement from eqn (21) to eqn (25) is significant at the same level as an improvement from eqn (20) to eqn (23), i.e. in both cases addition of the second parameter is significant at $\alpha = 0.01$. In the first case, however, the precision of the improved eqn (23) is with $r_{21} = 0.942$ much higher than in the second case with $r_{23} = 0.825$ only.

Therefore, we stop our analysis at eqn (23) since the percentage of the explanation of variance for variation of ε is $r^2 \cdot 100 = 88.7\%$. Since the experimental errors in the determination of solvent parameters are in the order of up to 10%, it is not reasonable to carry out further analysis steps. Moreover, in eqns (24) and (25) the added $1/\varepsilon$-term is not statistically significant.

REFERENCES

[1] L. R. Snyder, *J. Chromatogr.* **8**, 178 (1962); L. R. Snyder, *Principles of Adsorption Chromatography*. Dekker, New York (1968).

[2] L. R. Snyder, *Solvent Selection for Separation Processes*. In *Techniques of Chemistry* (3rd Ed.) (Edited by E. S. Perry and A. Weissberger. Vol. XII, Chap. II, p. 25 ff. Wiley-Interscience, New York (1978).

[3] K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann.* **661**, 1 (1963); C. Reichardt, *Ibid.* **752**, 64 (1971).

[4] L. Rohrschneider, *Analyt. Chem.* **45**, 1241 (1973).

[5] L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*. Wiley, New York (1974).

[6] A. F. M. Barton, *Chem. Rev.* **75**, 731 (1975).

[7] B. L. Karger, L. R. Snyder, and C. Eon, *J. Chromatogr.* **125**, 71 (1976); *Analyt. Chem.* **50**, 2126 (1978).

[8] C. Reichardt, *Angew. Chem.* **91**, 119 (1979); *Ibid.* Int. Ed. Engl. **18**, 98 (1979).

[9] C. Reichardt, *Solvent Effects in Organic Chemistry*. Chapter 7, p. 225 ff. Verlag Chemie, Weinheim, New York (1979).

[10] *Advances in Linear Free Energy Relationships* (Edited by N. B. Chapman and J. Shorter). Plenum Press, London, New York (1972); *Correlation Analysis in Chemistry—Recent Advances* (Edited by N. B. Chapman and J. Shorter). Plenum Press, London, New York (1978).

[11] I. A. Koppel and V. A. Pal'm, in *Advances in Linear Free Energy Relationships*, Chap. 5, p. 203 ff. (Edited by N. B. Chapman and J. Shorter). Plenum Press, London, New York (1972).

[12] T. M. Krygowski and W. R. Fawcett, *J. Am. Chem. Soc.* **97**, 2143 (1975); *Austr. J. Chem.* **28**, 2115 (1975); *Can. J. Chem.* **54**, 3283 (1976).

[13] N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter and R. Wilkinson, *J. Chem. Soc.* Perkin Trans. II 962 (1974).

[14] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.* **70**, 846 (1948).

[15] E. M. Kosower, *Ibid.* **80**, 3253 (1958).

[16] I. A. Koppel and V. A. Pal'm, *Reakts. Sposobnost. Org. Soedin.* **8**, 291 (1971); *Organic Reactivity* **8**, 296 (1971); *Chem. Abstr.* **76**, 28418 k (1972); I. A. Koppel and A. I. Paju, *Reakts. Sposobnost. Org. Soedin.* **11**, 139 (1974); *Organic Reactivity* **11**, 137 (1974); *Chem. Abstr.* **82**, 42806 r (1975).

[17] W. Gordy and S. C. Stanford, *J. Chem. Phys.* **9**, 204 (1941).

[18] I. A. Koppel and A. I. Paju, *Reakts. Sposobnost. Org. Soedin.* **11**, 121 (1974); *Organic Reactivity* **11**, 121 (1974); *Chem. Abstr.* **82**, 42805 q (1975).

[19] V. Gutmann and A. Scherhaufer, *Montsh. Chem.* **99**, 335 (1968); V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*. Plenum Press, New York (1978).

[20] M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.* **98**, 377 (1976).

[21] T. M. Krygowski, E. Milczarek, and P. K. Wrona, submitted to *J. Chem. Soc.* Perkin Trans. II.

[22] G. W. Snedecor and W. G. Cochran, *Statistical Methods*. The Iowa State University Press, Ames (1975).

[23] J. A. Riddick and W. B. Bunger, *Organic Solvents*. (3rd Edition) in *Techniques of Chemistry* (Edited by A. Weissberger), Vol. II. Wiley-Interscience, New York (1970).

[24] For details of the statistics as well as F-values see ref 22.

[25] A. I. Vogel, *A Textbook of Practical Organic Chemistry*. Longmans, Green, London (1961).