Coordination Chemistry Reviews, 29 (1979) 129—211

CORRELATIONS AMONG SOLVENT POLARITY SCALES, DIELECTRIC CONSTANT AND DIPOLE MOMENT, AND A MEANS TO RELIABLE PREDICTIONS OF POLARITY SCALE VALUES FROM CURRENT DATA

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(Received 10 August 1978)

CONTENTS

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A. INTRODUCTION

The considerable variations observed in chemical reactivity have long been known to be influenced by the solvent medium. As early as 1890, Menschutkin stated that a reaction cannot be separated from the medium in which it takes place [1]. In addition, he postulated a relationship between the rate of reaction and the structure of the solvent. However, it was another fifty years before the effect of single-component solvents on reaction rates was studied in any detail. Correlations were attempted with functions of bulk (or macroscopic) properties of the solvent. More recently, the widespread use of spectroscopic techniques has resulted in a wealth of empirical scales of solvent polarity, and an examination of intimate molecular interactions.

The last general reviews on solvent polarity scales were written in the mid-1960's and were not extensive [2—4]. In 1976 Dack [5] considered the influence of solvent on chemical reactivity and included a reasonably detailed up to date discussion on the main original scales. Many books and reviews in recent years on solvent sensitive phenomena usually contain mention of two or three of the most well known and oldest solvent polarity scales, but little on the more recent scales. References [6]—[27] contain a representative selection of such articles. Many articles report a linear relationship between the two most popular scales, Z values [28] and E_T values [29], but are reluctant to give or use values obtainable from this relationship. One of the purposes of this review is to examine critically and statistically linear relationships among the various scales so that predicted values may be reported and used with confidence. The authors of most solvent polarity scales have generally not extended substantially the list of solvents contained in their original publication, and there is little incentive for others to do so. However, in this review we include the experimental values for the Z values of over 40 new solvents, and these are compared with their predicted values.

This review will be arranged into three main components. First, the various attempts at solvent classification will be examined, and a summary of the various solvent polarity scales given (including those based on nmr-measurements, which have not previously been reviewed); second, inter-correlations between

the scales will be investigated; and third, the relationships with bulk solvent properties and the value and applications of solvent polarity scales will be considered. Solvent polarity parameters for mixed solvent systems will not in general be covered. We should add here that attempts are now being made to separate electrostatic and specific contributions to the overall solvent effects in reactions by employing multiparameter equations, and with some success [30]. However, results have been limited by the use of only *measured* parameters. In general the more parameters involved in an equation then the fewer solvents there are that can be considered regarding the reliability of the proposed equation. This arises because in establishing a scale the solvents for which the data are measured are generally limited, rather than exhaustive, because solvents have to be suitable for the phenomenon studied, and available at the time of the measurements. It is thus our hope and aim that confidently *predicted* data, and our discussion, will encourage more attempts at the multiple-correlation method of separating solvent effects, and make easier the evaluation of the best solvent for a desired chemical reaction.

B. SOLVENT CLASSIFICATION

(i) Bulk properties

Bulk properties are most frequently used as a basis for solvent classification. The more obvious bulk solvent properties considered include dielectric constant, dipole moment, acidity or basicity and hydrogen bonding ability.

One of the earliest schemes for solvent classification was suggested by Brönsted [31] in 1928. He considered the acidic and basic properties of a solvent, as well as its dielectric constant, and proposed a division of solvents into eight groups (Table 1). Solvents belonging to group 1 (e.g. water and methanol) were 'completely active protolytically', being both proton donors and acceptors. At the other end of the scale, group 8 solvents (e.g., benzene and carbon tetrachloride) were referred to as aprotic, to indicate that they were 'completely indifferent protolytically'. The terms 'protic' and 'aprotic' have since passed into common usage, and they are probably the best general distinction between the two main classes of solvent [25].

Parker [32] later reviewed the effects of solvation on the properties of anions in dipolar aprotic solvents. These he defined as solvents with dielectric constant $\epsilon > 15$, and which, although they may contain hydrogen atoms, cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds with an appropriate species. Solvents which fall into this category include acetonitrile, dimethyl sulphoxide and nitrobenzene.

In a review of the conductance of hydrogen halides in anhydrous polar organic solvents Janz and Danyluck [33] distinguished two groups of solvents: (1) levelling solvents in which members of a series of electrolytes are of approximately the same strength, e.g. hydrogen halides in methanol; and (2) differentiating solvents in which the members possess markedly different strengths,

TABLE 1

Brönsted's scheme for solvent classification

Group number	Dielectric constant	Relative acidity	Relative basicity
1	+	+	+
2	+	+	—
3	+	—	+
4	+	—	—
5	—	+	+
6	—	+	—
7	—	—	+
8	—	—	—

Positive and negative signs indicate a comparatively high or low value, respectively, for the property under consideration. The dividing line between high and low dielectric constant was arbitrarily set at 20.

e.g., hydrogen halides in acetonitrile, dimethyl sulphoxide and nitrobenzene. Parker [32] suggested that differentiating solvents possess this property because, being dipolar aprotic, they do not efficiently solvate small anions, but are slightly more efficient for large anions. The levelling (protic) solvents strongly solvate small anions because of hydrogen bonding solvent—anion interactions.

(ii) Initial approach to electrostatic solvation

In general, the static dielectric constant ϵ is the bulk property first considered, since it often parallels the dissolving power of the solvent, the higher the dielectric constant the better the solvent often is at dissolving polar and ionic compounds. However this generalisation is modified on consideration of another parameter, usually relating to specific interactions between solvent and solute molecules. For example, Dack [5] has extended the observation that solvents of similar dielectric constant usually have similar dipole moments μ by considering, for the common solvents used in organic reaction systems, their electrostatic factor EF, defined as the product of ϵ and μ, and which is considered to take into account the influence of both properties on the electrostatic solvation of solutes. From these EF values he proposed four classes of solvent, as follows.

		ϵ	EF
Class I	Hydrocarbon solvents	0 — 2.5	0— 2
Class II	Electron-donor solvents	3.5— 10	2—20
Class III	Hydroxylic solvents	10 — 35	15—50
Class IV	Dipolar aprotic solvents	17 —>100	⩾50

These divisions arose from a consideration of the role of the solvent, for

classes II to IV, in the electrostatic solvation of polar molecules and ions and it was concluded that 'a solvent chosen on the grounds of solute solubility will probably give a good reaction rate as well'. Internal pressure effects were considered to govern the role of solvents in electroneutral reactions.

Berman and Stengle [34] have considered dielectric constant coupled with Gutmann's donor number [35] as an indicator of contact ion pair association. Generally a low dielectric constant is taken to indicate that ion pairing will predominate for solutions of ionic solutes, but more than one type of ion pair is now known to occur in solution [24]. The electrostatic factor approach does not take into consideration the nature of the solute species when in solution before any reaction takes place.

Consider, for example, an ionic halide, such as iodide. In order that it be soluble in a wide range of solvents an appropriate counter ion would be tetra-n-butylammonium (Bu_4N^+). In reactions involving iodide the extent of its solvation or the nature of the iodide—solvent interactions are not necessarily the sole or main considerations: the counter ion may have a part to play. In other words, the nature and extent of ion-pairing must be evaluated.

It is of course recognised that in solution molecules must travel through a solvent to their reaction partner before reacting, and need to present a sufficiently or momentarily unsolvated site for collision. But then to conclude that a several million-fold rate change on changing the solvent is due only to the solvent governing the movement and energy of the reacting species [5] neglects the role of the solvent, largely through its dielectric constant, in affecting the interactions between ions and ions or polarizable molecules *before* reaction.

(iii) Dielectric constant and ion pairing

Griffiths and Wijayanayake [36] have studied the charge-transfer-to-solvent (ctts) spectrum of iodide in some 40 solvents and concluded, against their original expectations, that the nature of the various ion pairs arising was dependent upon the dielectric constant of the medium. They found, for alkali metal and quaternary ammonium iodides, four divisions, based on dielectric constant values: (a) $\epsilon > 23$, free ions and solvent separated ion pairs are present in solution; (b) $23 < \epsilon > 11$, solvent separated and solvent shared ion pairs predominate; (c) $11 < \epsilon > 5$, solvent shared ion pairs are present, and (d) $\epsilon < 5$, only contact ion pairs are expected.

Contact ion pairs are defined as anion and cation in contact, with essentially no covalent bonding, the stability of the species being due to electrostatic interaction only; solvent shared ion pairs have anion and cation linked electrostatically through a single (oriented) solvent molecule, which is part of the primary solvation shell of both ions; solvent separated ion pairs are separated by more than one solvent molecule; and free ions are solvated and essentially independent of all other ions. Later work [37,38] added support to this dielectric constant classification. There are apparent similarities with

the classes I—IV of Dack [5] but the main differences here are that the dielectric constant divisions are abrupt at the values noted above, and hence in the critical region $23 < \epsilon > 11$ both protic and dipolar aprotic solvents show similar behaviour. However, it will be established later that when the same species is made to occur in a wide range of solvents, then the solvents divide into essentially two classes, protic and aprotic: it is sometimes useful to recognise a subdivision of the latter into dipolar aprotic and non-polar aprotic.

(iv) Other approaches

Pimental and McClellan [39] have reviewed solute—solvent hydrogen bonding and divided the hydrogen bonding solvents into four classes.

(a) Proton donors	Chloroform
(b) Proton acceptors	Ketones, aldehydes, esters, ethers, *t*-amines, olefins and some aromatic hydrocarbons
(c) Proton donors and acceptors	Water, alcohols, carboxylic acids and primary and secondary amines
(d) Non-hydrogen bonding	Paraffins, carbon disulphide and carbon tetrachloride

Classes (a) and (b) are essentially dipolar aprotic, class (d) non-polar aprotic and class (c) protic. Other accounts and reviews on solvent classification, written around 1970, have discussed electrostatic and specific solvation effects [40,41], boiling, freezing and flash points, ignition temperature and chemical structure [42], and electrostatic factor, viscosity and solvent structure on dipole—dipole reactions [43].

The most recent account we have seen [44] of an examination of solute—solvent interactions, by electrochemical transport studies, takes the approach that ions are moving through a bulk medium, and specific effects of solvating ions are not considered, because they cannot be. Ion association is discussed as dependent on the dielectric constant and the ion size. Polar solvents are classified into four groups, on the basis of association patterns, viz., (a) basic solvents — which interact effectively with cations through their lone pairs but have no sharply defined positive sites for interaction with anions; (b) strongly acidic solvents — that have well-defined positive sites for solvation of anions but no distinct negative sites available; (c) hydrogen bonded liquids — which have both acidic and basic sites, and thereby effectively solvate both cations and anions; and (d) neutral solvents — which appear not to interact strongly with either cations or anions.

Kay et al. [44] then point out that adjustments of continuum theory are unlikely to explain the facts, and turn to specific solvent effects. However, they decided that the best theory was that of Bjerrum as a base for considering the magnitude of association constants because although ion pairs of the contact and solvent separated type can occur, such species do not contribute to the conductivity of a solution: they did not, however, consider triple ions

and other ion aggregates with a net charge. They state that the 'main factors affecting ionic mobilities are the ionic size and charge and the solvent size, viscosity and dielectric constant', and they conclude that ion—solvent interaction can be evaluated by using transport measurements; association constants are useful in this endeavour, but ionic mobilities are not yet reliable as useful probes.

Rao et al. [45] have recently reviewed non-specific solute—solvent interactions through changes in spectra and concentrated on solvent shifts correlated with functions of dipole moment, refractive index and dielectric constant, particularly functions involving $(n^2 - 1)/(n^2 + 2)$, $(n^2 - 1)(2n^2 + 1)$, $(\epsilon - 1)/(\epsilon + 2)$ and $(\epsilon - 1)(2\epsilon + 1)$. However, no plots were given of the various correlations, or any correlation coefficients, and such functions are examined in a later section. They conclude that in the absence of specific interactions between solute and solvent molecules it is possible to correlate solvent-induced spectral shifts with bulk properties of solvents. However, among the examples they give specific solute—solvent interactions can be considered to take place. Very recently Symons and co-workers [46] have advanced spectroscopic evidence in favour of the concept of continuous hydrogen-bonding from anions into bulk solvent with no intervention of an intermediate structureless region.

The concept that bulk properties and specific solute—solvent interactions *together* will be the way to understand electrolyte solutions and predict chemical reactivity is thus the current approach. We, therefore, now investigate specific solute—solvent interactions by examining the various solvent polarity scales, as a prelude to examining their relationships with bulk properties.

C. EMPIRICAL MEASURES OF SOLVENT POLARITY

The term 'solvent polarity' lacks an exact definition, but it is generally used, and used here, to encompass all the intermolecular interactions of which the solvent is capable [2]. We have seen that a simplistic application of solvent dielectric constant fails to represent electrostatic solute—solvent interactions, or provide a reliable guide for predicting suitable solvent media for chemical reactions. Naturally, alternative measures of these interactions, and specific solute—solvent interactions, have appeared, and there is now a wide variety of solvent polarity scales based on empirical parameters.

In developing these scales a model system is chosen, and changes in one of its parameters are recorded when the solvent is changed. At the present time, all parameters used to describe solvents arise from experimental results. The parameters are generally rate constants for a reaction, or spectral shifts in spectroscopic studies, which have recently been augmented by several scales based on nmr chemical shifts.

The model process must be chosen with care, and represent properly the interactions of the system, yet no one scale can be universal and useful for all

kinds of reactions. Indeed, it is our contention that only by comparing these 'incomplete' parameters can one ascertain the better model processes. On more theoretical considerations, the best model processes maximize solvent effects. One which converts an ion pair (maximum interaction with the solvent) into a neutral species (zero interaction with solvent) achieves this result. This, or its reverse, can be found in some chemical processes: an electronic transition in an ion pair to produce a neutral species is another example (but not its reverse, due to the Franck–Condon principle) [4].

