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RE-EVALUATION OF THE SOLVENT TRIANGLE AND COMPARISON TO SOLVATOCHROMIC BASED SCALES OF SOLVENT STRENGTH AND SELECTIVITY

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SUMMARY

The principal thrust of this work is to explore the validity of the major assumptions made in developing the solvent triangle and to examine the relationship between the selectivity parameters derived from the solvent triangle and independently determined, solvatochromically based measures of dipolarity, hydrogen bond acidity, and basicity. It is shown that the original solvent triangle classification scheme is only slightly modified by the use of a much more rigorous correction for the behavior of a reference alkane. These results are based on new experimental measurements of the gas-liquid partition coefficients of Rohrschneiders' probe solutes and a set of alkanes (*n*-pentane–*n*-octane). More fundamentally we have shown that the original selectivity parameters based on the properties of ethanol, dioxane and nitromethane are all lumped parameters composed of dipolar, hydrogen bond acidity and hydrogen bond basicity terms. Perhaps most importantly the original probe solutes used to develop the solvent triangle are shown to be inefficient choices in terms of their ability to discriminate between similar solvents. This is an important limitation in that the primary use of the solvent triangle has been for the optimization of selectivity and the classification of phases.

INTRODUCTION

A qualitative and quantitative understanding of the nature and strength of solute-solvent interactions is obviously important in chromatography. A major goal of many studies has been the development of schemes for classifying solvents to facilitate the selection of an optimum mobile phase for use in liquid chromatography.

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Similarly, the classification of stationary phases in gas chromatography requires the use of a set of probe solutes that explore different types of physicochemical interactions with the stationary phase. Accordingly, many approaches have been developed for separating the contributions of dipolarity, hydrogen bond acidity (HBA) and hydrogen bond basicity (HBD) to the overall solvent strength. Intuitively, any two phases that are similar in all three of the above properties should behave similarly in terms of their retention properties. The Snyder solvent triangle approach has been used very widely in chromatography^{1,2}. In contrast, in chemical engineering, the separation of the cohesive energy density (solubility parameters) into similar types of terms has received considerable attention^{3,4}, most recently by Thomas and Eckert⁵. The solubility parameter approach has also been used extensively in chromatography^{6,7}. A third approach, the use of the phenomenon of solvatochromism, in conjunction with linear solvation energy relationships (LSER), is widely used by physical organic chemists to rationalize, correlate and predict the effect of solvent on the rates and equilibria of chemical reactions⁸⁻¹⁰. This last approach has also been used to unravel the role of specific chemical processes in gas-liquid and liquid-liquid partitioning^{8,11,12}.

Several of the studies described above made extensive use of Rohrschneider's gas-liquid partition data for six prototypical solutes (octane, toluene, nitromethane, ethanol, dioxane and 2-butanone) in 81 common liquids¹³. The approach taken by Snyder is based entirely on this data set. In Snyder's approach, the P' polarity scale is a global or overall measure of solvent strength that is a composite of all types of solute-solvent interactions, except for dispersive interactions. Other workers have used the Rohrschneider data set to test their models¹¹. Recently many of the above data have been redetermined by a methodology which circumvents most of the shortcomings and assumptions inherent in Rohrschneider's measurements¹⁴. In addition, the gas-liquid partition coefficients of a set of alkanes in the same solvents have been measured¹⁵.

The purpose of this paper is to examine, in light of this new data, two of the approaches used to classify and quantify solvent properties. The first method is the solvent triangle and P' scale^{1,2}. The second approach is that of Kamlet and Taft⁸, in which gas-liquid partition coefficients are correlated with the solvatochromic scales describing solvent dipolarity-polarizability (π^*), hydrogen bond acidity (α) and basicity (β). In this study, we employ an additional term to account for solvent reorganization effects in self-associating solvents¹⁶. In addition, we have evaluated the suitability of each of these two methods for ranking and classifying solvents, and discuss appropriate modifications to these solvent strength scales and classification methods.

THEORY

P' polarity scale

Snyder's approach^{1,2} is based on the assumption that the dispersive interactions and cavity formation contributions can be eliminated from the partition coefficient by first multiplying the partition coefficient by the solvent molar volume, V_s , as shown in eqn. 1, and then referencing this quantity to that which would result for a hypothetical alkane with the same molar volume as the solute,

$$\log K'_{i,s} = \log(K_{i,s}V_s) \quad (1)$$

$$\log K''_{i,s} = \log K'_{i,s} - (V_i/163) \log(K_{0,s}V_s) \quad (2)$$

Here $K_{i,s}$ is the gas-liquid partition coefficient of solute i in solvent s , V_s is the solvent molar volume, $K_{0,s}$ is the gas-liquid partition coefficient for octane in solvent s , and V_i is the molar volume of the probe solute. The term 163 is the molar volume of octane. In the absence of measured values for the partition coefficients for a series of n -alkanes, the above correction is the best available expedient. The accuracy of this approach, however, is entirely contingent upon the validity of Snyder's assumption that the intercept of a plot of the log of the partition coefficient for the n -alkanes vs. the molar volume (V_{alkane}) is insignificant.

