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CLASSIFICATION OF THE SOLVENT PROPERTIES OF COMMON LIQUIDS

L. R. SNYDER
Technicon Instruments Corp., Tarrytown, N.Y. (U.S.A.)
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SUMMARY

Solubility data reported by Rohrschneider for 82 solvents and several test solutes have been transformed into a corresponding set of solvent characterization parameters: P', x_e, x_d and x_n values. These latter parameters are approximately corrected for dispersion interactions and for molecular weight effects, and allow the separate characterization of solvent strength (polarity) and selectivity in liquid–liquid chromatography.

INTRODUCTION

Chromatographers rely on solvents for a variety of purposes: to dissolve solid samples prior to further processing, for carrying out preliminary sample cleanups by solvent extraction, for use as mobile or stationary phases in liquid–liquid chromatography (LLC), etc. In each of these various applications, it is useful to be able to predict the relative solubility of a compound of interest in different common solvents as this in turn determines the preferred solvent(s) for a given application.

Several solvent classification schemes have been described during the past 30 years, *viz.*, the Hildebrand solubility parameter treatment[1], various extensions of this treatment to recognize specific intermolecular interactions (*e.g.*, refs. 2 and 3), the Rohrschneider scheme for gas chromatographic (GC) phases[4], to name but a few of many. It is probably fair to state that each of these previous approaches leaves something to be desired in terms of ease of application, reliability, and other considerations.

Recently, Rohrschneider[5] has reported solubility data for six test solutes in 82 volatile liquids, including most of the commonly used solvents. The resulting data for each solvent in effect constitute a solvent classification scheme, one which is particularly valuable because it avoids any dependence on the present less-than-adequate theory of liquid mixtures. However, in their present form, the data of ref. 5 are somewhat difficult to apply to practical problems. Thus, the raw data are a function of the molecular weights of the particular solvents and test solutes used —and (indirectly) of solute vapor pressures. In some applications (such as LLC), it is useful to distinguish solvent strength from solvent selectivity. The strength of a solvent depends upon its

"polarity", or ability to preferentially dissolve more polar compounds such as nitriles and alcohols. Solvent selectivity refers to the ability of a given solvent to selectively dissolve one compound as opposed to another, where the "polarities" of the two compounds are not obviously different. Thus one of two polar solvents might preferentially dissolve nitriles, the other alcohols.

The present Rohrschneider data do not readily lend themselves to distinguishing between solvent strength and selectivity. In the present communication I will describe a simple transformation of the data of ref. 5 into what appears to be a more convenient and useful form for classifying the solvent properties of the various solvents studies by Rohrschneider.

TRANSFORMATION OF THE ROHRSCHNEIDER PARAMETERS

The first objective is to remove the dependence of these solubility constants K_g (so-called gas–liquid partition coefficients) on the molecular weights of solvent and solute. The effect of the solvent molecular weight arises from the use of concentration distribution constants K_g in ref. 5, rather than corresponding mole fraction constants K_g', where

$$K_g' = K_g \cdot V_s \tag{1}$$

V_s is the molar volume (ml/mole) of the solvent. It is assumed here that Raoult's law holds for solvents of similar chemical composition and differing molecular weights, which seems a reasonable first approximation. Thus, the K_g values for the various saturated hydrocarbon solvents of ref. 5 vary from 3512 (squalane) to 13,500 (cyclohexane), or by an overall factor of 3.9. The corresponding K_g' values show a smaller variation, by a factor of only 1.5, which can reasonably be attributed to actual differences in the intermolecular interactions in these saturated hydrocarbon solvents.

The molecular weight effect of the solute on its K_g' value can likewise be removed by dividing K_g' by the estimated K_g' value (K_v) of an *n*-alkane whose molar volume is the same as that of the solute:

$$K_g'' = K_g'/K_v$$

or

$$\log K_g'' = \log K_g - \log K_v \tag{2}$$

Here K_g'' refers to the solute solubility constant corrected for the molecular weights of both solvent and solute. K_g'' is therefore a measure of the excess retention of the solute relative to an *n*-alkane of equivalent molar volume. The resulting parameter K_g'' is largely corrected for the effect of dispersion interactions on K_g'.