Another approach to solute–solvent interactions would be to identify the energy of interaction between a standard solute and a variety of (single) solvent molecules, by monitoring their reaction in an inert medium. Such a scale would be expected to correlate only with other similar scales, yet they should be able to assist in decomposing a solvent polarity parameter into its component parts. Further, these scales should be valuable when setting up multiparameter equations, and some attempts have been successfully made [47].

Probably the first attempt in this field was in 1965, when Drago and Wayland [78] proposed a two-parameter equation, and though reasonably successful, the E and C parameters derived have not so far been incorporated into multiparameter equations.

One of the most publicized scales of this type is that of donor number, devised by Gutmann and Wychera [35], but probably because it has mainly been concerned with its applicability to inorganic reactions in rather exotic non-aqueous media it has not yet been incorporated in the multiparameter equations of organic chemists. We shall discuss their and similar scales shortly, and therefrom predict many donor numbers for solvents of interest to organic chemists.

Historically the first empirical scales were from the rate constant studies of Grunwald and Winstein [48] in 1948 but such scales are now out-numbered by scales based on spectroscopic measurements. It is interesting that many scales are associated with letters of the alphabet. The first important scale was the Y values of Grunwald and Winstein [48], soon followed by Kosower's Z values [28], then X values [49], R and S values [3], Q values [50,51], P values [52,53], G values [54] and F values [55], in generally reverse alphabetical order. The early rate constant scales rarely reached double figures for the number of solvents that could be studied. It was the first reported linear relationship between a spectroscopic measurement, for a static system, viz., Kosower's Z values, and a dynamic system, Winstein's Y values, that opened the door to the search for many more spectroscopic scales, since the values obtained are generally measured quickly and with more precision and ease than rate constants. Also, spectroscopic scales cover a much wider range of solvents. We have therefore chosen to discuss first these scales, which are based on a shift in the absorption band maximum with solvent change, then those based on enthalpy measurements, on basicities, on nmr chemical shifts, and finally on rate constant determinations.

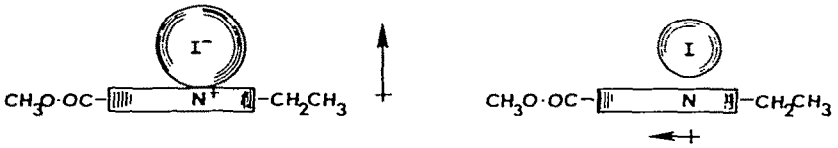
D. POLARITY SCALES FROM SPECTROSCOPIC MEASUREMENTS

(i) Z values of Kosower

It has long been known that dissolution of an absorbing species results in a change in the position, intensity and shape of absorption bands relative to those of the species in the gas phase. Early work in this area has been reviewed by Sheppard [56]. The solvent effect is due to the difference in stabilization of the ground and excited states, which leads to a change in the excitation energies, and depends primarily on the nature of the electronic transition. This phenomenon was termed *solvatochromism* by Hantzsch [57].

The first suggestion that solvatochromic dyes could be used as a measure of solvent polarity was made by Brooker et al. [58] but Kosower [28] was the first to establish a comprehensive polarity scale using such species. He found that concentrated solutions of 1-alkylpyridinium iodides exhibited a pronounced solvatochromism [59,60], and used 1-ethyl-4-carbomethoxypyridinium iodide (chosen because of its solubility in a wide variety of solvents) to establish a solvent polarity scale [28,61,62]. He monitored the ultraviolet and visible absorption spectrum of this solute in a variety of solvents, and termed the transition energy (in kcal mol^{-1}) of the longest wavelength absorption band the Z value.

The explanation of the solvent dependence was as follows. The electronic transition monitored was assumed to be that of the ion pair, involving the transfer of an electron from the iodide ion to the pyridinium ring. Accompanying this transition would be a 'dipole flip'. In the ground state the iodide ion



is proposed situated above the pyridine ring in the neighbourhood of the positive nitrogen centre, and thus the dipole is perpendicular to the plane of the ring. Strong interaction of this dipole with the surrounding solvent molecules leads to their orientation, and thus to a stabilization of the ground state. On excitation, the electron is transferred to the pyridine ring, causing the dipole to 'flip' into the plane of the ring. The dipole moment of the species is thus decreased considerably, but not necessarily to zero (as required by the best model). According to the Franck—Condon principle, the excitation time is too short to allow for solvent rearrangement. Thus the dipole of the excited state is perpendicular to that created by the oriented solvent molecules. As mutually perpendicular dipoles do not interact, the excited state becomes destabilized. Combination of the two factors, stabilization of the ground state and destabilization of the excited state, causes a large increase in the transition energies with increasing solvent polarity. The stronger the stabilizing

effect of the solvent on the ion pair in the ground state relative to that in the less polar excited state the lower the wavelength of the charge transfer band, and thus the higher the transition energy, and the Z value.

The experimental Z values are therefore considered a direct empirical measure of solvent behaviour. However, some of the basic assumptions concerning the nature of the electronic transition can be questioned. It is not always made clear that the Z value transition only appears in concentrated solutions. The spectrum of a dilute (10^{-5} M) solution of the pyridinium iodide in common solvents [38] contains no visible band but only, in the ultraviolet, absorption due to the pyridinium ring and the ctts spectrum of iodide, the latter shifted in the expected manner, and by the expected amount, with temperature increase. Concentrations of around 10^{-2} M are required to produce the ion pair band, and on dilution its position was found, for several solvents, to be concentration dependent. The reported Z values were those obtained on extrapolation to infinite dilution. In the remaining solvents the band intensity obeyed Beer's law over most of the concentration range in which it was observable. It was also reported that Z values vary with temperature [28], but this was only described for chloroform, the solvent that was most concentration dependent. Our individual studies have shown no temperature effect in the alcohols and acetonitrile [38] and in the alkyl phosphates [63]. Thus to attribute every measured Z value to the contact ion pair charge transfer transition cannot be correct: a solvent molecule may at times be intimately involved [64] (e.g., in a solvent shared ion pair), or, because of the high concentrations required, nearby ions and ion pairs may participate in the ground state by dipolar interactions, or may aggregate to form clusters. It is therefore perhaps surprising that the measured Z values correlate as well as they do with other scales: that they do must mean that the orientation and interactions of solvent molecules around an ion pair are not particularly sensitive to the magnitude of the dipole on the ion pair.

Z values range from 54.0 in benzene to 94.6 in water. However, Z values above 86.4 may not be measured directly, as the (low intensity) charge transfer band is masked by the intense absorption of the pyridinium cation. The value of 86.4 refers to a 70% solution of ethanol in water, and to date only two substances (water and silica gel) have been found with a greater Z value. The value for water (94.6) was obtained by extrapolating from the correlation with Y values [48] of binary solvent mixtures. That for silica gel (88) refers to a slurry of silica gel in chloroform, and no attempt was made to extrapolate to zero chloroform concentration [65]. This value must therefore be treated with caution.

1-Ethyl-4-carbomethoxypyridinium iodide is insufficiently soluble in certain non-polar solvents (e.g., hexane) for direct measurement of the Z value. This problem can be overcome in all but the most non-polar solvents by careful use of 1-ethyl-4-carbo-*t*-butoxypyridinium iodide [4], which has greater solubility in non-polar solvents than its methoxy analogue. A good linear correlation is obtained between the transition energies for the ion pair band

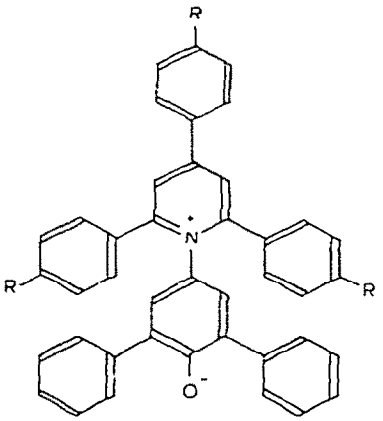
for these two solutes. An alternative solute is pyridine-1-oxide, but the correlation between the transition energy for this solute and the Z value is only moderately good. Thus this solute was used but sparingly by Kosower to obtain Z values.

The correlations reported were not obtained by a least squares best fit, nor are the predicted Z values, or concentration dependent values, subsequently identified; they are all attributed, by implication and common usage, the same precision.

Some 45 individual Z values are now known, excluding binary solvent mixtures: later in this review we report 40 more.

(ii) E_T values of Dimroth et al.

To date, the most comprehensive solvent polarity scale is almost certainly that given by the E_T values of Dimroth et al. [29]. This scale is based on the solvatochromic band of the pyridinium-*N*-phenolbetaines (I) and (II). The E_T



(I) R = H
(II) R = CH_3

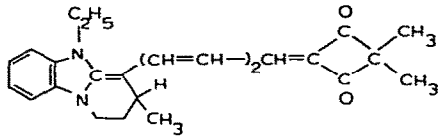
value is the transition energy (again in kcal mol^{-1}) of the intramolecular charge transfer band of (I). The solvatochromic shift of this band is the largest for any compound yet investigated, ranging from 63.1 (equivalent to 453 nm) in water to 35.3 (810 nm) in diphenyl ether. Compound (I) is insoluble in aliphatic and aromatic hydrocarbons, but the scale may be extended using the more soluble compound (II). An excellent correlation exists [2] between the transition energies of (I) and (II), and the E_T scale has thus been extended to include the value of 30.9 for n-hexane.

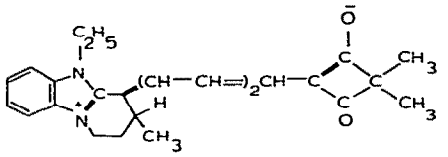
No E_T value may be measured for acidic solvents, as these protonate the oxygen atom of (I) and (II), and the long-wave band disappears. Since the solvatochromic band lies in the visible region of the spectrum, it is even possible to make a visual estimation of solvent polarity, e.g., in highly polar methanol (I) appears red, while in the less polar acetone it is green. E_T values are temperature sensitive and decrease with increasing temperature, owing to the pronounced thermochromism of the pyridinium-*N*-phenolbetaines [66].

To date E_T values have been reported [2,29] for some 62 solvents. A plot of E_T vs. Z value is well known and linear, no solvent being more than 2 kcal mol^{-1} from the line.

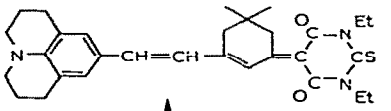
(iii) X_B *and* X_R *values of Brooker et al.*

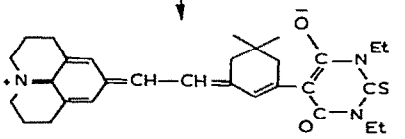
We remarked earlier that the first suggestion that solvatochromic dyes could be used as a measure of solvent polarity was made in 1951 by Brooker et al. [58]. Since then they [67] have proposed two solvent polarity scales, X_B and X_R, based on the shifts of the merocyanines (III) and (IV). The merocyanine dyes they originally [67] considered were of limited usefulness because of their insolubility in solvents of low polarity. This problem also arises in (III), but not with (IV). However (IV) is insoluble in strongly stabiliz-





III





IV

ing solvents, such as those which are highly aqueous. Compound (III) exhibits blue shifts, and (IV) red shifts, and thus Brooker et al. [67] proposed that the transition energies in kcal mol^{-1} of (III) and (IV) be designated X_B and X_R, respectively, and used as criteria of gross solvent polarity. The maximum observed shift in the X_B and X_R values (ΔX_B = 27.2 kcal mol^{-1} and ΔX_R = 17.3 kcal mol^{-1}) is less than that for the E_T values (ΔE_T = 32.2 kcal mol^{-1}) and the

Z values (ΔZ = 48.0 kcal mol^{-1}), but even so they are useful indicators of solvent polarity.

The χ_B values do not correlate well with the χ_R values, the correlation coefficient for all the solvents common to both scales being only 0.620 [67]. They suggest that it is not unreasonable to associate this behaviour with the complex nature of solvent stabilization, where the separate factors of hydrogen bonding and of solute—solvent dipole interaction may be distinguished, as well as solute—solvent polarizability interaction (dispersion forces) [68]. In spite of this poor correlation, the two scales independently correlate well with other solvent polarity scales, e.g., χ_B with Z and E_T values, and χ_R with the rate data (log k values) of Pincock [69] on the influence of non-polar solvents on the base-catalysed decomposition of t-butyl peroxyformate. These, and other correlations, will be discussed later.

χ_B values have been reported for 12 solvents, and χ_R values for 58 solvents [67]. Suprisingly, although the ten common χ_B values correlate well with Z (Correlation coefficient = 0.989) [67], Kosower does not consider χ_B values of general applicability, because of 'uncertainty about the nature and solvation of the Franck—Condon state' [4].

(iv) F values of Dubois et al.

Dubois et al. [55] have examined the effect of solvents on the n → π^* transition of saturated ketones, and found that the absorption maxima in the 33,000—38,000 cm^{-1} region were dependent on both the solvent and the structure of the ketone. MacRae's formula [70] (relating the spectral band shift to various macroscopic properties of the solute and solvent) was not directly applicable to the experimental data, without first introducing serious restrictions as to its generality (a point omitted by Rao et al. [45]).

Their study was based on the specific properties of a ketone series for a solvent (8 aliphatic ketones in 14 solvents) linked with a linear free energy postulate and resulted in the development of an excellent description of the absorption maxima in terms of the nature of the solvent and the structure of the ketone. The correlations between the behaviour of the ketone series in various solvents and that in hexane result in a meaningful generalized description of the solute—solvent system.