In Snyder's approach, the $\log K''_{i,s}$ value given in eqn. 2 was then modified by subtracting the average of the $\log K''_{i,s}$ values for the i th solute in the solvents hexane, cyclohexane, and isooctane ($\log K'_{i,\text{hci}}$) as shown in eqn. 3

$$P'x_i = \log K''_{i,s} - \log K'_{i,\text{hci}} \quad (3)$$

The calculations described by eqns. 1-3 were done using ethanol ($P'x_e$), p -dioxane ($P'x_d$) and nitromethane ($P'x_n$) as solutes, where the following condition holds

$$1 = x_e + x_d + x_n \quad (4)$$

Snyder suggested that x_e , x_d and x_n should be measures of the solvent hydrogen bond basicity, the solvent hydrogen bond acidity and the solvent dipolarity, respectively.

Poppe and Slaats¹⁷ proposed two modifications to the approach described above. First, they suggested that a Flory-Huggins correction factor be included in eqn. 1 to account for the entropic contribution to the partition coefficient due to differences in molecular size. The net effect of this correction is to arithmetically completely eliminate the dependence on the molar volume of the solvent introduced in eqn. 1, so that the final equation for $P'x_i$ becomes

$$P'x_i = \log K_{i,s} - (V_i/163) \log K_{0,s} - \log K_{i,\text{hci}} + (V_0/163) \log K_{0,\text{hci}} \quad (5)$$

In general, the magnitude of the Flory-Huggins factor is relatively small for molecules with similar sizes. The second correction proposed by these authors involves an improvement in the estimate of the contribution from a hypothetical n -alkane with the same molar volume as the solute, so that the expression for $P'x_i$ then becomes

$$P'x_i = \log K_{i,s} - (V_i/163) \log K_{0,s} - \log K_{i,\text{hci}} + \\ + (V_0/163) \log K_{0,\text{hci}} + (\beta_{\text{hci}} - \beta_s) [1 - (V_i/163)] \quad (6)$$

where β_s is a term which takes into account the fact that a plot of $\log K_{\text{alkane},s}$ vs. V_{alkane} may have a non-zero intercept. These authors found that the Flory-Huggins correction (equivalent to the omission of the original V_s correction) produced $P'x_i$ values for the non-polar alkane solvents that were virtually independent of the solvent. More importantly, changes in the P' values and the x_e , x_d and x_n factors were negligible

in terms of the solvent classification scheme¹⁷. These authors were unable to evaluate the proposed correction given in eqn. 6, due to the difficulty in estimating the β_s values.

Recently, gas-liquid partition coefficient data for a series of alkanes in the Rohrschneider solvents have become available¹⁵. These data permit the estimation of the contribution from a non-zero intercept. In all solvents studied, the data for at least four *n*-alkanes (pentane to octane) give rise to precise linear relationships of the following form,

$$\log K_{\text{alkane},s} = m_s V_{\text{alkane}} + b_s \quad (7)$$

where m_s and b_s are the solvent dependent slope and intercept, respectively. In addition, limited data for a few of the solvents studied here show linear behavior with carbon number and hard core volume down to a carbon number of two, although the relationship with molar volume is not as linear¹⁸. It can therefore be argued that the solute volume parameter used in eqn. 7 should be a molecular hard core volume (*e.g.*, based on the Bondi-group contribution method¹⁹), rather than a molar volume as is employed here. This was investigated briefly, however the approach, although quantitatively different, showed no changes in the final classification scheme.

If the linear extrapolation given by eqn. 7 is assumed to be valid, and the V_s correction introduced in eqn. 1 is omitted, as is suggested by the theoretical work of Ben-Naim¹⁸, the following expression for $P'x_i$ is obtained

$$P'x_i = \log K_{i,s} - m_s V_i - b_s - \log K_{i,\text{hcl}} + m_{\text{hcl}} V_i + b_{\text{hcl}} \quad (8)$$

This approach is somewhat different from that proposed by Poppe and Slaats as given in eqn. 6.

Correlation with solvatochromic parameters

A second solvent characterization scheme has been reported by Kamlet *et al.*⁸ that is similar to the approach described above; it is based on a dissection of the partition coefficient into contributions from solvent dipolarity, hydrogen bond basicity and hydrogen bond acidity. Here, the partition coefficient data were corrected for dispersion and cavity formation by referencing to an alkane of similar size to the solute. These values were then correlated with the solvatochromic scales. The parameters π^* , α , β and δ are the solvatochromic parameters describing the solvent dipolarity-polarizability, hydrogen bond acidity, hydrogen bond basicity, and the polarizability correction factor, respectively. These solvent parameters were then used as linear energy parameters in an LSER. For aliphatic solvents, the correlation takes the form

$$\log K_{i,s} - \log K_{\text{alkane},s} = SP_0 + s\pi^* + \alpha\alpha + b\beta \quad (9)$$

or alternatively (in aromatic and polyhalogenated solvents), to correct for differences in the polarizability contribution (δ) to π^*

$$\log K_{i,s} - \log K_{\text{alkane},s} = SP_0 + s\pi^* + d\delta + \alpha\alpha + b\beta \quad (10)$$

where δ is 0 for non-chlorinated, aliphatic solvents, 0.5 for polychlorinated, aliphatic solvents, and 1.0 for aromatic solvents. Here, SP_0 is the solute dependent intercept, which corresponds to the corrected $\log K$ value for a solvent with zero values for π^* , α , β and δ (*i.e.*, cyclohexane). The coefficients s , a , b and d are the solute dependent coefficients which can be determined from multiple linear regression; these coefficients should describe the solute dipolarity–polarizability, hydrogen bond basicity, hydrogen bond acidity, and the contribution from the polarizability correction factor for the solute, respectively.