We next assume that $\log K_v$ for different *n*-alkanes is proportional to molar volume, which is approximately the case (*e.g.*, heats and free energies of vaporization for the *n*-alkanes increase linearly with carbon number). Therefore the value of log

K_v for an *n*-alkane of volume V_x is calculable from K_0, the value of K_g for *n*-octane ($V_x = 163$) as

$$\log K_v = (V_x/163) \cdot \log K_0 \tag{2a}$$

Given values of V_x for the solute in question, and K_0 from ref. 5 for the particular solvent, it is then possible to calculate K_v and K_g'' from eqns. 2 and 2a for any solute–solvent combination. Log K_g'' is in turn proportional to the free energy of vaporization of the solute from that solvent, relative to an *n*-alkane solute of equal molar volume.

Application of eqns. 1–2a to the saturated solvents of ref. 5 yields small residual values of log K_g'' for the various test solutes; *e.g.*, for *n*-hexane as solvent, −0.29 for ethanol, −0.19 for dioxane, and 0.11 for nitromethane. These represent a combination of incomplete cancellation of terms in the above treatment, plus dipole induction interactions, which we have ignored. We next arbitrarily adjust all log K_g'' values to zero for the reference solvent *n*-hexane, by adding 0.29, 0.19 and −0.11 to the log K_g'' values for ethanol, dioxane and nitromethane, respectively, as solutes (in each solvent). This has the effect of making these selective interaction terms (log K_g'') zero in the nonselective solvent hexane.

We next define the polarity index, P', which is a measure of the ability of the solvent to interact with various polar test solutes:

$$P' = \log (K_g'')_{\text{ethanol}} + \log (K_g'')_{\text{dioxane}} + \log (K_g'')_{\text{nitromethane}}$$

Data for methyl ethyl ketone are excluded from this relationship because it was found that log K_g'' values for this solute correlate with values for ethanol as solute, and therefore give little added information on solvent properties. Table I lists the various Rohrschneider solvents in order of their P' values. Values of P' for some of the more polar solvents (*e.g.*, water) are approximate because insufficient data are reported in ref. 5.

Finally we define various selectivity parameters, *viz.*, x_e, x_d and x_n:

$$x_e = \log (K_g'')_{\text{ethanol}}/P' \tag{3a}$$
$$x_d = \log (K_g'')_{\text{dioxane}}/P' \tag{3b}$$
$$x_n = \log (K_g'')_{\text{nitromethane}}/P' \tag{3c}$$

The quantities x_e, x_d and x_n represent the fraction of P' contributed by interactions associated with ethanol, dioxane and nitromethane, respectively.

DISCUSSION

Three questions require consideration:

(1) What is the significance of the various parameters listed in Table I?

(2) How can we be sure of their reliability?

(3) How can these parameters be applied in practice?

The parameter P' increases with solvent polarity, *i.e.*, the ability of the solvent to take part in strong intermolecular interactions with other like molecules. P' can be compared with the Hildebrand solubility parameter δ (ref. 1), in that values of P' roughly

TABLE I

SOLVENT PARAMETERS DERIVED FROM ROHRSCHNEIDER DATA[5,*]

*Solvent***	*P'*	x_e	x_d	x_n
Squalane	−0.8			
Isooctane	−0.4			
n-Decane	−0.3			
Cyclohexane	0.0			
n-Hexane	0.0			
Carbon disulfide (VIb)	1.0			
Carbon tetrachloride (VIb)	1.7	0.30	0.38	0.32
Dibutyl ether (I)	1.7	0.53	0.08	0.39
Triethylamine (I)	1.8	0.61	0.07	0.32
Diisoprophyl ether (I)	2.2	0.54	0.11	0.35
Toluene (VIb)	2.3	0.32	0.24	0.44
p-Xylene (VIb)	2.4	0.32	0.24	0.44
Chlorobenzene (VII)	2.7	0.24	0.34	0.42
Bromobenzene (VII)	2.7	0.24	0.34	0.42
Iodobenzene (VII)	2.7	0.24	0.36	0.40
Diphenyl ether (VII)	2.8	0.25	0.33	0.42
Ethoxybenzene (VIb)	2.9	0.27	0.29	0.44
Diethyl ether (I)	2.9	0.55	0.11	0.34
Benzene (VIb)	3.0	0.29	0.28	0.43
Tricresyl phosphate (V)	3.1	0.35	0.18	0.47
Ethyl bromide (VIa)	3.1	0.32	0.28	0.40
n-Octanol (II)	3.2	0.61	0.14	0.25
Fluorobenzene (VII)	3.3	0.24	0.33	0.43
Dibenzyl ether (VIb)	3.3	0.27	0.27	0.46
Methylene chloride (V)	3.4	0.34	0.17	0.49
Methoxybenzene (VIb)	3.5	0.28	0.31	0.41
Isopentanol (II)	3.6	0.58	0.17	0.25
Ethylene chloride (V)	3.7	0.36	0.19	0.45
Bis(2-ethoxyethyl) ether (VIa)	3.9	0.35	0.19	0.46
tert.-Butanol (II)	3.9	0.55	0.23	0.22
n-Butanol (II)	3.9	0.53	0.21	0.26
n-Propanol (II)	3.9	0.53	0.21	0.26
Tetrahydrofuran (III)	4.2	0.41	0.19	0.40
2,6-Lutidine (III)	4.3	0.47	0.18	0.35
Ethyl acetate (VIa)	4.3	0.34	0.25	0.42
Isopropanol (II)	4.3	0.54	0.20	0.26
Chloroform (VIII)	4.4	0.28	0.39	0.33
Acetophenone (VIa)	4.4	0.33	0.27	0.40
Methyl ethyl ketone (VIa)	4.5	0.36	0.17	0.47
Cyclohexanone (VIa)	4.5	0.35	0.23	0.42
Nitrobenzene (VIb)	4.5	0.30	0.27	0.43
Benzonitrile (VIa)	4.6	0.35	0.26	0.39
Dioxane (VIa)	4.8	0.38	0.21	0.41
2-Picoline (III)	4.8	0.51	0.19	0.30
Tetramethylurea (III)	5.0	0.46	0.14	0.40