Hexane was chosen as the reference solvent as it is non-polar and not polarizable, and thus solute—solvent interactions are reduced to a minimum. All of the solvents used could be described by an expression of the form

$$\nu^s = A^s \nu^H + B^s \qquad (1)$$

where ν^s is the absorption frequency of a ketone in the solvent under consideration, ν^H the absorption frequency of the same ketone in hexane, and A^s and B^s are parameters characteristic of the solvent.

A more refined treatment made it possible to isolate the influence of the

solvent on the n → π^* transition of the ketones by

$$\nu^s - \nu^{II} = F(\nu^{II} - \nu^I), \quad (2)$$

where ν^I = 33,374 cm^{-1}. This value for ν^I is the frequency below which solvent effects are no longer discernible. It was obtained by extrapolation of the correlations between ν^s and ν^{II} to a common point of intersection. The correlations for all solvents, except water, pass within 100 cm^{-1} of this point. The F value is thus a measure of the solvent effect on the n → π^* transition of saturated ketones, and to date has been measured for 13 solvents. No value is obtained for water, due to the above mentioned poor correlation.

(v) $\Delta\nu_D$ and $\Delta\nu_A$ values of Kagiya et al.

Kagiya et al. [71] made a quantitative study of the electron-donating and electron-accepting nature of more than 90 liquid organic compounds using infrared techniques. The relative magnitude of the electron-donating or -accepting power of a compound (solvent) was compared by measurement of the perturbation it produced on the O—D vibrational band of methanol-d or the C=O vibrational band of acetophenone. This power was defined as the relative difference, in wavenumbers, of the O—D or C=O absorption frequency absorbed in the compound from that in benzene, i.e.,

$$\text{Electron-donating power: } \Delta\nu_D = \nu_D(\text{benzene}) - \nu_D(\text{solvent}) \quad (3)$$

$$\text{Electron-accepting power: } \Delta\nu_A = \nu_A(\text{benzene}) - \nu_A(\text{solvent}) \quad (4)$$

Thus for benzene both $\Delta\nu_D$ and $\Delta\nu_A$ are zero.

$\Delta\nu_D$ is much more sensitive than $\Delta\nu_A$ to the solvent environment, as may be seen from the relative magnitudes of these two parameters: $\Delta\nu_D$ varies from −21 in carbon tetrachloride to 242 in di-n-propylamine, while $\Delta\nu_A$ varies from −5.9 in tetrahydropyran to 9.0 in nitrobenzene. However, much higher values are observed for $\Delta\nu_A$ in inorganic halides, such as antimony pentachloride ($\Delta\nu_A$ = 125.2).

Within a homologous series the electron-donating power decreases with an increase in the ionization potential in the gas phase, or with an increase in the pK_b in the liquid phase. Similarly, the electron-accepting power increases with an increase in the electron affinity in the gas phase, and decreases with increase in the pK_a value in the liquid phase.

Not surprisingly the $\Delta\nu_D$ and $\Delta\nu_A$ values do not correlate with each other, (but they do correlate, independently, with other polarity scales, see later). However, Kagiya et al. [71] have used this non-correlation to give a somewhat dubious classification of solvents into four groups: (1) amphoteric; (2) nucleophilic; (3) electrophilic and (4) non-philic. They plotted $\Delta\nu_D$ against $\Delta\nu_A$ and arbitrarily chose a 'standard point', where $\Delta\nu_D$ = 35 cm^{-1} and $\Delta\nu_A$ = 3 cm^{-1}. Amphoteric liquids have both larger $\Delta\nu_D$ and $\Delta\nu_A$ values than the standard point, while in non-philic liquids both are smaller; nucleophilic liquids have larger $\Delta\nu_D$ and smaller $\Delta\nu_A$, while the reverse applies for electrophilic liquids. They suggest that this *quantitative* (our italics) classification

is useful as a unifying interpretation for many kinds of experimental results, but we have used their data in a later section another way.

(vi) G values of Allerhand and Schleyer

Another solvent polarity scale based on infrared measurements is the G scale of Allerhand and Schleyer [54]. These workers studied the effect of solvents on the stretching vibrations of hydrogen bonded systems and found, contrary to previously held ideas, that the frequencies of hydrogen bonded bands were very solvent sensitive for many intra- and intermolecular hydrogen bonds. The solvent shifts of OH···O bonds were found to be proportional to C=O and other X=O solvent shifts, indicating a possible similarity of mode of interaction of solvents with these chromophores. As existing theories [72,73] of solvent shifts did not explain this behaviour, they proposed an empirical linear free energy equation,

$$G = (\nu^0 - \nu^s)/a\nu^0, \tag{5}$$

for the accurate prediction of the positions of a large number of solvent sensitive infrared bands. ν^0 and ν^s are the stretching vibration frequencies in the gas phase and in solution, respectively; a is a function of the particular infrared vibration of a given molecule and is a measure of its solvent sensitivity; and G is a function of the solvent only. Values of G were determined from the best fit of solvent shifts given in the literature by Bellamy et al. for the carbonyl bands of dimethylformamide and benzophenone [74], and the sulphonyl band of dimethyl sulphoxide [75]. An arbitrary value of 100 was assigned to dichloromethane to fix the scale, the other fixed point being zero for the gas phase.

The accuracy of these G values could, however, now be improved. While Bellamy and his group were reporting the most accurate infrared data available in 1959, far better than the broad bands of Gordy and Stanford (1940) [76], recent advances in infrared spectrophotometers mean that the bands they measured can now be recorded as even narrower bands, and hence with more precision in the peak maximum. It is therefore now an appropriate time to recalculate and extend G values, but we have not yet done so.

E. POLARITY SCALES FROM ENTHALPY DATA

The first discussion of the constituent thermodynamic steps involved in the enthalpy of a donor—acceptor reaction, where the donor was the solvent, was presented by Drago and Wayland [78], who formulated their coordination model for non-aqueous solvents. A two-parameter equation was proposed to correlate enthalpies of adduct formation in the gas phase and poor solvating solvents, viz., $-\Delta H = E_A E_B + C_A C_B$ where the subscripts A and B refer to acceptor and donor, respectively, and E and C are two empirically derived parameters assigned to each.

Originally E and C parameters were determined mainly from the enthalpy data of iodine and phenol. The above equation was solved using experimental enthalpies for iodine interacting with a series of alkyl amines, and empirical values obtained for the amine E and C parameters by setting $C_A = E_A = 1.00$ for iodine and $C_B = aR_D$ and $E_B = bu$ for the amines. R_D was the total distortion polarisation and u the ground state dipole moment. With sufficient enthalpy data all the unknowns could be determined, and checks made on the entire procedure. Subsequently the best set of E and C parameters was determined, by computer program, using the available enthalpy data, and a least squares fit analysis, yielding values for 33 acids and 48 bases [126].

E and C were initially interpreted as being related to the electrostatic and covalent bond forming abilities of acids and bases, normalised to $E_A = C_A = 1$ for iodine. Drago [126] now states that they "are very complicated quantities". Although they do support intuitive trends, predict enthalpies, and can illumine certain reactions there are a significant number of interactions where the observed and predicted enthalpies do not agree, and for which the investigators have no explanation. E and C values are not polarity scales and therefore have not been included in subsequent correlations. They are an attempt to redefine the term 'solvent polarity' (Section C) as two effects, *coordination* and *non-specific solvation*. We do not accept this as a necessarily reasonable and feasible subdivision of all experimentally determined values which relate to enthalpy, and other solvent dependent data, particularly in the light of the successes of multi-parameter equations [30] to separate *electrostatic* and *specific contributions* to the overall solvent effects in chemical reactions, though we recognise the two systems are not identical. We therefore have in this review stressed *experimental* values, and have included the above for completeness, because the measured enthalpy values determined by Gutmann and Wychera [35], originally termed donor numbers, are interpreted and used differently, and consequently their approach has been criticised by Drago [126].

(i) Donor numbers of Gutmann

The concept of donor numbers (or donicity, as it is often now termed) was proposed by Gutmann and Wychera [35] to express, in at least a semi-quantitative manner, the donor-strength of a solvent. Donor number was defined as the absolute value of the enthalpy (in kcal mol^{-1}) of the reaction,

$$SbCl_5(\text{dissolved}) + D(\text{dissolved}) \rightleftharpoons D \cdot SbCl_5(\text{dissolved}) \qquad (6)$$

measured calorimetrically for dilute solutions in an inert medium such as 1,2-dichloroethane. Since $SbCl_5$ is such a strong electron pair acceptor (see for example ref. 71), it is considered that the equilibrium is displaced essentially completely to the right. Thus

$$DN_{SbCl_5} \equiv -\Delta H_{D \cdot SbCl_5} \text{ (kcal mol}^{-1}\text{)} \qquad (7)$$

where D represents the electron pair donor molecule.

The majority of the 16 donor solvents used in the original study were of a somewhat exotic nature, and would not normally be considered as media for organic reactions, but more for inorganic and organo-metallic preparations. Since then, the donor numbers of more common solvents have been measured, and 45 values recently reported, including some obtained indirectly [16,77].

Gutmann [16] has also examined the approximately linear relationship between donor number and $-\Delta H_{D \cdot A}$ values of various acceptors (A) as an empirical method of predicting $-\Delta H_{D \cdot A}$ values. On inspection, however, the average difference between observed and calculated values was ±3 kcal mol^{-1}.

(ii) Q_m values of Marvel, and also Searles

Another empirical scale based on enthalpies in 1,2-dichloroethane was commenced by Marvel et al. [50], continued by Searles and Tamres [51], and compiled and reviewed by Arnett [79]. Q_m is the heat of mixing of the solvent with 50 mol % chloroform at 25°C. These values, because the interaction between a solvent and a chloroform molecule is not expected to be strong, are low, ranging from 0.1 to 1 kcal mol^{-1}. The directly comparable Gutmann donor numbers [35] generally range between 10 and 40 kcal mol^{-1}. There is a good linear relationship between Q_m and DN_{SbCl_5}, and also $\Delta\nu_D$, which will be discussed in Section I.

F. POLARITY SCALES FROM BASICITY MEASUREMENTS

(i) Proton affinity (PA) values of Long and Munseon

Proton-affinity values (in kcal mol^{-1}) were calculated by Long and Munseon [80] from equilibrium constants, from mass spectroscopy experiments, for various gaseous proton-transfer reactions with various solvents. The results reflect the effect of solvent structure on the intrinsic basicity of the solvents [5]. PA values increase steadily down a homologous series, but viewed overall the order is surprising, e.g., benzene comes between methanol and formic acid which is above the lowest member, water. Obviously deviations must be expected from the gas-phase values in liquid solvents containing hydrogen bonding and other solvent—solvent interactions.

(ii) HCl_{sol} values of Gerrard et al.

Another scale that appears to be a direct measure of solvent basicity comes from solubility measurements of hydrogen chloride in various solvents at 10°C by Gerrard et al. [81]. Arnett [79] has also examined these values. On comparing HCl_{sol} values with PA values, where one might expect a correlation, the only linear correlation found was for solvents with the same functional group, viz., the alcohols. HCl_{sol} values are perhaps better related to the conductance studies of HCl in anhydrous polar organic solvents by Janz and Danyluck [33].

G. POLARITY SCALES FROM NMR CHEMICAL SHIFTS

Recently several polarity scales have been developed from the solvent effects on certain nuclei, as measured by nmr techniques. The magnitude, direction and concentration dependence of the chemical shifts of these nuclei are strongly influenced by the solvating ability (or donicity) of the solvents.

Numerous studies of ionic solvation have used proton chemical shifts in the elucidation of the structures of electrolyte solutions. The information obtained is somewhat limited since the measurements are usually performed on the resonance of either the solvent protons or on protons of solvating species dissolved in an "inert" solvent, and, for the early work, usually at quite high concentrations. The observed protons are often several atoms removed from the interaction site, as in studies of oxygen—solute interactions in dimethyl sulphoxide [82]. As a consequence, the chemical shifts are only weakly affected by solvation. Thus much better information may be obtained if the resonance of the solvated ions is observed directly. We divide this section according to the resonating nuclei.

(i) Protons

The ΔR scale of Anderson and Symons [64] is based on a very carefully chosen cation. They studied the proton nmr spectra of some 1,4-diethylpyridinium halides, and in addition to considering the individual proton shifts they measured the *difference* between the 2,6- and 3,5-ring proton shifts. They assumed that the anion was held electrostatically above the positively charged nitrogen atom of the cation in an ion pair structure (cf. the solutes used by Kosower [28]), the tightness of which decreased with increasing solvent polarity and anion size. Thus the proton shifts will be directly affected by solvation, and the difference between ring proton shifts, designated ΔR, will be independent of any solvent effects that are mutual to both pairs of protons. Thus ΔR values are a direct measure of solvating ability, i.e., solvent polarity.

This study necessitated relatively high solute concentrations to permit the formation of the contact ion-pair being studied, but even so, ΔR values were markedly concentration dependent, in general increasing by about 10% on increasing the concentration from 0.2 to 10% mol fraction of solute. Although the data were found to correlate well with Kosower's Z values we note that, at the maximum concentration employed, ΔR values were not constant, and a ΔR value at 1% mol fraction was generally used: the measured Z values were either concentration independent, or obtained from extrapolation to infinite dilution.

The other nmr studies, particularly those involving ions, required dilute solutions to avoid ion-pairing or clustering influencing chemical shifts, and normally were extrapolated to infinite dilution. There is therefore some imprecision in the data in the literature, but recent developments in instrumen-

tation now make possible measurements, in high dielectric constant solvents, at sufficiently low concentrations so that ion-pairing is not statistically significant.

(ii) Alkali metal nuclei

A nucleus particularly well suited to the direct observation of the resonance of solvated ions is ^{23}Na. The relative sensitivity of 0.1 with respect to ^{1}H facilitates measurements in fairly dilute solutions. Also, the large quadrupole moment results in the sodium nucleus being a sensitive probe of the neighbouring electronic environment.