In the work of Kamlet *et al.*⁸ ethane was used as the reference alkane solute for ethanol and nitromethane, propane the reference for 2-butanone and *p*-dioxane, and butane the reference for toluene. A similar analysis of the newer experimental results has been carried out, using the Hildebrand solubility parameter to estimate the relative contribution of the cavity formation step²⁰.

In this work, instead of referencing with respect to an alkane with similar size, the gas–liquid partition coefficients are referenced with respect to a hypothetical alkane with a molar volume equal to the solute molar volume, obtained from the regression results calculated using eqn. 7. The appropriate equation for the examination of the selectivity parameters in terms of the solvatochromic parameters can then be given as

$$P'x_i = SP_0 + s\pi^* + d\delta + a\alpha + b\beta \quad (11)$$

Since the terms involving the averages of the solvent characteristics for hexane, cyclohexane, and isooctane (*hci*) in eqn. 8 are constants, the correlation given by eqn. 11 differs from that given in eqn. 10 by a constant. In this work, all correlations are based on the product $P'x_i$, rather than x_i , since this should yield coefficients which can be interpreted based on known solute properties, and is consistent with an analysis of the units involved (energy), whereas the x_i values are normalized, dimensionless quantities.

Recent work has demonstrated that an additional term must be added to eqn. 11 to adequately model the gas–liquid partition behavior for the wide range of solvents employed here¹⁶. An additional parameter, $\alpha\beta$, which is the product of the solvent hydrogen bond basicity and acidity, is included to give the following equation

$$P'x_i = SP_0 + s\pi^* + d\delta + a\alpha + b\beta + h\alpha\beta \quad (12)$$

This term is required to account for the additional reorganization of self-associating solvents which occurs when the solute is capable of hydrogen bonding.

EXPERIMENTAL

Data for 65 solvents were evaluated in the reassessment of Snyder's P' scale. In this case, only those solvents for which gas–liquid partition coefficients were available for octane, ethanol, *p*-dioxane and nitromethane were included in the data set. For those solvents for which data were not determined in the more recent study¹⁴, values from the original Rohrschneider set¹³ were used, so that each of the 65 solvents was characterized by four gas–liquid partition coefficient values. In addition, data for *n*-alkane solutes were available for 58 of these solvents¹⁵. A list of these solvents is given in Table I.

TABLE I
RE-EVALUATION OF P' AND x_i VALUES*

<i>Solvent</i>	P'	x_e	x_d	x_n
Hexane**	-0.14			
Decane**	0.06			
Hexadecane**	0.20			
Isooctane**	-0.03			
Squalane**	0.44			
Cyclohexane**	0.17			
Triethylamine	2.19	0.66	0.08	0.26
Carbon disulfide	1.07	0.22	0.39	0.39
Diethyl ether	3.15	0.53	0.13	0.34
Dibutyl ether	1.65	0.48	0.14	0.38
Diisopropyl ether	1.83	0.51	0.10	0.39
Tetrahydrofuran	4.28	0.41	0.19	0.40
<i>p</i> -Dioxane	5.27	0.37	0.23	0.40
Bis-2-ethoxyethyl ether	4.13	0.38	0.20	0.42
2-Butanone	4.62	0.36	0.20	0.43
Cyclohexanone	4.72	0.37	0.21	0.41
Ethyl acetate	4.24	0.36	0.22	0.42
Acetonitrile	5.64	0.33	0.25	0.42
Butyronitrile	4.60	0.35	0.23	0.42
Nonanenitrile	3.66	0.36	0.22	0.42
Pentadecanenitrile	2.84	0.36	0.21	0.43
<i>N,N</i> -Dimethylformamide	6.31	0.40	0.21	0.39
<i>N,N</i> -Dimethylacetamide	6.45	0.41	0.20	0.38
Hexamethylphosphoramide	7.10	0.47	0.16	0.37
γ -Butyrolactone	6.27	0.34	0.26	0.40
<i>N</i> -Methylpyrrolidone	6.45	0.41	0.21	0.39
Nitromethane	5.78	0.29	0.30	0.41
Dimethylsulfoxide	7.29	0.40	0.22	0.37
Benzene	3.19	0.27	0.28	0.45
Toluene	2.68	0.28	0.27	0.45
<i>p</i> -Xylene	2.55	0.28	0.26	0.45
Acetophenone	4.95	0.35	0.25	0.40
Ethoxybenzene	3.34	0.30	0.27	0.43
Benzonitrile	4.77	0.32	0.26	0.41
Nitrobenzene	4.74	0.29	0.29	0.43
Pyridine	5.53	0.42	0.22	0.36
2-Picoline	5.15	0.44	0.20	0.36
Anisole	3.87	0.30	0.28	0.42
Methylene chloride	4.29	0.27	0.33	0.40
Chloroform	4.31	0.31	0.35	0.34
Carbon tetrachloride	1.56	0.26	0.40	0.34
Methylene iodide	4.31	0.28	0.37	0.35
Fluorobenzene	3.03	0.26	0.29	0.44
Chlorobenzene	3.02	0.27	0.30	0.43
Bromobenzene	3.14	0.28	0.31	0.42
Ethanol	4.40	0.52	0.19	0.29
Propanol	4.13	0.54	0.19	0.27
Butanol	4.11	0.54	0.18	0.28
Octanol	3.23	0.58	0.17	0.25
Isopropanol	3.92	0.57	0.17	0.26
<i>tert.</i> -Butanol	4.03	0.56	0.20	0.24