TABLE I *(continued)*

*Solvent***	P'	x_e	x_d	x_n
Diethylene glycol (IV)	5.0	0.43	0.24	0.33
Triethylene glycol (IV)	5.1	0.43	0.24	0.33
Ethanol (II)	5.2	0.51	0.21	0.28
Quinoline (III)	5.2	0.40	0.27	0.33
Pyridine (III)	5.3	0.43	0.21	0.36
Nitroethane (VIb)	5.3	0.31	0.27	0.42
Acetone (VIa)	5.4	0.36	0.24	0.40
Ethylene glycol (IV)	5.4***	0.47	0.23	0.30
Benzyl alcohol (IV)	5.5	0.42	0.28	0.30
Tetramethylguanidine (I)	5.5	0.52	0.11	0.37
Methoxyethanol (IV)	5.7	0.39	0.25	0.36
Tris(cyanoethoxy)propane (VIa)	5.8	0.34	0.25	0.41
Propylene carbonate (VIb)	6.0	0.31	0.28	0.41
Oxydipropionitrile (VIa)	6.2	0.33	0.28	0.39
Aniline (VIa)	6.2	0.34	0.30	0.36
Methyl formamide (III)	6.2	0.43	0.21	0.36
Acetic acid (IV)	6.2	0.41	0.29	0.30
Acetonitrile (VIa)	6.2	0.33	0.26	0.41
N,N-Dimethylacetamide (III)	6.3	0.43	0.20	0.37
Dimethyl formamide (III)	6.4	0.41	0.21	0.38
Tetrahydrothiophene-1,1-dioxide (VIa)	6.5	0.35	0.27	0.38
Dimethyl sulfoxide (VIa)	6.5	0.35	0.27	0.38
N-Methyl-2-pyrrolidone (III)	6.5	0.41	0.21	0.28
Hexamethyl phosphoric acid triamide (III)	6.6	0.49	0.15	0.36
Methanol (II)	6.6	0.51	0.19	0.30
Nitromethane (VIb)	6.8	0.28	0.30	0.42
m-Cresol (VIII)	7.0	0.39	0.36	0.25
Formamide (IV)	7.3***	0.40	0.28	0.32
Dodecafluoroheptanol (VIII)	7.9	0.35	0.40	0.25
Water (VIII)	9 ***	0.40	0.34	0.26
Tetrafluoropropanol (VIII)	9.3	0.36	0.34	0.30
Range		0.24–0.61	0.07–0.40	0.22–0.49

* A parameter x_m for methyl ethyl ketone can also be derived, but is found to correlate closely with x_e.

** Roman numerals refer to a solvent group, defined as in Table II and Fig. 1.

*** Incomplete data, estimated values.

parallel values of δ, and have a similar significance. The main difference between P' and δ is that δ is measured for the pure solvent, and can only reflect interactions that exist in the pure solvent. P', on the other hand, is measured against a variety of solutes that encompass all possible types of interaction. Thus, the value of δ for the solvent diethyl ether is rather low ($\delta = 7.4$), and virtually the same as for the non-polar solvent hexane ($\delta = 7.3$). It is known, however, that diethyl ether is a good proton acceptor and a moderately polar solvent. In the pure liquid, where no proton-donor molecules are present, the basicity of diethyl ether is essentially "wasted", and the resulting value of δ is artificially low. In Table I, on the other hand, we see that P' for diethyl ether is significantly larger ($P' = 2.9$) than for the saturated hydrocarbon solvents ($-0.8 \leqslant P' \leqslant 0.0$), accurately reflecting its moderately polar characteristics.