An early study of ionic solvation using the ^{23}Na nucleus was performed by Bloor and Kidd [83], using various concentrations of NaI in a series of oxygen- or nitrogen-donor organic solvents. The chemical shifts were concentration dependent, and when extrapolated to infinite solution, Bloor and Kidd suggested a scale (δ_0, ppm) relative to infinitely dilute aqueous NaI, for which δ_0 was assigned the value zero ppm. This work was extended by Popov and co-workers [84,85] to include the shifts of sodium tetraphenylborate, perchlorate, iodide and thiocyanate. For the first two salts the shift was concentration independent.

More recently Popov and co-workers [86] have measured the chemical shifts of the ^{7}Li nucleus for a series of lithium salts in a variety of non-aqueous solvents. The shifts (δ ppm) relative to aqueous lithium perchlorate did not correlate with the δ_0 values [83] for ^{23}Na. This was explained in terms of the relative magnitudes of the paramagnetic and diamagnetic screening constants of the two nuclei. However, they found [85] an excellent correlation between the ^{23}Na chemical shifts and Gutmann's donor numbers [35].

(iii) Halogen nuclei

Halogen nuclei, especially ^{19}F, have also been used in the study of the solvating ability of solvents. Taft et al. have examined the solvent effects on the fluorine resonance in *meta*- [52] and *para*-substituted [53] fluorobenzenes, and have defined the *P* value of a solvent as the chemical shift of *p*-nitrofluorobenzene in that solvent relative to the shift in the standard solvent cyclohexane. Gurka and Taft [87] have further used the ^{19}F nucleus to study hydrogen bond complex formation between *p*-fluorophenol in that solvent (i.e., the shift of the completely formed complex) relative to that in carbon tetrachloride (i.e., the shift of the uncomplexed *p*-fluorophenol), termed Δ ppm.

Spaziante and Gutmann [88] measured the ^{19}F chemical shift of CF_3I in a series of electron pair donor solvents relative to CCl_3F as an external standard. A linear correlation was obtained between the shifts at infinite dilution and the donicity [35] of the solvent.

Langford and co-workers [89] have measured the chemical shifts of the

TABLE 2

Solvent polarity scales from nmr measurements

	ΔR(Hz)	δ_0(ppm)	δ(ppm)	P(ppm)	Δ(ppm)	δ(ppm)[a]	Acceptor number (AN)
Nucleus	^{1}H	^{23}Na	^{7}Li	^{19}F	^{19}F	^{19}F	^{31}P
Standard	TMS[b]	NaI[c]	$LiClO_4$[d]	C_6H_{12}[e]	CCl_4	CCl_3F	Ph_2POCl[f]
Number of values	19	15	12	52	55	28	34
Minimum value	47.3	−13.1	−2.54	−0.40	1.10	ca. 4.5	0.0
Solvent of minimum value	D_2O	en[g]	Py[h]	3-mp[i]	Et_2S	Thionyl chloride[j]	Hexane
Maximum value	87.1	9.9	2.80	2.70	3.71	ca. 14.5	129.1
Solvent of maximum value	$CDCl_3$	Ac_2O	CH_3CN	TMS[b]	HMPA[k]	HMPA[k]	TFMS[l]
Reference	64	83	86	53	87	88	91

[a] Spaziante and Gutmann presented their data graphically and thus only approximate δ values are available. [b] Tetramethylsilane. [c] Infinitely dilute aqueous NaI. [d] 4 M aqueous $LiClO_4$. [e] Cyclohexane. [f] Diphenylphosphonic chloride. [g] Ethylenediamine. [h] Pyridine. [i] 3-Methylpentane. [j] Although this name is given Gutmann has attributed the formula of sulphuryl chloride to it (ref. 16). [k] Hexamethylphosphoramide. [l] Trifluoromethyl sulphonic acid.

^{35}Cl, ^{79}Br and ^{127}I nuclei in a series of solvents relative to aqueous solution and reported a close correlation between the shifts and the ctts absorption band energies [90]. The data covered five pure solvents and two binary solvent mixtures.

(iv) ^{31}P *nucleus*

Gutmann and co-workers [91] have very recently introduced the acceptor number (AN) as a quantitative measure of the electrophilic properties of solvents. This is analogous to the donor number [35], which attempts to quantify the nucleophilic properties of solvents. The acceptor number of a solvent is defined as the chemical shift of the ^{31}P nucleus of triethylphosphine oxide relative to diphenyl phosphinic chloride as an external standard. However, the probe nucleus of this solute is remote from the actual place of solute—solvent interaction, viz., the basic oxygen atom. Gutmann and co-workers [91] suggested this was an important factor, as "theoretically ill-definable contact contributions to the chemical shift values are thus eliminated". It also results in the solvation effects on the chemical shift being reduced.

All the above solvent polarity scales from nmr measurements are summarised in Table 2.

H. POLARITY SCALES FROM RATE CONSTANT DETERMINATIONS

(i) General

A basic reason in the search for solvent polarity parameters has been the predictive potential a suitable scale, embracing many solvents, would have upon the most appropriate solvent for a reaction. Thus the earliest studies on this topic were investigations into the effect of solvent on various organic reactions, hoping to find an appropriate, and versatile, reaction. We have left this group of polarity scales until now because the number of solvents that can be used in rate constant determinations are usually few and in single figures, and because we shall shortly show how the data for this range can be confidently and vastly extended.

Dack [5] has recently published a review on the influence of solvent on chemical reactivity. We shall therefore confine our remarks to the nature and scope of these scales.

(ii) Y *and log* k_{ion} *values of Winstein*

An investigation of the solvolyses of aliphatic compounds proceeding by an S_N1 mechanism led Grunwald and Winstein [48] to derive Y values as a quantitative measure of the ionising power of a solvent. The relationship

between Y and the rate of solvolysis is given by

$$\log(k_A/k_B) = m(Y_A - Y_B) \tag{8}$$

where k_A and k_B are the rate constants of an S_N1 solvolysis in solvents A and B, respectively and m is a function of the compound being solvolysed. Since this equation is concerned only with the difference in Y values, the absolute Y values can be arbitrarily fixed by reference to a standard reaction. This was chosen as the solvolysis of t-butyl chloride at 25°C, and Y was defined as

$$Y = \log k^{t\text{-BuCl}} - \log k_0^{t\text{-BuCl}} \tag{9}$$

where k and k_0 are the rate constants of the solvolysis in a given solvent and a standard solvent, respectively. The standard solvent selected was 80% aqueous ethanol, for which Y, by definition, is zero. Equation (9) thus reduces to

$$\log(k/k_0) = mY \tag{10}$$

By definition, m for t-butyl chloride is 1.0. Y values range from 3.493 in water to −2.033 in ethanol: the larger the Y value, the greater is the ionizing power of the solvent. Due to experimental difficulties, Y values were measured for only 6 pure solvents and a series of binary mixtures. However, the scale can be extended, provided values for m for other reactions are obtainable. In this way Y values for iso-propanol and t-butanol were obtained via the solvolysis of t-butyl bromide [92].

There is an obvious analogy between eqn. (10) and the Hammett equation [93]

$$\log(k/k_0) = \rho\sigma \tag{11}$$

with m and Y corresponding to ρ and σ, where ρ is the reaction constant and σ the substituent constant. The Hammett equation was proposed as an empirical relation suggested by the parallelism of the effects of substituents in many different side-chain reactions of benzene derivatives.

Later Winstein and co-workers [94] introduced another standard reaction for characterizing the polarity of solvents, the ionization of p-methoxyneophyl-p-toluenesulphonate. The rate of this reaction at 75°C was termed the $\log k_{ion}$ value and was determined for a series of non-hydroxylic solvents and solvent mixtures. The $\log k_{ion}$ values provided a measure of the solvating power of non-hydroxylic solvents as good as that provided by the Y values for hydroxylic solvents.

(iii) X values of Gielen and Nasielski

It is possible, using eqn. (8), to measure the ionizing power of a solvent towards electrophilic aliphatic substitutions at a saturated carbon atom. Gielen and Nasielski [49] showed this for the reaction of halogen with tetraalkyl tin

compounds, which proceeds by an S_E2 mechanism. They formulated this as

$$\log(k/k_0) = p \cdot X \qquad (12)$$

where k and k_0 are the rate constants of an electrophilic aliphatic substitution on an organo-metallic compound in, respectively, the solvent under consideration and the reference solvent (in this case glacial acetic acid), p is a constant dependent on the electrophile and the organometallic compound and X is a measure of the solvent polarity. Again there is an obvious analogy with the Hammett equation (11).

Gielen and Nasielski chose as standard reaction that between bromine and tetramethyltin, for which p was assigned a value of unity, and the reference solvent a value of zero for X. To date, however, X values are known for only 7 solvents (excluding the reference solvent).

(iv) Ω values of Berson et al.

Berson et al. [95] have proposed a polarity scale based on the slight solvent dependence of the rate of Diels—Alder addition reactions, since in the addition of cyclopentadiene to methyl acrylate, the ratio of the *endo* product (N) to the *exo* product (X) is solvent dependent. Since the reaction is kinetically controlled, the product ratio is equal to that of the specific rate constants. Thus

$$\log(k_N/k_X) = \log(N/X) = \Omega \qquad (13)$$

where Ω is the proposed empirical parameter of solvent polarity. This scale is limited by the low solubility of the reactants in polar media.

The Ω value is directly proportional to the free energy difference between the *endo* and *exo* transition states. The dipole moment of the former is greater than that of the latter. Hence an increase in the polarity of the solvent will result in a better solvation of the *endo* transition state, thus lowering the free energy to a greater extent (i.e., a greater stabilization of the *endo* transition state) and leading to preferential *endo* addition. The Ω value therefore increases with increasing solvent polarity. Eleven solvents have been assigned Ω values, and these give reasonable correlations with Z and E_T.

(v) Rate constants k of Pincock

Pincock [69] has measured the effects of non-polar solvents on the ionic decomposition of *t*-butylperoxy formate. In chlorobenzene this compound undergoes relatively slow unimolecular thermal decomposition and generates formyloxy and *t*-butoxy radicals by simple cleavage of the peroxide bond, while in n-butyl ether a first-order induced decomposition occurs which involves attack by radicals on the peroxide oxygen atoms. However, in the presence of pyridine a bimolecular ionic elimination reaction proceeds, with the formation of *t*-butanol and carbon dioxide. The rate k of this reaction in

non-hydroxylic solvents depends extensively on the solvent. Values for k (at 90°C) vary by a factor of 140 (from 0.00152 in n-heptane to 0.212 in nitrobenzene), and are related to the dielectric constant and polarizability of the solvents. The solvent dependence of the reaction rate is interpreted in terms of a system in which a dipolar transition state is formed from relatively non-polar initial states. The reaction rate has been measured for 20 solvents.

(vi) S and R values of Brownstein

The final polarity scale to be considered in this section is that of Brownstein [3], which he designated S values. The m parameter in the Y value scheme of Grunwald and Winstein relates the susceptibility of a given reaction to changes in Y. Since spectroscopically derived polarity scales measure a static rather than a dynamic feature no equivalent parameter can be associated with such scales. Brownstein endeavoured to overcome this by defining a general scale, by formal analogy with Hammett's linear free energy relationship (eqn. 11), which correlated the effect of solvents on a wide variety of equilibria, reaction rates and spectral shifts,

$$\log(k_{\mathrm{solv}}/k_{\mathrm{EtOH}}) = SR \qquad (14)$$

where k_{solv} is the appropriate parameter in a given solvent, and k_{EtOH} the corresponding parameter in absolute alcohol, chosen as standard as it was a widely used solvent of medium dielectric constant and polarity. S is a constant, characteristic of a given solvent (by definition, $S = 0.00$ for absolute ethanol) or solvent mixture, and R a constant reflecting the sensitivity of a given system to solvent effects. Brownstein assigned an R value of 1.00 to Kosower's spectroscopic Z value system, because at that time it was the system covering the widest range of solvents, the E_{T} values of Dimroth et al. [29] had yet to be proposed.

From Kosower's data [28] 58 S values were calculated and used to determine R values for 9 systems, which in turn were used to calculate further S values. Altogether, Brownstein calculated 158 S values and 78 R values.

A large number of experimental data correlated quite well, but, as with all the empirically derived solvent parameters, eqn. (14) is inadequate when the specific solute—solvent interactions differ between the reference solvent and the solvent under consideration. Little use has been made of these values since they were proposed, partly because they seemed less precise than measured values. Further, Kosower [4] was somewhat critical of S values because "they cannot be related to a specific model process". More recently it has been suggested [96] that S and R values have been little used because Z and E_{T} values, although fewer in number, have been quite adequate, and that smoothing correlations of this type can cause some loss of mechanistic information gleanable from individual solvent polarity scales [5]. We now examine intercorrelations between scales to extend individual scales, and consider the reliability of predicted solvent polarity values.

I. INTERCORRELATION OF SOLVENT POLARITY PARAMETERS

(i) General

In order to allow further development of the above relationships between solvent polarity data and bulk solvent properties, and of the multiple-correlation method of separating solvent effects, we need to extend the number of solvents for which there are measured solvent polarity parameters on the various scales. Once a scale has been published the likelihood that the number of solvents covered will be extended by other workers is low (the exception is Kosower's Z values). We now consider interrelationships between the various empirical solvent polarity scales, and the validity and justification for predicting solvent polarity parameters.

Several good linear correlations between parameters for pure solvents have been noted, but only four groups of workers [2,67,94,95] have formulated the correlations in terms of the equation of a straight line, i.e.,

$$\text{ordinate(parameter 1)} = \text{gradient} \times \text{abscissa(parameter 2)} + \text{intercept} \qquad (17)$$

The gradient and intercept are usually determined by least squares analysis. Suggestions are sometimes made that additional parameters can thereby be obtained but the point has not been further developed, except once [95] when one predicted value was confirmed by direct measurement.