TABLE I (continued)

Solvent	P'	x_e	x_d	x_n
Isopentanol	3.46	0.58	0.17	0.25
Methoxy ethanol	5.71	0.41	0.22	0.36
Benzyl alcohol	6.06	0.40	0.29	0.31
Trifluoroethanol	7.55	0.40	0.33	0.27
Hexafluoroisopropanol	8.68	0.45	0.27	0.27
Aniline	6.31	0.33	0.31	0.36
Acetic acid	6.13	0.41	0.30	0.30
Perfluorohexane**	-0.84			
Nitroethane***				
Ethylene glycol***				
Diethylene glycol***				
<i>m</i> -Cresol***				
Benzyl ether***				
2,6-Lutidine***				
Iodobenzene***				

* These values were calculated using eqn. 8, based on the linear correlation of the *n*-alkane partition coefficients.

** This solvent has a value for P' which is too small to obtain reliable x_e , x_d and x_n values.

*** Data for the partition coefficients for the *n*-alkane solutes in these solvents were not available, so P' , x_e , x_d and x_n values based on eqn. 8 could not be calculated.

Data for 44 solvents were used in the calculation of the coefficients for the solvatochromic regression equations. These solvents were chosen based on the availability of π^* , α and β values for these liquids. These solvents, along with the corresponding values for π^* , α and β^{21} are given in Table II. All multiple linear regression results were obtained using the Kalman filter, a recursive, least-squares algorithm^{22,23}. The regression program was written in Pascal, and run on an IBM PC compatible computer with an 8087 coprocessor and 384K of memory.

RESULTS AND DISCUSSION

P' polarity scale

Snyder's P' values and the selectivity parameters, x_e , x_d and x_n were reevaluated using the new partition coefficient data for the Rohrschneider solvents. Three different calculation approaches based on eqns. 3, 5 and 8 were employed. As will be demonstrated, there were few significant differences in the resulting classification scheme. For 57 of 65 solvents considered by Snyder given in Table I¹, the newer experimental partition coefficient values are used to compute new P' values via eqn. 3 (the original approach used by Snyder). The following regression equation was obtained for the correlation of the new P' values (P'_{new}) based on eqn. 3, with the original values reported by Snyder (P'_{old}).

$$P'_{\text{new}} = (0.921 \pm 0.017) P'_{\text{old}} + (0.040 \pm 0.073) \quad (13)$$

$$r^2 = 0.983 \quad s = 0.236 \quad n = 57$$

The value for the slope (0.921) in eqn. 13 is explained by the fact that the P'_{old} values

TABLE II
SOLVENT SOLVATOCHROMIC PARAMETERS*

<i>Solvent</i>	π^*	α	β
Pentane	-0.08	0	0
Hexane	-0.04	0	0
Heptane	-0.02	0	0
Decane	0.03	0	0
Hexadecane	0.08	0	0
Isooctane	-0.04	0	0
Cyclohexane	0	0	0
Triethylamine	0.14	0	0.71
Diethyl ether	0.27	0	0.47
Dibutyl ether	0.24	0	0.46
Diisopropyl ether	0.27	0	0.49
Tetrahydrofuran	0.58	0	0.55
<i>p</i> -Dioxane	0.55	0	0.37
Acetone	0.71	0.08	0.48
2-Butanone	0.67	0.06	0.48
Cyclohexanone	0.76	0	0.53
Ethyl acetate	0.55	0	0.45
Acetonitrile	0.75	0.19	0.31
N,N-Dimethylformamide	0.88	0	0.69
N,N-Dimethylacetamide	0.88	0	0.76
Hexamethylphosphoramide	0.87	0	1.01
γ -Butyrolactone	0.87	0	0.49
Nitromethane	0.85	0.22	0.25
Dimethylsulfoxide	1.00	0	0.76
Benzene	0.59	0	0.10
Toluene	0.55	0	0.11
<i>p</i> -Xylene	0.51	0	0.12
Acetophenone	0.90	0	0.49
Benzonitrile	0.90	0	0.41
Nitrobenzene	1.01	0	0.39
Pyridine	0.87	0	0.64
Anisole	0.73	0	0.22
Methylene chloride	0.82	0.30	0
Chloroform	0.58	0.44	0
Carbon tetrachloride	0.28	0	0
Ethylene chloride	0.81	0	0
Fluorobenzene	0.62	0	0.07
Chlorobenzene	0.71	0	0.07
Bromobenzene	0.79	0	0.06
Methanol	0.60	0.93	0.62
Ethanol	0.54	0.83	0.77
Butanol	0.47	0.79	0.88
Isopropanol	0.48	0.76	0.95
<i>tert.</i> -Butanol	0.40	0.68	1.01

* Solvatochromic parameters from ref. 21.