It is useful (but not precise) to consider the selectivity parameters x_e, x_d and x_n as reflecting the relative ability of the solvent to function, respectively, as a proton acceptor, a proton donor, or a strong dipole interactor. Thus, solvents with large x_e values will interact more strongly with ethanol than with dioxane or nitromethane, presumably via hydrogen bonding between ethanol and proton-acceptor solvents. Similarly, solvents with large x_n values interact relatively more strongly with the polar (*i.e.*, large dipole moment) nitromethane molecule. It should be noted that the selectivity parameters of Table I are normalized (eqns. 3a–c), so that the total (selective) interaction strength of the solvent with ethanol is given as $P' x_e$ (or $P' x_d$ for dioxane, $P' x_n$ for interaction with nitromethane).

Consider next the classification of the solvents of Table I within the triangular diagram of Fig. 1. We will first argue that this grouping of solvents in Fig. 1 represents a validation of the present solvent classification scheme. Then we will examine the practical utility of Fig. 1.

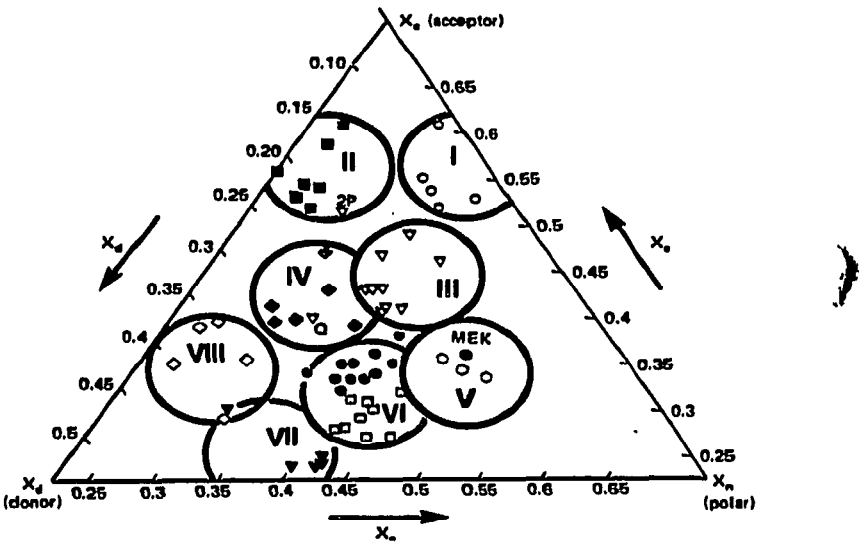

Fig. 1. Classification of solvent selectivity (see also Tables I and II). 2P = 2-Picoline; MEK = methyl ethyl ketone; Q = quinoline.

The parameters x_e, x_d and x_n reflect the relative importance of different intermolecular interactions, and these in turn are determined by the functional group(s) present in the solvent molecule. Therefore we should expect to find solvents with the same chemical functionality in the same regions of the selectivity triangle of Fig. 1. As seen in the classification of Table II, this is generally the case. Compounds of a given type fall within one of the groups or circles of Fig. 1 (maximum variations in x_e, x_d or $x_n = \pm 0.05$ units), with only a few minor exceptions (*e.g.*, 2-picoline, labelled 2P in circle II of Fig. 1, but belonging to group III).

Similarly, various functional groups can in some cases be categorized as good proton acceptors (large x_e), good donors (large x_d), or having large dipole moments (large x_n), without reference to the data of Table I or Fig. 1. The positions of these