Kosower obtained some of his Z values from linear (but not least squares) correlations between various pyridinium iodides, where direct relationships are to be expected. A linear relationship observed by Erlich and Popov [85], with only a small amount of scatter, between ^{23}Na nmr chemical shifts and Gutmann's donor numbers, enabled them to suggest donor numbers for methanol, ethanol and formamide, which have now been generally accepted. However this correlation excluded Gutmann's measured value for water (18): to be on the line the value would have to be 33. Herlem and Popov [97] later extrapolated this correlation, above the highest measured value, stating that should there be a continuance of linearity, then they could predict donor numbers for seven amines. Gutmann and co-workers have not yet incorporated these solvents into their writings.

We have assembled a comprehensive listing of the available measured parameters and calculated the correlation constants for as many linear correlations as possible. They are listed in Table 3, together with their correlation coefficients (r).

Inspection of Table 3 shows 7 linear correlations between E_T values and other empirical scales. As one of these is the Z value scale linear correlations are expected between Z values and the remaining 6 scales. This is indeed the case for 5 of the scales (viz., X_B [58]; Ω [95]; log k_{ion} [94]; F [55] and S [3]), but it was not originally possible to establish a correlation with the sixth scale (log k [69]) as there were only three solvents common to both scales. This is not surprising as log k values were determined for non-hydroxylic solvents of

TABLE 3

Correlation of empirical solvent polarity parameters

Ordinate	Abscissa	Number of points	Gradient	Intercept	Correlation coefficient	Ref.
Z	E_T	—	1.259	13.76	—	2
Z	E_T	15	1.330	10.47	0.998	a
$\log k_{ion}$	E_T	—	0.179	−12.35	—	2
$\log k_{ion}$	E_T	14	0.205	13.59	0.966	a
Ω	E_T	—	0.0154	−0.0389	—	2
S	E_T	—	0.0134	−0.704	—	2
Z	χ_B	10	1.45	−6.34	0.989	67
Z	χ_B	11	1.368	−2.032	0.993	a
$\log k_{ion}$	χ_B	7	0.179	−13.8	0.982	67
$\log k_{ion}$	χ_B	7	0.185	−14.15	0.983	a
E_T	χ_B	12	1.03	−8.86	0.991	67
E_T	χ_B	12	1.04	−9.60	0.991	a
P	χ_B	6	−0.0108	10.9	0.232	67
χ_B	χ_R	38	−1.44	118.4	0.620	67
Z	χ_R	17	−1.94	159.8	0.524	67
P	χ_R	19	−0.189	18.7	0.812	67
$\log k$	χ_R	16	−0.236	12.4	0.958	67
Z	Ω	9	71.7	22.1	0.972	95
Z	Ω	9	76.0	20.25	0.955	a
$\log k_{ion}$	Ω	8	10.8	−10.5	0.936	95
Z	$\log k_{ion}$	10	8.11	104.2	0.971	94
Z	$\log k_{ion}$	14	5.979	96.84	0.965	a
DN	$\Delta\nu_D$	15	0.20	3.03	0.984	38
Y	Z	8	0.304	−25.60	0.959	a
$\log k_{ion}$	Y	5	0.362	−2.45	0.998	a
$\log k$	E_T	9	0.0063	−0.200	0.973	a
$\log k$	G	7	0.00077	−0.040	0.964	a
G	$\Delta\nu_A$	8	4.337	80.00	0.951	a
S	G	15	0.00398	−0.525	0.995	a
F	G	5	0.00314	−0.147	0.965	a
F	Z	9	0.0126	−0.734	0.983	a
F	E_T	11	0.0124	−0.391	0.953	a
F	S	10	0.812	0.256	0.967	a
PA	HCl_{sol}	5	0.0160	−2.05	0.998	a
DN	$D(H,I)$	5	10.11	−12.17	0.995	a
$\Delta\nu_{PFP}$	DN	9	0.0809	−1.694	0.969	a
$\Delta\nu_{PFP}$	Δppm	9	0.00732	0.116	0.887	a
Q_m	$\Delta\nu_D$	16	0.134	−8.83	0.947	a
$\Delta\nu_{PFP}$	$\Delta\nu_D$	11	0.403	−15.3	0.984	a
Q_m	DN	8	2.63	3.18	0.977	a
AN	$\Delta\nu_A$	9	0.547	−4.63	0.777	a
AN	E_T	27	0.574	32.5	0.918	a
ΔR [b]	Z	8	−0.197	81.0	0.911	a
ΔR [c]	Z	10	−0.846	131.0	0.968	a
ΔR_∞ [d]	Z	7	−0.189	79.0	0.927	a
ΔR_∞ [e]	Z	10	−0.873	131.3	0.962	a

TABLE 3 (continued)

Ordinate	Abscissa	Number of points	Gradient	Intercept	Correlation coefficient	Ref.
Z	δ [h]	13	3.60	32.3	0.912	98
E_T [f]	δ [h]	21	2.135	20.0	0.920	98
E_T [g]	δ [h]	18	3.13	5.98	0.948	98
Ω	δ [h]	7	0.471	0.133	0.952	98
S	δ [h]	34	0.046	−0.624	0.919	98
Y	δ [h]	5	0.524	−8.75	0.9998	98
Δ_{ppm}	DN	11	12.3	−5.85	0.903	a
δ_0 [i]	DN	8	−0.780	22.15	0.598	a
δ [j]	DN	9	−2.65	20.18	0.433	a
δ [k]	DN	10	−1.80	32.11	0.966	a
δ [l]	DN	10	−1.89	33.71	0.939	a
p [m]	log k	12	0.676	3.51	0.932	a
p [m]	E_T	27	5.19	30.54	0.914	a

[a] This work. [b] 1% mole fraction for dipolar aprotic solvents. [c] 1% mole fraction for protic solvents. [d] Extrapolated to infinite dilution for dipolar aprotic solvents. [e] Extrapolated to infinite dilution for protic solvents. [f] E_T values at 30°C. [g] E_T values at 26°C. [h] Hildebrand's solubility parameter [99]. [i] Chemical shifts for ^{23}Na [83]. [j] Chemical shifts for ^{7}Li [86]. [k] Chemical shifts for ^{23}Na (0.5 M $NaBPh_4$ solns.) [85]. [l] Chemical shifts for ^{23}Na (0.5 M $NaClO_4$ solns.) [85]. [m] Dipolar aprotic and non-polar solvents only.

low or zero polarity, whereas Z values relate to more polar solvents, hydroxylic solvents and solvent mixtures.

Herbrandson and Neufeld [98] have proposed that δ, the solubility parameter of Hildebrand [99], provides a measure of the effect of solvent on organic reactions, and thus a measure of solvent polarity. It is derived from the cohesive energy density, a direct measure of the total molecular cohesion per cc of liquid, and is measured by the molal energy of vapourization to a gas at zero pressure, $-E$, per molal volume of liquid, V^1: $\delta^2 = -E/V^1$. The square root of the cohesive energy density is termed the solubility parameter, δ, because of its value in correlating and predicting solubility behaviour of non-electrolytes [99]. Herbrandson and Neufeld calculated a fair correlation between δ and Z, E_T, Ω and S, and their results are included in Table 3. They found an excellent correlation with Y, $r = 0.9998$, but only four alcohols and water were used in the calculation. In the light of our comments in Section C (iii) it is not surprising that a poor relationship between δ and X_B has been found, and that the correlations with X_R separated solvents into essentially protic and dipolar aprotic groups [100].

A linear relationship between δ and the Arrhenius activation energy for the isomerization of *cis*-azobenzene to the *trans* isomer has been reported [101] for 15 solvents. However, the rate of racemization of 1,1'-binaphthyl did not increase regularly with δ [102]. Some 150 δ values have been determined, many at more than one temperature [103—107].

We have indicated earlier that Gutmann's donor numbers, because they represent a 1 : 1 solute—solvent interaction, do not correlate with the solvating scales such as Z and E_T. Table 3 does show, however, that similar specific scales do inter-correlate, and with donor numbers. However donor numbers do correlate well with the spectroscopic scale $\Delta\nu_D$. Donor numbers do not correlate with acceptor numbers so it is not surprising that acceptor numbers have only a poor correlation with the corresponding $\Delta\nu_A$ values, and interestingly quite a good correlation is obtained between AN and E_T values. The best correlation with donor numbers is obtained with Q_m values, a scale also based on enthalpy measurements in 1,2-dichloroethane.

Gutmann [16] has also noted a linear relationship between his donor numbers and the spectrophotometric measurements of Selbin and Ortolano [108], who estimated the degree of interaction between various solvents and vanadylbisacetylacetonate [$VO(acac)_2$], which has one ligand site available. Selbin [109] has since reviewed the electronic spectrum changes on addition of donor band I moves to higher energies and band II to lower. From the energy difference, D(II,I), the degree of interaction of the solvent (and donor) with $VO(acac)_2$ is estimated. Gutmann elected to take two solvents, propanediol-1,2-carbonate and dimethyl sulphoxide, for which donor numbers are known and, assuming a linear relationship between these reference points, has compared calculated with known donor numbers, and predicted others, for non-hydrogen bonding solvents. Unfortunately, in his Fig. 7 (ref. 16) half his data points are incorrect or incorrectly plotted. Figure 1 shows a least squares fit for all the mutually common data points reported, except the nitrocompounds, and r is 0.995.

It is obviously inappropriate to comment in detail on each correlation obtained. In generating the data in Table 3, unless otherwise subsequently stated,

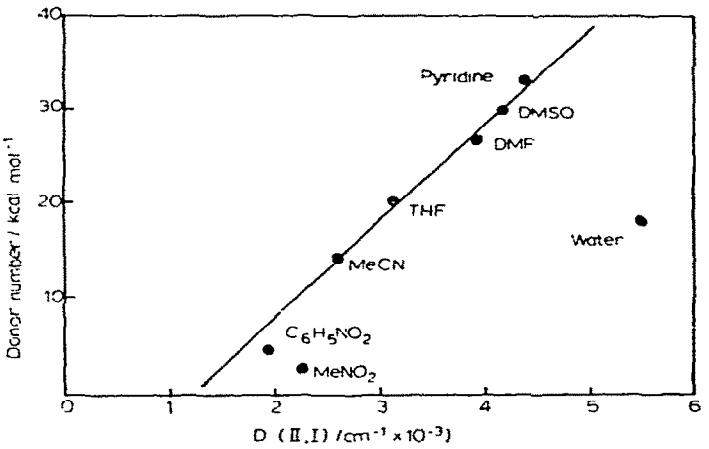


Fig. 1. Correlation between donor number (DN) and D(II,I) for various solvents. Least squares calculated line given by the equation DN = 10.11 (D(II,I)) — 12.17.

all available data were incorporated in the least squares analyses. Occasionally, if two disparate values for a solvent were available then judgement was exercised, and either the solvent was dropped from the analysis, or the value obtained by the authors of the scale was used.

(ii) Reliability of predicted solvent polarity parameters

Kosower [28] originally measured Z values for 21 pure solvents and 35 binary solvent mixtures. This scale has since been extended [65,95,100,110—114] to include 45 pure solvents, but only 5 of these also have a value for log k. (The E_T values for 42 pure solvents [29] have since been extended by one of the originators [2] to 62 solvents.) We have measured [63] Z values for a further 43 pure solvents (Table 4). However, due to solubility problems with low polarity solvents, Z values could only be measured for two more solvents for which Pincock [69] had measured log k values. This brought the number of solvents common to both scales to 7, but the correlation observed was poor (r = 0.152). Better correlations were found, following Pincock's suggestions, for log k with S and G values (r = 0.738 and 0.964, respectively).

The correlation between Z and E_T values has been known for some time [29], and Reichardt has published [2] the constants for the correlation (Table 3). Unfortunately he never stated the number of solvents used, or the correlation coefficient obtained. We have therefore re-examined this relationship. For any solvent for which there was doubt, one or both of the parameters was not included in the correlation. For example, the Z value of dimethyl sulphoxide has been quoted as 71.1 [28] and 70.4 [29], while the E_T value for t-butanol was measured [29] at 30°C, and E_T values are temperature dependent and normally measured at 25°C. This left a total of 15 solvents common to both scales, and these are plotted in Fig. 2. The correlation parameters, obtained by least squares analysis, are given in Table 3, including the excellent correlation coefficient r = 0.998.

From this correlation were calculated Z values for 27 solvents and E_T values for 13 solvents. Subsequently, Z values have been measured for 16 of these solvents [63]. The observed and calculated Z values are given in Table 5, together with the percentage error of the calculated relative to the observed value. For 10 of the 16 solvents the calculated Z value is within 2% of the observed value, and for only three solvents (benzene, 1,4-dioxan and pentan-1-ol) is the error greater than 5%.