were multiplied by 1.1 before tabulation. The intercept is not significantly different from zero. These data are shown in Fig. 1. There are five solvents for which the absolute discrepancy between the P' scale based on the new and old Rohrschneider

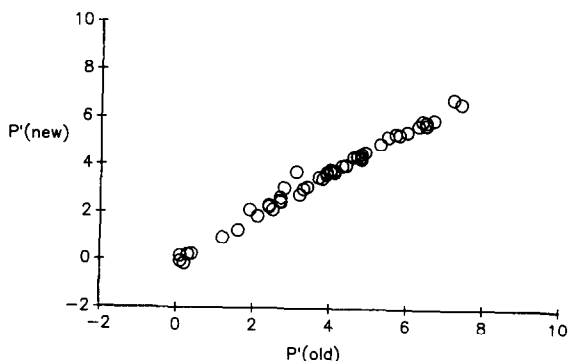


Fig. 1. Plot of new P' values calculated using eqn. 3 vs. the original values reported by Snyder in ref. 1.

data is greater than ± 0.3 : diethylene glycol, ethylene glycol, triethylamine, methylene chloride and ethyl ether. The discrepancy in the values for the glycols is not surprising; these solvents are very viscous, and the difficulty of making accurate gas-liquid partition coefficient determinations on them has been previously noted¹⁴. The value for the partition coefficient for *p*-dioxane in methylene chloride in Rohrschneider's original data set is also in error¹⁴. In general, the new and old values for the x_e , x_d and x_n selectivity scales are in agreement within ± 0.03 .

The most marked deviations for the Snyder selectivity parameters were observed for triethylamine and methylene chloride, which were not correctly classified in the original solvent triangle, and for chloroform. The original solvent triangle is shown in 2, where the changes for these three solvents are indicated. These modifications, which

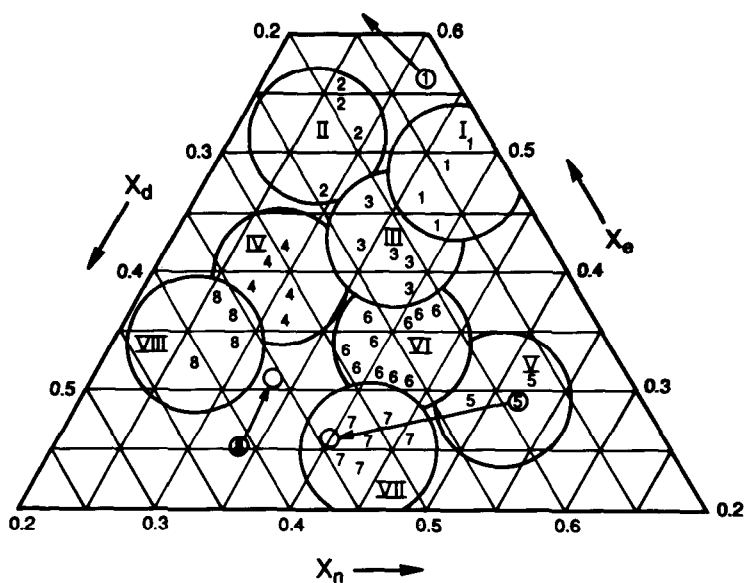


Fig. 2. Original solvent triangle, with modifications for triethylamine (1), methylene chloride (5), and chloroform (8). Reproduced from *J. Chromatogr. Sci.* (ref. 1) by permission of Preston Publications, A Division of Preston Industries, Inc.

result from the use of the new data, are consistent with the known chemistry of these compounds. For example, triethylamine (1), a good hydrogen bond acceptor ($\beta = 0.71$), is shifted toward the basic corner of the triangle, methylene chloride (5), a slightly acidic compound, is shifted away from ethylene chloride towards the acidic corner of the triangle, and chloroform, a moderately strong hydrogen bond donor ($\alpha = 0.44$) is shifted closer to group VIII which consists of the strong hydrogen bond acids, fluoroalkanol, water and *m*-cresol.

The two alternate formulations (Poppe's and our own) used for calculation of the P' values are given by eqns. 5 and 8. It is difficult to evaluate the merits of the modified scales relative to Snyder's original approach (eqn. 3), since there were not very many differences between the three methods. The calculations based on eqns. 3 and 8 (the original approach, and the method proposed here) gave a range of P' values within the homologous series of *n*-alkane solvents, while the method based on eqn. 5 (Poppe's approach) gave essentially identical P' values for all of the alkanes. Since we cannot completely account for dispersion interactions and solute dipole-solvent induced dipole interactions, it appears that eqns. 3 and 8 give more realistic estimates of the relative P' values for these compounds. In addition, carbon disulfide, benzene and carbon tetrachloride, which are non-polar, non-hydrogen bonding solvents, all yield P' values significantly larger than those of the alkanes using all methods. These P' values presumably reflect larger dipole-induced dipole interactions between the polar solutes and these non-polar, but highly polarizable solvents.

In general, the differences between the x_o , x_d , and x_n values for the three different approaches used for computation of the x_i values were small, and did not appear to provide any insight as to whether any of the three approaches is superior. For all three calculation methods, the x_i values within the homologous series were consistent with the original observations; the x_i values were similar within a given series, except that the first few members of the series tended to have slightly different values relative to the rest of the series.