TABLE II

CLASSIFICATION OF SOLVENTS IN TABLE I AND FIG. 1

Group	*Solvents*
I	Aliphatic ethers, trialkyl amines, tetramethylguanidine
II	Aliphatic alcohols
III	Pyridines, tetrahydrofuran, amides (except the more acidic formamide)
IV	Glycols, glycol ethers, benzyl alcohol, formamide, acetic acid
V	Methylene chloride, ethylene chloride, tricresyl phosphate
VIa	Alkyl halides, ketones, esters, nitriles, sulfoxides, sulfones, aniline and dioxane
VIb	Nitro compounds, propylene carbonate, phenyl alkyl ethers, aromatic hydrocarbons
VII	Halobenzenes, diphenyl ether
VIII	Fluoroalkanols, *m*-cresol, chloroform, water

solvents within Fig. 1 should reflect these selective solvent properties, and in general this appears to be the case. For example, the ethers, amines and substituted guanidines of group I are all strong proton acceptors, weak donors and have intermediate dipole moments. The large x_e values for this group of solvents are consistent with this classification. Similarly, the alcohols (group II) are known to be strong proton acceptors and donors, which is consistent with the placement of group II to the left of group I in Fig. 1. The glycols, glycol ethers, and benzyl alcohol are expected on chemical grounds to be more acidic and less basic than the alcohols, which is borne out by the position of group IV in Fig. 1. Methylene chloride and ethylene chloride are compounds whose dipole interactions clearly outweigh any interactions by hydrogen bonding; their inclusion in group V with large x_n values is consistent with these facts. Group VIII (large x_d) includes all the solutes which are relatively strong donors: fluoroalcohols, *m*-cresol, chloroform and water*. Other correlations (and a few apparent exceptions) between Fig. 1 and independent evidence of selective solvent interaction tendencies can readily be drawn by the experienced reader. At the moment there are no compelling reasons to suspect the general reliability of this classification scheme.

Fig. 1 and Table I can be used in various ways (see ref. 6 for a detailed discussion of its application in LLC). Basically this approach to solvent classification describes the solvent properties of different liquids in terms of degree (value of P') and kind (x_e, x_d, x_n), and follows in the path laid out by Hansen[2] and others (*e.g.*, refs. 3 and 7) for the extended solubility parameter treatment. For example, the similarity of P' and δ as thermodynamic quantities suggests (as in the case of δ) that P' for a solvent mixture A–B will be given as

$$P' = \Phi_a P_a + \Phi_b P_b \tag{4}$$

where Φ_a and Φ_b are volume fractions of solvents A and B in the solvent mixture, and

* By "relatively strong donors" we mean solvents whose donor properties are relatively more pronounced than their acceptor or dipole moment properties. Water may appear rather unlike chloroform in terms of selectivity, but this is largely because of the great differences in polarity of the two solvents. If it were possible to dissolve significant amounts of water in a non-polar solvent, the solubility properties of that solvent mixture would be predicted to be rather like those of a solution of chloroform in the non-polar solvent, when the concentrations of water and chloroform are adjusted to give solutions of similar polarity or P' value.

P_a and P_b are the P' values of the pure solvents A and B. If solvent A is non-polar (P' small) and B is polar (P' moderately large), dilution of B by A should not affect the selectivity of B significantly; *i.e.*, mixtures of acetone–hexane would remain in group VIa of Fig. 1. This provides a continuous range of P' values (as binary mixtures) within each of the selectivity groups of Fig. 1.

In seeking the best solvent for a given application, it is useful to separate the effects of P' and selectivity on the operation in question, *e.g.*, dissolution of a solid sample. This can be done by first determining the effect of P' on the operation in question, which is conveniently accomplished by studying the performance of a series of blends of a particular polar and non-polar solvent pair (*e.g.*, 25, 50, 75 and 100% methanol–hexane). Having established the optimum value of P' for the operation in question (*e.g.*, 50% methanol–hexane, $P' = 3.3$, gives maximum solubility for the solid sample), the effect of solvent selectivity can next be explored by using solvents of similar P' (3.3) but different selectivity. These should be chosen from other selectivity groups (*e.g.*, V, VIII). Solvents from the same selectivity group II would be unlikely to give significantly improved performance (greater solubility of the solid sample in this case).

The grouping of solvents in Table II suggests that many of these have similar solvency properties. Therefore, a relatively small number of total solvents should be sufficient for most applications requiring a given type of solvent. Table II and Fig. 1 provide a rapid means for classifying and rejecting redundant solvents.

REFERENCES

1 J. H. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes*, Dover Publications, New York, 3rd ed., 1964; *Regular Solutions*, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.
2 C. Hansen, *Ind. Eng. Chem., Prod. Res. Develop.*, 8 (1969) 2.
3 R. A. Keller, B. L. Karger and L. R. Snyder, in R. Stock and S. G. Perry (Editors), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 125.
4 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
5 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
6 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley-Interscience, New York, 1974.
7 L. R. Snyder, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley-Interscience, New York, 1971, Ch. 4.