Berson et al. [95] observed a linear relationship between their Ω values and Z values, from which they predicted a Z value for 1,2-dimethoxyethane of 61.7 kcal mol^{-1}. The spectrophotometric value was subsequently measured as 62.1 kcal mol^{-1}, thus the predicted Z value was within 1% of the observed value. They suggested the advantage that Z values could be obtained for solvents which absorb in the region of the charge transfer band, and predicted a Z value of 71.2 kcal mol^{-1} for nitromethane. This compares favourably with

TABLE 4

New Z values measured at 25°C

Solvent	λ_{max}(nm)	Z(kcal mol^{-1})
1,2-Dibromoethane	476.3	60.0
Tri-n-butyl phosphate	466.4	61.3
Dimethyl digol	464.7	61.5
Di-n-butyl sulphoxide [a]	464.1	61.6
Dibromomethane	455.0	62.8
Pentane nitrile	452.7	63.2
Methyl-n-propyl ketone	451.9	63.3
2-Methylcyclohexanone	451.4	63.3
Methyl ethyl ketone	446.9	64.0
Di-n-butyl ether	446.6	64.0
Ethyl acetate	446.6	64.0
Triethyl phosphate	443.2	64.5
1,4-Dioxan	442.9	64.6
Diethyl carbonate	442.3	64.6
Dimethyl carbonate [b]	441.7	64.7
Methyl-n-pentyl ketone	438.4	65.2
Methyl chloroacetate	430.8	66.4
Di-n-butyl sulphone [c]	424.1	67.4
n-Propylamine	421.9	67.8
n-Butyronitrile	421.5	67.8
Dimethyl sulphoxide	407.2	70.2
Trimethyl phosphate	406.2	70.4
Sulpholane	404.9	70.6
t-Pentanol	404.2	70.7
Triethyl phosphite	402.3	71.1
2-Methylcyclohexanol	387.2	73.8
Dimethyl sulphone [d]	384.5	74.4
Butyl digol	381.2	75.0
sec-Butanol	379.2	75.4
4-Chlorobutyronitrile	378.5	75.5
3,5,5-Trimethylhexan-1-ol	377.5	75.7
1-Hexanol	373.8	76.5
2-Methylpentan-2,4-diol	372.7	76.7
Dipropylene glycol	372.4	76.8
2-Ethoxyethanol	370.9	77.1
1-Pentanol	368.4	77.6
i-Butanol	368.0	77.7
2-Methoxyethanol	364.2	78.5
Pentan-1,5-diol	363.1	78.7
1-Bromo-2-propanol	362.4	78.9
3-Chloropropionitrile	358.1	79.8
Propan-1,2-diol	356.1	80.3
Glycerol	345.6	82.7

[a] 39.1°C. [b] Concentration dependent — extrapolated to infinite dilution. [c] 59.0°C. [d] 125.0°C.

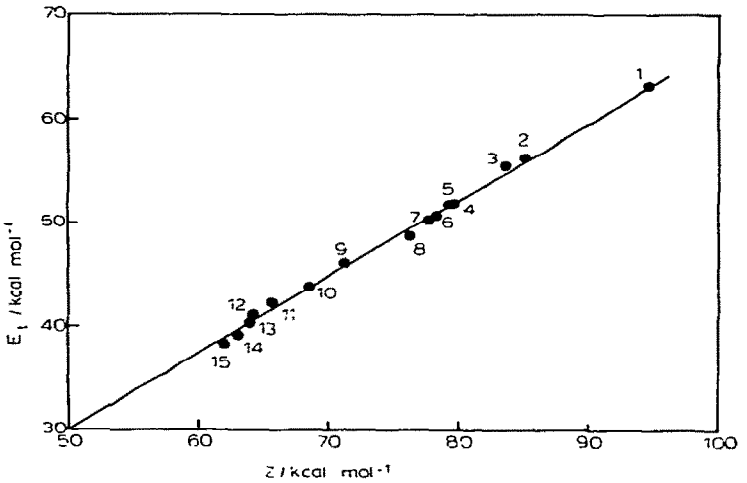


Fig. 2. Correlation between Z values and E_T values: 1, water; 2, 1,2-ethane diol; 3, methanol; 4, ethanol; 5, acetic acid; 6, propan-1-ol; 7, butan-1-ol; 8, propan-2-ol; 9, acetonitrile; 10, dimethylformamide; 11, acetone; 12, dichloromethane; 13, pyridine; 14, chloroform; 15, 1,2-dimethoxyethane.

TABLE 5

Observed and calculated Z values

Solvent	Z(obs)	Z(calc)	Percentage difference [a]	Ref.
Benzene	54.0	63.2	15.4	4
Chlorobenzene	58.0	60.4	4.1	110
Bromobenzene	59.2	60.4	2.0	110
Fluorobenzene	60.2	61.2	1.7	110
1,2-Dichloroethane	63.4	66.5	4.9	111
cis-Dichloroethylene	63.9	61.5	−3.8	110
Ethyl acetate	64.0	63.8	−0.3	[b]
1,4-Dioxan	64.5	58.4	−9.5	[b]
Benzonitrile	65.0	66.3	2.0	110
Dimethyl sulphoxide	70.2	70.4	0.3	[b]
Sulpholane	70.6	69.3	−1.8	[b]
2-Methylcyclohexan-1-ol	73.8	73.0	−1.1	[b]
1-Pentanol	77.6	73.0	−5.9	[b]
2-Methyl-1-propanol	77.7	76.5	−1.5	[b]
Benzyl alcohol	78.4	78.1	−0.4	112
2-Methoxyethanol	78.5	80.0	1.9	[b]

[a] Calculated from $[(Z(\text{calc}) - Z(\text{obs}))/Z(\text{obs})]\ 100$. [b] This work.

the value of 72.0 kcal mol^{-1} we have predicted from the correlation between Z and E_T values.

It is therefore concluded that the prediction of non-measured and unmeasurable parameters from linear correlations with Z values is validated. Accordingly, the new Z values here reported (Table 4) were used to predict E_T values and values for the five other parameters for which linear correlations with Z values were obtained. The 6 predicted values for each of the 43 solvents are included in Table 5, except for Y values, which are only valid for protic solvents, and they have been predicted accordingly.

(iii) Determination of polarity values for water

The values declared for water on various scales do not always, as we have already seen, correlate well between scales. This is no doubt due to the anomalous nature of liquid water compared with all other solvents, and that it experiences dielectric saturation in the first solvent shell about an ion. In addition, the value for water cannot always be measured directly, so it may then be extrapolated from binary aqueous mixtures. The measured parameter is plotted against the mole fraction or similar ratio, of water, but any preferential solvation of the solute is ignored.

For example, the correlation between Y and Z values was early used to predict [28] the Z value for water. It is not possible to measure this directly as the charge-transfer band, from which the Z value is calculated, is hidden beneath the intense absorption band of the pyridinium cation. Accordingly, Kosower [28] measured Z values for three binary solvent mixtures, and compared them graphically with the Y values for solvent mixtures of the same compositions. In the plot of Y against Z the three sets of data converged, within experimental error, at the independently determined [48] Y value for water, but only two sets were linear over the range studied. The convergent point corresponded to a Z value of 94.6 kcal mol^{-1}, but the measured Y value [48] had previously been obtained with difficulty and with considerably less precision than the other Y values. Further, the maximum water content of the three binary mixtures was 40 volume %, and thus the lines were extrapolated a considerable distance. A plot of Z value against mole fraction of water (Fig. 3) does not indicate a common point of convergence.

Brownstein's scale of S values [3] was based on the original Kosower Z values [28], and thus a linear correlation would be expected between the two scales. This is indeed the case for most solvents (Fig. 4), but not for water. The S value for water corresponds to a Z value of 91.8 kcal mol^{-1}, i.e., 2.8 kcal mol^{-1} less than that obtained by Kosower. Inspection of the other correlations (Table 3) involving Z values leads us to favour this value of 91.8 kcal mol^{-1} for water. Figure 5 shows the correlation between χ_B [67] and Z, with both values for Z being plotted. The 'best' line, by least squares criteria, passes much closer to the new lower Z value. This is also reflected in the corre-

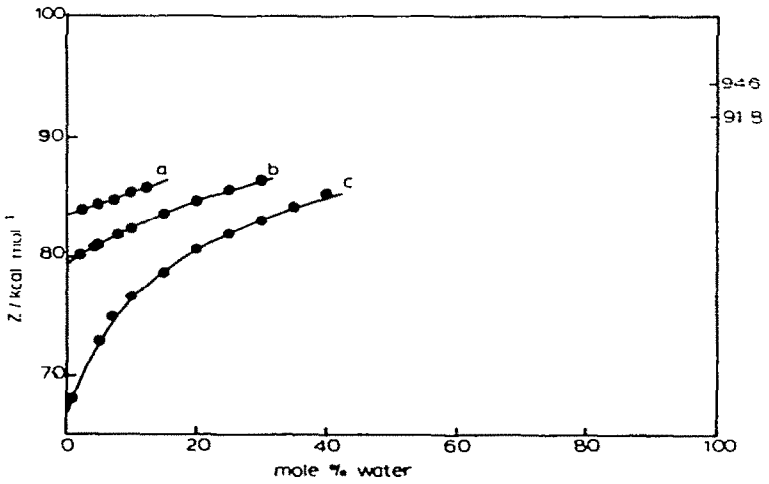


Fig. 3. Variation of Z value with mole fraction of water: (a) methanol—water; (b) ethanol—water; (c) acetone—water.

lation coefficient, which increases from 0.990 to 0.993 on going from 94.6 to 91.8 for the Z value of water.

(iv) Relationships with nmr chemical shift scales

Correlations between polarity scales derived from nmr measurements and other polarity scales have but rarely been reported. Anderson and Symons [64] observed a linear relationship between their ΔR values and Z values, for most of the solvents studied. However, they did not differentiate between protic and aprotic solvents. On replotting their data (Fig. 6), and making this distinction, we now find all the data fall close to two lines. Anderson and Symons had suggested that the deviations were probably due, in part, to incomplete ion pairing, but this is unlikely since their three main deviators, dimethyl sulphoxide, acetonitrile and tetramethylene sulphone, all have relatively high dielectric constants.

Using our classification we find protic solvents correlate with Z with a correlation coefficient of 0.968, and dipolar aprotic with 0.911 (Table 3). However, these values were obtained using ΔR values at 1% mol fraction solute, the concentration arbitarily chosen by Anderson and Symons. Using ΔR values at other concentrations, or after extrapolation to infinite dilution alters these values, slightly for protic, but increasing significantly for dipolar aprotic (0.962 and 0.927, respectively).

Water was omitted in performing the protic solvent correlation, but it is interesting to note that predicting Z for water from this correlation favours a lower Z value.

Popov and co-workers [84,97], we remarked earlier, have observed a reason-

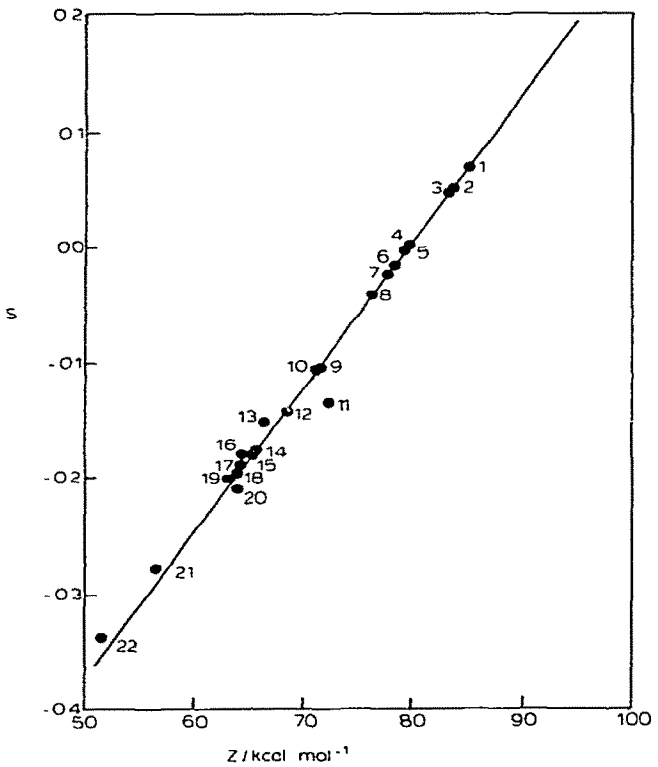


Fig. 4. Correlation between Z values and S values: 1, 1,2-ethane diol; 2, methanol; 3, formamide; 4, ethanol; 5, acetic acid; 6, propan-1-ol; 7, butan-1-ol; 8, propan-2-ol; 9, acetonitrile; 10, 2-methylpropan-2-ol; 11, nitromethane; 12, dimethylformamide; 13, 1,2-dichloroethane; 14, acetone; 15, cyclopropyl methyl ketone; 16, 1,4-dioxan; 17, dichloromethane; 18, pyridine; 19, chloroform; 20, ethyl acetate; 21, diethyl ether; 22, n-hexane.

able correlation between the ^{23}Na chemical shifts for solutions of tetraphenylborate and donor numbers [35], from which they tentatively proposed donor numbers for a series of amines. These proposals may now be partially checked since a good correlation is here reported between donor numbers and the $\Delta\nu_D$ values of Kagiya et al. [71]. This is shown in Fig. 7. Here again, to obtain high donor numbers a continuance of linearity has to be assumed, but in this case there is additional evidence. A least squares correlation between log ($\Delta\nu_D$) and log (DN) has a slope of 1.187, indicating a first order relationship and an insignificant amount of curvature. Also, the $\Delta\nu_D$ value for hexamethylphosphoramide, the solvent for which the highest donor number, 38.8, has been measured, was estimated as 179 cm^{-1} and measured [38] as 180 cm^{-1}. For the mutually common amine solvents the predicted donor numbers (of around 50) were acceptably close, and those from $\Delta\nu_D$ were always the lower. Thus predicted high donor numbers, especially from $\Delta\nu_D$ measurements, may be viewed with reasonable confidence.