There can be no "true" or unique ranking for any single parameter solvent strength scale, such as the P' scale, since the scale will depend on differences in the relative contributions of dispersion, dipole-dipole, dipole-induced dipole, and hydrogen bonding interactions, which must be solute dependent²⁴. From this point, we assume that the method based on subtracting out the contribution due to a hypothetical alkane of identical size to the probe solute is the most appropriate approach (eqn. 8). This is consistent with the observations described above, since we expect that there will be at least some small variations of P' within the *n*-alkane solvent set due to variations in induced dipole interactions (a 0.34 variation in P' between hexane and hexadecane was observed). This is true of other solvent strength scales as well, including the π^* solvatochromic scale and the scales based on the cohesive energy density³.

The following regression equation was obtained for the correlation of the P' values obtained using eqn. 8 (based on the correction calculated from a hypothetical *n*-alkane), with the original values reported by Snyder (P'_{old}).

$$P' = (0.994 \pm 0.025) P'_{old} + (0.06 \pm 0.11) \quad (14)$$

$$r^2 = 0.970 \quad s = 0.341 \quad n = 50$$

Only 50 solvents were used here, since data for the *n*-alkane solutes for the last seven of the solvents listed in Table I were not measured¹⁵. The slope obtained in this comparison is close to one, as opposed to the value of 0.921 given in eqn. 13. This is due to the omission of the volume correction introduced in eqn. 1. The intercept is not significantly different from zero. The final values for P' and the selectivity parameters, x_e , x_d and x_n using eqn. 8 are given in Table I.

As mentioned earlier, there is also very good agreement between the original x_i values reported by Snyder, and those calculated using eqn. 8, shown in Table I. This implies that many of the observations made by Snyder in the original reports are valid for these values as well. The values in Table I show tight clustering of the x_i values with in the homologous series (the alkylnitriles and the *n*-alcohols). However, if comparisons are made between classes, some confusion can arise. For example, if it is assumed, as Snyder proposed, the values for x_d indicate the relative solvent hydrogen bond acidity, the x_d for benzene (a non-acidic compound, $\alpha = 0$) should be less than that for ethanol ($\alpha = 0.33$). In fact, the x_d for benzene is 0.28 and the x_d for ethanol is 0.19. Similar inconsistencies can be found throughout Table I. It was these inconsistencies which led us to investigate the correlation of the $P'x_i$ values with the solvatochromic parameters.

Correlation with solvatochromic parameters

Snyder originally proposed, as described in the Theory section, that x_e , x_d and x_n should describe the hydrogen bond basicity of the solvent, the hydrogen bond acidity of the solvent, and the dipolarity of the solvent, respectively. If this were true, then x_e , x_d and x_n should correlate strongly with β , α and π^* , respectively. As Fig. 3 demonstrates, there is disappointingly little correlation of the selectivity factors with the individual solvatochromic parameters.

We realized first that the descriptor which relates to these solvatochromic parameters should be $P'x_i$, rather than x_i , as seen by inspection of the derivation leading to eqn. 12. However, there was little change in the quality of the correlation with the solvatochromic parameters with this modification. Next, multiple linear regression was used to evaluate the relationship between the $P'x_i$ values for 2-butanone, ethanol, toluene, *p*-dioxane, and nitromethane and the solvatochromic parameters, π^* , α and β . All correlations were based on eqn. 12, and the regression results are given in Table III. All solutes were sensitive to the solvent dipolarity-polarizability, with the strongest dependence observed for nitromethane, as expected based on its π^* and bond dipole moment¹⁰. The s coefficient for nitromethane was 2.29, as compared to 1.65 for 2-butanone, 1.44 for *p*-dioxane, 1.32 for ethanol, and 0.97 for toluene. These coefficients were correlated with the π^* values for these solutes, as shown in Table IV. A moderate dependence on solvent α was observed for 2-butanone, ethanol, and *p*-dioxane, while a weaker dependence was observed for toluene and nitromethane. These coefficient values are again consistent with the values for solute β , as given in Table IV. In addition, a strong dependence on solvent β was observed for ethanol ($b = 1.88$), and a weaker dependence on solvent β ($b = 0.55$) was observed for nitromethane. The values for solute α are consistent with these observations. Fig. 4 shows plots of the $P'x_i$ values vs. the $P'x_i$ values predicted from the regression calculation.

These results indicate that the assumption that of the three solutes ethanol is the