Spaziante and Gutmann [88] have reported a linear correlation between the

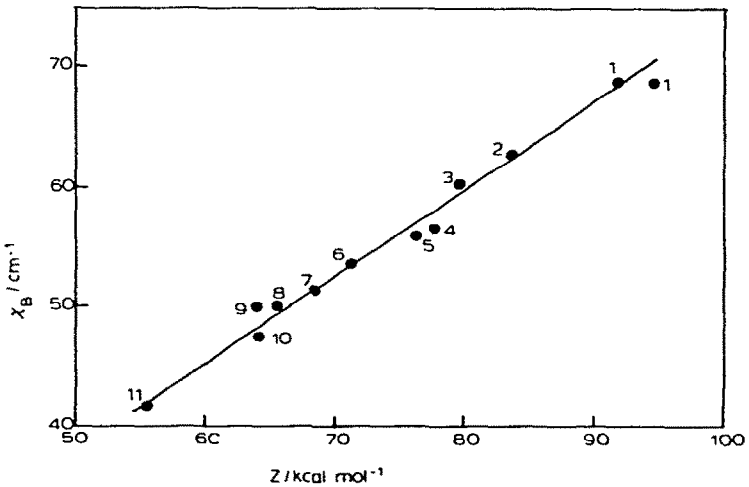


Fig. 5. Correlation between X_B values and Z values: 1, water (see Section I(iii)); 2, methanol; 3, ethanol; 4, butan-1-ol; 5, propan-2-ol; 6, acetonitrile; 7, dimethylformamide; 8, acetone; 9, pyridine; 10, dichloromethane; 11, toluene.

^{19}F chemical shift of CF_3I with donor number, and we have applied a least squares analysis and found $r = 0.903$ (Table 3). If chemical shifts were measured in amines, then this would provide another test of the above predicted high donor numbers.

The P scale of Taft et al. [52,53], also based on ^{19}F, has been compared by Brooker et al. [67] with their X_B and X_R values. Other empirical scales correlated well, but not the P scale (Table 3). However, since most nmr measurements are taken at high solute concentrations the observed chemical shifts may contain a significant contribution of other influences, such as variation in the amount of ion pairing in different solvents. Popov and co-workers are currently seeking to eliminate these problems.

(v) Predicted donor numbers

We have remarked above on the correlation between donor number and $\Delta\nu_D$, and earlier that with D(II,I) [Section I(i)]. Table 6 gives the observed and calculated donor numbers obtainable from these correlations. The original 37 measured donor numbers are now extended to 132 solvents. Some interesting points now arise between certain predicted donor numbers.

Donor numbers have not been measured for hydrocarbon compounds but the values predicted from $\Delta\nu_D$ and D(II,I) measurements are remarkably similar. Both correlations place carbon tetrachloride as the solvent with the least donor ability, with a negative donor number, but they are at variance over the donor ability of chloroform. Possibly steric reasons may affect the coordination of this molecule in the sixth site on $VO(acac)_2$. However we do have one reservation or warning. Advocates of donor numbers are now tending

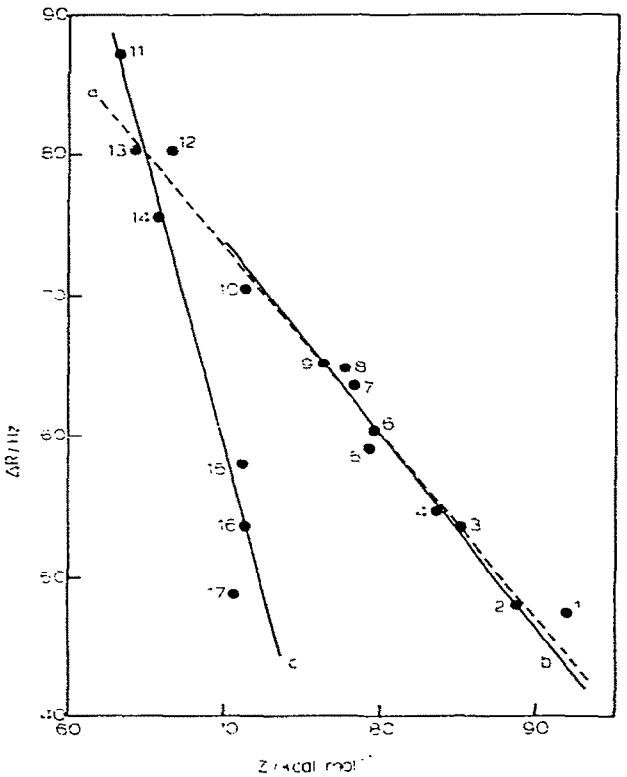


Fig. 6. Correlation between ΔR values and Z values: (a) original correlation, (b) protic solvents, (c) aprotic solvents; 1, water; 2, formic acid; 3, 1,2-ethane diol; 4, methanol; 5, ethanol; 6, acetic acid; 7, propan-1-ol; 8, butan-1-ol; 9, propan-2-ol; 10, 2-methylpropan-2-ol; 11, chloroform; 12, 1,2-dichloroethane; 13, dichloromethane; 14, acetone; 15, dimethyl sulphoxide; 16, acetonitrile; 17, sulpholane.

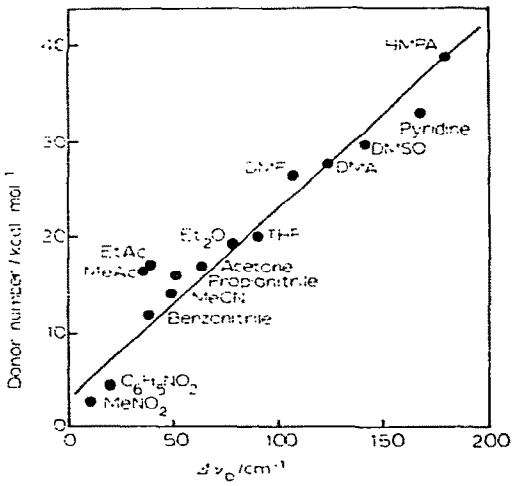


Fig. 7. Correlation between donor numbers and $\Delta\nu_D$ values.

TABLE 6

Observed and calculated donor numbers, $\Delta\nu_D$ and $D(II,I)$ values

No.	Solvent	Donor number			$\Delta\nu_D$		$D(II,I)$		
		Obs. (ref. 77)	Calc. from $\Delta\nu_D$	Calc. from $D(II,I)$[b]	Obs. (ref. 71)	Calc. from DN	Obs. (ref. 108)	Calc. from DN	Obs.[a]
Aromatic hydrocarbons and derivatives									
1	Benzene	0.1	3.0	3.8	0	−15	1.58	1.21	1.85
2	Toluene		3.4	3.5	2		1.55		
3	Ethylbenzene		3.8		4				
4	*m*-Xylene			3.0			1.50		
5	Styrene		3.4		2				
6	α-Methylstyrene		2.8		4				
7	*p*-Methylstyrene		3.4		2				
8	Chlorobenzene		2.6		−2				1.85
9	Bromobenzene		2.8		−1				
10	*o*-Dichlorobenzene		0.8		−11				
11	*m*-Dichlorobenzene		0.0		−15				
Aliphatic hydrocarbons and derivatives									
12	n-Hexane		3.2		1				
13	n-Heptane		3.0		0				
14	Carbon disulphide			3.8			1.58		1.95
15	Carbon tetrachloride		−1.2	−1.4	−21		1.07		2.0
16	Chloroform		−0.4	7.4	−17		1.94		1.95
17	Methylene chloride		0.6		−12				
18	Ethylene chloride	0.1	3.4		2	−15		1.21	
19	Ethylene sulphite	15.3				61		2.72	
20	1,1-Dichloroethane		0.6		−12				
Nitro compounds									
21	Nitromethane	2.7	4.2	10.7	6	−2	2.26	1.47	
22	Nitroethane		4.6		8				
23	Nitrobenzene	4.4	7.2	7.5	21	7	1.95	1.64	2.25

TABLE 6 (*Continued*)

No.	Solvent	Donor number			$\Delta\nu_D$		D(II,I)		
		Obs. (ref. 77)	Calc. from $\Delta\nu_D$	Calc. from D(II,I)[b]	Obs. (ref. 71)	Calc. from DN	Obs. (ref. 108)	Calc. from DN	Obs.[a]
Nitriles									
24	Acetonitrile	14.1	12.8	14.1	49	55	2.60	2.60	2.6
25	Propionitrile	16.1	13.4		52	65		2.80	
26	Acrylonitrile		10.4		37				
27	n-Butyronitrile	16.6				68		2.85	
28	iso-Butyronitrile	15.4				62		2.73	
29	Benzonitrile	11.9	10.6		38	44		2.38	
30	Phenylacetonitrile	15.1				60		2.70	
Esters									
31	Methyl acetate	16.5	10.2		36	67		2.84	
32	Ethyl acetate	17.1	10.8		39	70		2.90	
33	Methyl chloroacetate		8.4		27				
34	Methyl dichloroacetate		7.6		23				
35	Methyl propionate		9.6		33				
36	Ethyl propionate		9.4		32				
37	Methyl isobutyrate		9.4		32				
38	Vinyl acetate		7.2		21				
39	Methyl acrylate		9.0		30				
40	Ethyl acrylate		9.6		33				
41	Methyl methacrylate		10.4		37				
Lactones									
42	β-Propiolactone		9.8		34				
43	γ-Butyrolactone		16.3		66				
44	ε-Caprolactone		19.5		82				
Ketones									
45	Acetone	17.0	15.9		64	70		2.89	2.4
46	Methyl ethyl ketone		14.5		57				
47	Diethyl ketone		14.3		56				

48	Methyl vinyl ketone		20.9		89				
49	Cyclohexanone		16.3		66				
50	Acetophenone		14.3		56				
Ethers									
51	Diethyl ether	19.2	18.7		78	81		3.10	
52	Di-n-propyl ether		17.7		73				
53	Di-isopropyl ether		18.1		75				
54	Ethyl n-butyl ether		18.5		77				
55	Ethyl vinyl ether		9.2		31				
56	n-Butyl vinyl ether		9.6		33				
57	Isobutyl vinyl ether		9.6		33				
58	Diallyl ether		16.3		66				
59	1,2-Dimethoxyethane		17.3		71				
60	Anisole		8.2		26				
61	Phenetole		8.0		25				
62	Propylene oxide		14.9		59				
63	Epichlorohydrin		12.0		45				
64	Styrene oxide		13.3		51				
65	3,3-Bischloromethyl-oxetane		18.7		78				
66	Furan		3.8		4				
67	Tetrahydrofuran	20.0	21.1	19.56	90	85	3.14	3.18	3.4
68	1,3-Dioxolane		14.7		58				
69	2-Methyl-1,3-dioxolane		15.3		61				
70	4-Methyl-1,3-dioxolane		14.3		56				
71	2-Phenyl-1,3-dioxolane		14.3		56				
72	4-Chloromethyl-1,3-dioxolane		11.6		43				
73	Tetrahydropyran		21.7		93				
74	1,4-Dioxane		18.5	28.5	77		4.02		3.2
Aldehydes									
75	Acetaldehyde		18.9		79				
76	Propionaldehyde		20.1		85				
77	n-Butyraldehyde		19.7		83				
78	Acrolein		27.5		122				
79	Crotonaldehyde		18.1		75				
80	Benzaldehyde		13.7		53				

TABLE 6 (*Continued*)

No.	Solvent	Donor number			$\Delta\nu_D$		D(II,I)		
		Obs. (ref. 77)	Calc. from $\Delta\nu_D$	Calc. from D(II,I)[b]	Obs. (ref. 71)	Calc. from DN	Obs. (ref. 108)	Calc. from DN	Obs.[a]
Amines and derivatives									
81	Ammonia			34.5			4.62		4.1
82	Ethylamine		49.7	35.6	233		4.73		4.5
83	n-Propylamine		49.1	31.4	230		4.31		
84	Di-n-propylamine		51.5		242				
85	Triethylamine		50.7		238				
86	Aniline		34.7		158				3.3
87	*N*-Methylaniline		33.3		151				
88	*N*,*N*-Dimethylaniline		32.7		148				
89	Pyridine	33.1	36.7	32.2	168	150	4.39	4.48	4.3
90	α-Picoline		39.7		183				4.2
91	γ-Picoline		35.1		160				4.25
92	4-Ethylpyridine		38.9		179				4.2
93	*o*-Toluidine		32.1		145				
94	Piperidine		51.1	28.5	240		4.02		
95	4-Vinylpyridine		41.7		193				
96	Quinoline			30.4			4.21		
97	*N*-Methyl-ε-caprolactam	27.1				120		3.88	
98	*N*-Methyl-2-pyrrolidone	27.3				121		3.90	
Imines									
99	Ethylenimine		50.5		237				
100	*N*-Phenylethylenimine		40.3		186				
Amides									
101	Formamide			39.9			5.15		
102	*N*,*N*-Dimethylformamide	26.6	24.5	27.7	107	118	3.94	3.84	4.1
103	*N*,*N*-Dimethylacetamide	27.8	25.7		113	124		3.95	
104	*N*,*N*-Diethylformamide	30.9				139		4.26	
105	*N*,*N*-Diethylacetamide	32.2				146		4.39	
106	Hexamethylphosphoramide	38.8	39.1		180	179		5.04	3.6

Sulphoxides and sulphones									
107	Dimethyl sulphoxide	29.8	31.3	30.1	141	134	4.18	4.15	3.8
108	Tetramethylene sulphone	14.8				59		2.67	
Acids and derivatives									
109	Formic acid			20.7			3.25		
110	Acetic acid			25.1			3.69		3.8
111	Acetic anhydride	10.5				37		2.24	
112	Acetyl chloride	0.7				−12		1.27	
113	Benzoyl chloride	2.3				−4		1.43	
114	Benzoyl fluoride	2.0				−5		1.40	
Water and alcohols									
115	Water	18.0		43.3		75	5.49	2.99	5.4
116	Methanol	19.0		32.5		80	4.42	3.08	4.7
117	Ethanol			30.9			4.26		4.5
118	n-Butanol			29.3			4.1		4.25
119	n-Amyl alcohol			26.2			3.8		
Carbonates									
120	Ethylene carbonate	16.4				67		2.83	
121	Dichloroethylene carbonate	3.2				1		1.52	
122	Tetrachloroethylene carbonate	0.8				−11		1.28	
123	Propanediol-1,2-carbonate	15.0				60		2.70	3.4
Phosphates									
124	Trimethyl phosphate	23.0				100		3.48	
125	Tri-n-butyl phosphate	23.7				103		3.55	
Inorganic halides									
126	Sulphuryl chloride	0.1				−15		1.21	
127	Thionyl chloride	0.4				−13		1.24	
128	Selenium oxychloride	12.2				46		2.41	
129	Phosphorus oxychloride	11.7				43		2.36	
130	Phenylphosphonic difluoride	16.4				67		2.83	
131	Phenylphosphonic dichloride	18.5				77		3.03	
132	Diphenylphosphonic chloride	22.4				97		3.42	