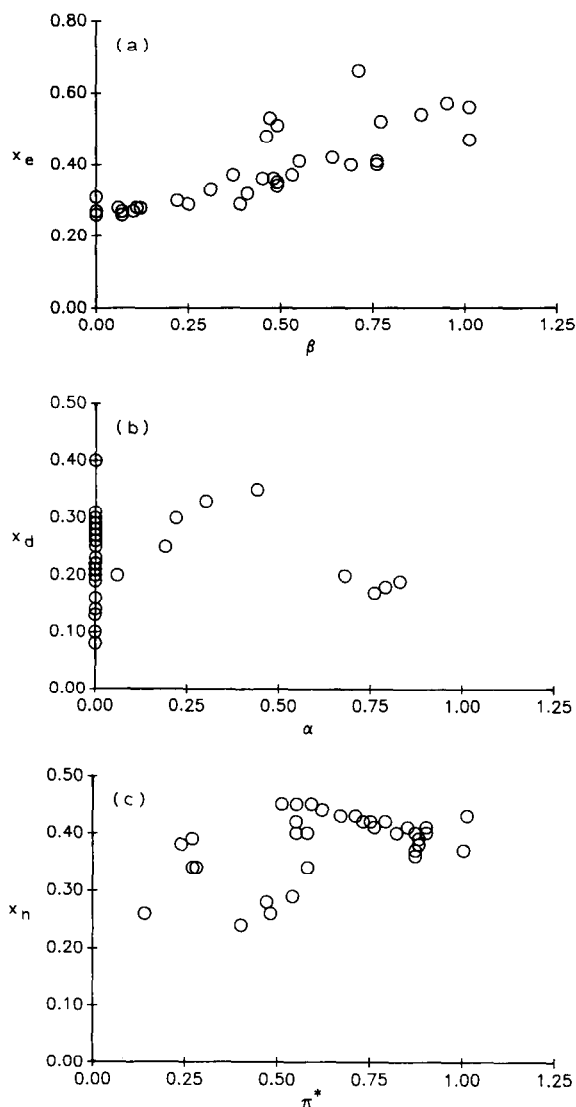


Fig. 3. (a) x_e vs. β ; (b) x_d vs. α ; (c) x_n vs. π^* . Snyder selectivity parameters are given in Table I.

main probe of solvent basicity is correct, however, the assumption that x_n is the main indicator of solvent dipolarity is incorrect, as all three solutes have appreciable dipolar interactions with the solvents. In addition, sensitivity to solvent hydrogen bond acidity is split approximately equally between ethanol and dioxane, with a small contribution from x_n .

Based on the observations described above, one can predict that the most basic solvents should lie at the top of the triangle, the most acidic solvents should lie towards the left edge of the triangle, and the polar solvents might be found almost anywhere in

TABLE III
MULTIPLE LINEAR REGRESSION RESULTS

Solute	Regression coefficients*						Standard error of the fit
	<i>s</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>h</i>	<i>SP₀</i>	
2-Butanone	1.65 (0.06)	-0.18 (0.05)	0.89 (0.24)	-**	-0.79 (0.28)	-0.18 (0.04)	0.103
Ethanol	1.32 (0.15)	-0.24 (0.10)	1.31 (0.38)	1.88 (0.17)	-1.59 (0.24)	0.00 (0.06)	0.173
Toluene	0.97 (0.03)	-0.13 (0.02)	0.13 (0.09)	-**	-0.54 (0.11)	0.01 (0.02)	0.053
<i>p</i> -Dioxane	1.44 (0.06)	-0.06 (0.05)	1.07 (0.18)	-**	-1.14 (0.23)	0.02 (0.04)	0.110
Nitromethane	2.29 (0.13)	-0.34 (0.08)	0.49 (0.27)	0.55 (0.14)	-1.27 (0.39)	0.04 (0.05)	0.138

* Standard deviations of the coefficients are given in parenthesis. Eqn. 12 is the regression equation employed.

** These coefficients were found to be not significantly different from zero and were omitted in the final fit.

the triangle. This can be seen in Fig. 2, where the basic groups (I, ethers; II, alkanols) are found at the top of the triangle, the most acidic groups (III, alkanols; IV, glycols, acetic acid, benzyl alcohol; VIII fluoroalkanols) are located near the left edge of the triangle, and the most polar groups (V, sulfoxides, amides, pyridines; VI, ketones, nitriles, esters; VII, ethylene chloride) are located in the center and somewhat towards the right corner of the triangle. In addition, since all solutes show some indication of solvent dipolarity, this indicates that the triangle should not allow very strong discrimination between solvents of differing dipolarity.

TABLE IV
SOLUTE SOLVATOCHROMIC PARAMETERS

From refs. 21 and 31.

Solute	π^*	α	β
2-Butanone	0.67	0.02	0.48
Ethanol	0.54	0.33	0.45
Toluene	0.42*	0	0.11
<i>p</i> -Dioxane	0.55	0	0.37
Nitromethane	0.85	0.12	0.25

* This value is modified by a $-\delta\delta$ correction term.

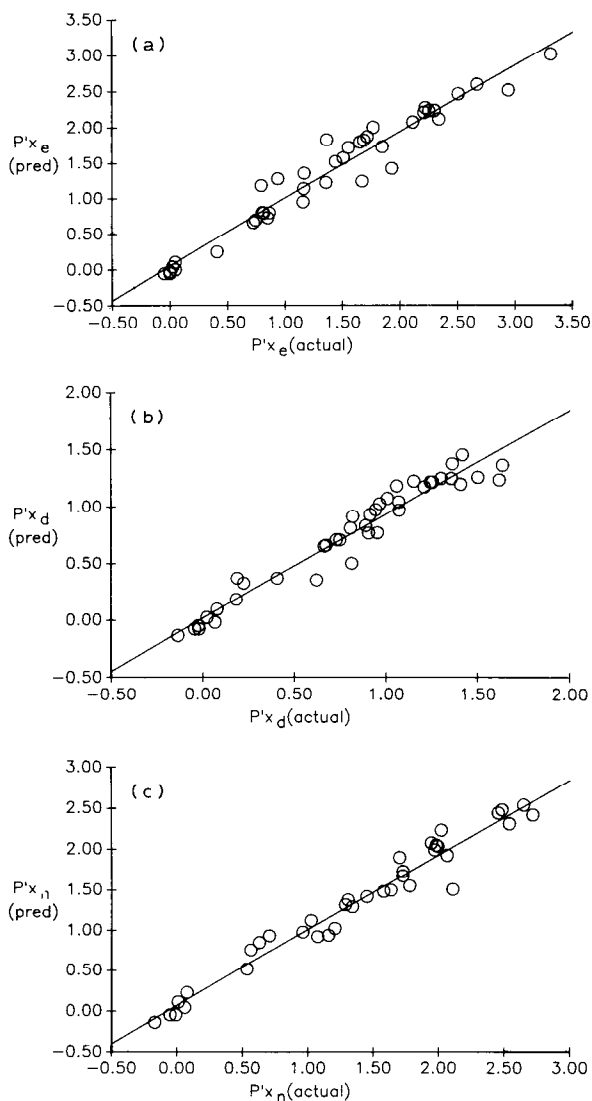


Fig. 4. (a) $P'x_e$ (pred) vs. $P'x_e$. (b) $P'x_d$ (pred) vs. $P'x_d$. (c) $P'x_n$ (pred) vs. $P'x_n$. All predicted values calculated using eqn. 12 and the regression results tabulated in Table III.

CONCLUSIONS

The above solvatochromic correlation results impact upon the use of the x_e , x_d and x_n selectivity parameters generated in Snyder's approach. As can be seen from the coefficients given in Table IV, the x_e values reflect a composite of solvent dipolarity-polarizability, hydrogen bond basicity, and hydrogen bond acidity, the x_d values reflect a composite of solvent dipolarity and solvent acidity, and the x_n values reflect

predominately solvent dipolarity, with small contributions from hydrogen bond basicity and acidity.

While the solvent triangle does allow classification on the basis of these three characteristics, it appears that knowledge of the solvatochromic parameters should permit the selection of more appropriate probe solutes for the development of a solvent triangle with better ability to allow discrimination between solvents. For example, triethylamine ($\pi^* = 0.14$, $\alpha = 0$, $\beta = 0.71$), a very basic, but relatively non-polar compound, and trifluoroethanol ($\pi^* = 0.73$, $\alpha = 1.51$, $\beta = 0$), a strongly acidic compound might be more suitable probe solutes. Selection of probe solutes such as these, based on information theory principles²⁵, should permit the development of a solvent triangle which allows for better distinction between the solvent classes.

Another limitation to the classification ability of the solvent triangle is the lack of an explicit selectivity parameter describing dispersive interactions. The work of Meyer and co-workers²⁶⁻²⁹ clearly shows that dispersive interactions predominate over all other interactions in organic solvents. Although the alkane correction reduces the dependence of the x_i factors on dispersion, residual variations in dispersive interactions undoubtedly contribute to the observed x_i factors.

One could also envision a triangle based directly on the solvatochromic π^* , α and β scales, however, this requires an arbitrary normalization and probably would not yield a triangle with high discriminating power, since so many of the common solvents have low hydrogen bond acidity. A better approach, which could be based directly on the solvatochromic parameters, would be to develop a classification scheme using cluster analysis methods³⁰. In this case, solvents would be determined to be in the same solvent class when the π^* , α and β values of the solvents are similar.

The above results demonstrate several points of interest to chromatographers seeking better methods for classifying solvents. First, the redetermination of the Rohrschneider gas-liquid partition coefficients has been found to change the P' scale and selectivity triangle in only a few instances. An improved method of calculation of the $P'x_e$, $P'x_d$ and $P'x_n$ based on newly determined partition coefficients for the n -alkanes in the Rohrschneider solvents has been examined, and determined to give similar values to the original approach. In addition, the values for $P'x_e$, $P'x_d$ and $P'x_n$, have been rationalized in terms of their correlations with the π^* , α and β solvatochromic parameters. Finally, some suggestions for improvements in solvent classification methods based on the Snyder selectivities and the solvatochromic parameters have been proposed.

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GLOSSARY

- $K_{i,s}$ gas-liquid partition coefficient of solute i in solvent s
 V_s molar volume of solvent s
 V_i molar volume of solute i

x_i	selectivity parameter
P'	polarity parameter
β_s	correction factor for non-zero slope of a plot of $\log K$ for n -alkanes in solvent s vs. solvent molar volume (Poppe's approach)
π^*	solvatochromic dipolarity–polarizability parameter
α	solvatochromic hydrogen bond acidity parameter
β	solvatochromic hydrogen bond basicity parameter
δ	solvatochromic polarizability correction parameter
s	coefficient for π^* parameter
d	coefficient for δ parameter
a	coefficient for α parameter
b	coefficient for β parameter
m_s	slope of plot of $\log K$ for n -alkanes in solvent s vs. solvent molar volume
b_s	intercept of plot of $\log K$ for n -alkanes in solvent s vs. solvent molar volume

Subscripts

o	octane
hci	average value for the solvents hexane, cyclohexane, and isooctane
e	ethanol
d	<i>p</i> -dioxane
n	nitromethane
s	solvent
i	solute

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