[a] Obtained from reported values of the maxima of the bands I and II of vanadyl acetylacetonate in various solvents [130].
[b] Using data from ref. 108 only.

towards quantitative applications. Donor numbers (enthalpy determinations at infinite dilution) are not easy to measure, and since they were originally determined more accurate and sensitive calorimeters have been marketed. Enthalpy measurements by other groups of workers [128,129] have not always yielded values within (the claimed) experimental error of the original workers [35]. Thus before this tendency is continued we consider it important that donor numbers should be remeasured, and the linear relationship with $\Delta\nu_D$ redetermined, before our predicted donor numbers are used extensively. Differences also appear in the predicted values for certain amines. We have just demonstrated that the DN—$\Delta\nu_D$ relationship may be used to predict with confidence high donor numbers. In this relationship we did not use the nitro-compounds (Fig. 1). All the solvents used had only one possible donor site on the molecule, usually an oxygen atom: the nitro-compounds have two neighbouring oxygen atoms containing lone pairs. Thus these compounds will have slightly different effects on bands I and II. The measured donor numbers of nitromethane and nitrobenzene are therefore the more appropriate to use, but they should be used with some circumspection since although they were employed in obtaining the DN—$\Delta\nu_D$ relationship (Table

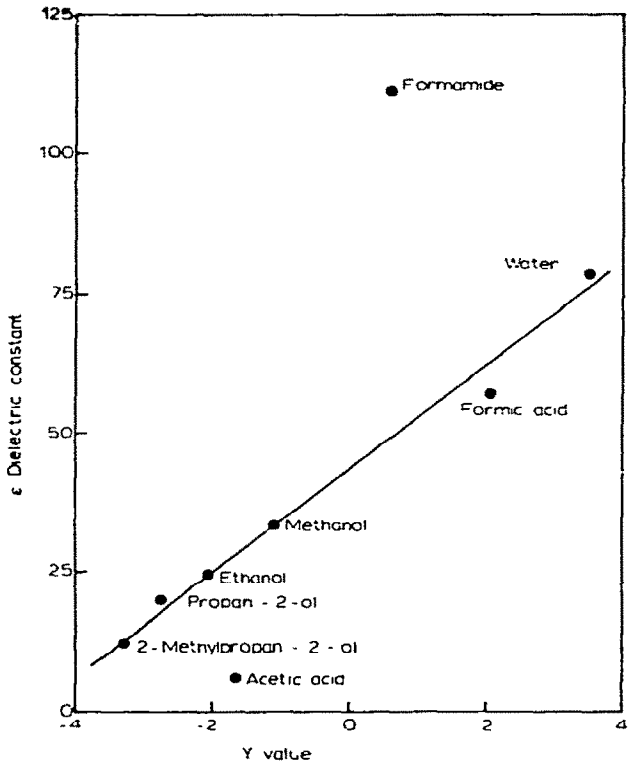


Fig. 8. Variation of Y values with dielectric constant.

3) the line obtained (Fig. 8) does not pass through their datum points.

The acetate esters were omitted in this relationship for chemical reasons. Deuteron transfer from CH_3OD can occur on to the ester molecule via keto—enol tautomerism. The value obtained for $\Delta\nu_D$ may be related to the O—D vibration of the deuterated enol form. It is unfortunate that donor numbers for formates, in which this tautomerism cannot occur, have not been reported. Thus the measured and calculated donor number values for esters in Table 6 should be treated with caution.

We also note that the D(II,I) values reported by Selbin and Ortolano [108] do *not* agree, with the one exception of acetonitrile, with those that may be derived from the data of Symons and co-workers [130]. In most cases the difference is quite marked (Table 6). A plot of these values against donor number produces a plot of greater scatter to that in Fig. 1, and slightly different slope. We therefore again advise caution for donor numbers predicted from D(II,I) data, but emphasise that, with our earlier proviso that donor numbers need to be redetermined on modern equipment, the measurement of $\Delta\nu_D$ values is currently recommended as a rapid and reliable method for deriving further donor numbers.

J. CORRELATIONS BETWEEN SOLVENT POLARITY DATA AND BULK SOLVENT PROPERTIES

We can now return to a consideration of the relationships between solute—solvent interactions and bulk solvent properties. Many attempts have been made to correlate rate constants (k) for reactions with macroscopic solvent parameters representing various aspects of solvation, the most widely used being the solvent dielectric constant ϵ. Scatchard, in an early review [115], considered the effect of dielectric constant on ion—ion reactions in terms of the Debye—Hückel theory, and predicted ln k to be inversely dependent upon ϵ. Amis [116] and Laidler and Landskroener [117] later deduced the same relationship, but both reasoning from different viewpoints.

Kirkwood [72] derived an expression for the change in free enthalpy when a molecule with dipole moment μ and radius r passes from a medium of dielectric constant unity to one of dielectric constant ϵ.

$$\Delta G = -\mu^2(\epsilon - 1)/r^3(2\epsilon + 1) \tag{15}$$

This equation can be extended, via transition state theory to include k, yielding

$$\ln k = \ln k_0 - U(\epsilon - 1)/(2\epsilon + 1) \tag{16}$$

where k_0 is the rate constant in a medium where $\epsilon = 1$, and U is a constant independent of the medium. A linear relationship is thus expected between ln k and $(\epsilon - 1)/(2\epsilon + 1)$. This has been found in many reactions between polar molecules in binary solvent mixtures [118]. However, both the Scatchard and the Kirkwood relationships usually break down when applied

to a series of one-component solvents [119], or to binary mixtures of low dielectric constant [120]. Dack [5] has suggested that correlations of this type appear to be useful only for reactions such as ion—ion, ion—dipole and dipole—dipole reactions, where general electrostatic interactions are dominant. He also notes [5] that those who have used multiparameter equations to separate electrostatic and specific contributions to the overall solvent effects in reactions have generally employed such functions of dielectric constant, viz., ϵ, $1/\epsilon$, $(\epsilon - 1)/(2\epsilon + 1)$ and $(\epsilon - 1)/(\epsilon + 2)$. We note that the latter two functions have an exaggerating effect on low dielectric constants and a levelling effect on high dielectric constants. For example, for the expression $(\epsilon - 1)/(2\epsilon + 1)$, for low ϵ values, from 2 to 7, this function changes from 0.2 to 0.4, but for $\epsilon > 20$ it is essentially constant, tending rapidly to 0.5, and only changing by 0.02 between ϵ values of 20 and 40. Plots of these two functions against a reaction or solvent sensitive parameter (are often said to) give a linear correlation [45].

Ito et al. [121] have plotted the experimental wavenumber shift of the $n \rightarrow \pi^*$ transition of various carbonyls in several non-hydrogen bonding solvents against $(\epsilon - 1)/(\epsilon + 2)$. A straight line was fitted to the data, but in each case a curve would have produced a better fit. Nicol [12] has reviewed solvent effects on spectra, maintaining this linear approach. In our view, his linear correlations have too much scatter for large numbers of data points, or would fit a curve better for few points, to encourage continuing this approach. We have therefore used the unadorned dielectric constant in seeking correlations, not necessarily linear, with solvent polarity scales.

A good linear correlation between dielectric constant and the Y values of Grunwald and Winstein has however been noted [122] (Fig. 8). The deviations from linearity for formamide and acetic acid may be rationalised in terms of internal hydrogen bonding effects, resulting, in the latter case, in dimerisation of the solvent.

Since it is well established that Y and Z values correlate well, it is not surprising that Z values also correlate reasonably well with dielectric constant, contrary to the claims of Reichardt [2]. Early criticisms of Z values are inadequate [127] and are therefore now shown to have been premature. But to understand the plot (Fig. 9) it is necessary to recognise the division of solvents into protic and aprotic (Section B. (iii)). Thus any scale that correlates with Z values, e.g., E_T values, also relates to dielectric constants in the same protic—aprotic way: Y values, with the exception of formamide, relate to protic solvents.

The increasing curvature of the Z vs. ϵ plot for dipolar aprotic solvents, compared with that for protic solvents (Fig. 9), reflects the inclusion of non-polar solvents in the former category. If they are omitted the curves are almost identical, in this and similar plots. It is interesting to note that for all polarity scales where the parameters are measured in kcal mol^{-1} the separation between the lines describing the two classes of solvent gradually increases, from around 10 kcal mol^{-1} at low dielectric constant to around 14 kcal mol^{-1}

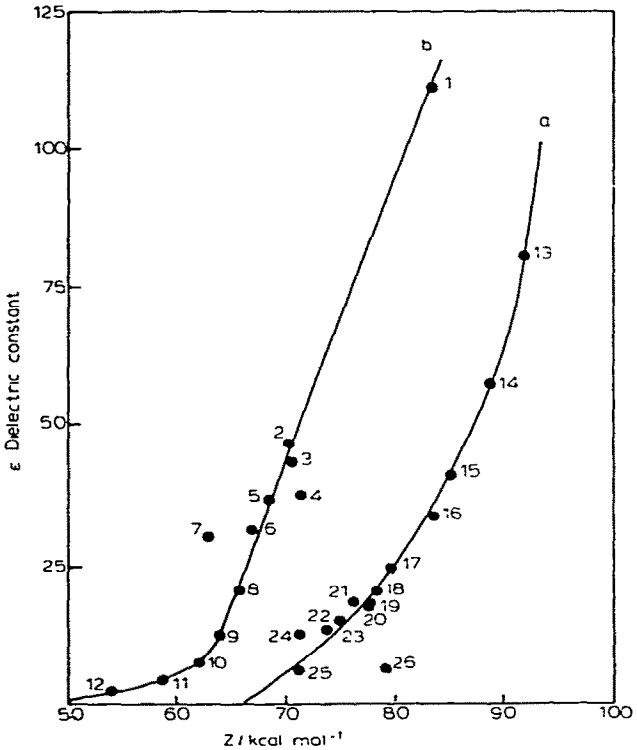


Fig. 9. Variation of Z values with dielectric constant: 1, formamide; 2, dimethyl sulphoxide; 3, sulpholane; 4, acetonitrile; 5, dimethyl formamide; 6, dimethyl acetamide; 7, hexamethylphosphoramide; 8, acetone; 9, pyridine; 10, 1,2-dimethoxyethane; 11, phenetole; 12, benzene; 13, water; 14, formic acid; 15, 1,2-ethane diol; 16, methanol; 17, ethanol; 18, propan-1-ol; 19, 2-methylpropan-1-ol; 20, butan-1-ol; 21, propan-2-ol; 22, cyclohexanol; 23, 2-methylcyclohexan-1-ol; 24, 2-methylpropan-2-ol; 25, 2-methylbutan-2-ol; 26, acetic acid.

at high values. This separation approximates closely the energy of hydrogen bonding. Using several plots of ϵ vs. a solvent polarity parameter, and classifying a solvent as protic or aprotic, it has been possible to predict with reasonable accuracy the dielectric constant of several solvents, which were later measured [38].

A related correlation is that of Griffiths and Wijayanayake [37] of the energy difference between the first ultraviolet absorption maximum of sodium iodide and tetra-n-hexylammonium iodide in a given solvent with the reciprocal of the dielectric constant of that solvent (Fig. 10). In the range $11 < \epsilon > 5$, in which only solvent shared ion pairs were found (Section B. (iii)) the anion—cation separation was confirmed by calculations that used the *bulk* dielectric constant for the intervening solvent molecule.

It is still being suggested [5] that the microscopic dielectric constant of the solvent molecules contiguous to the solute should be of relevance. This is

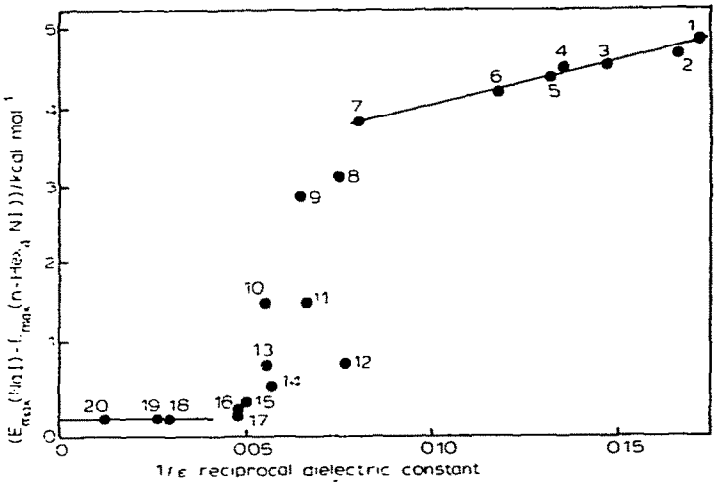


Fig. 10. Partitioning of ΔE_{max} values as a function of the reciprocal of the dielectric constant: 1, 2-methylbutan-2-ol; 2, ethyl acetate; 3, tri-n-butyl phosphate; 4, 1-chlorobutane; 5, tetrahydrofuran; 6, methyl formate; 7, 2-methylpropan-2-ol; 8, 2-methylcyclohexan-1-ol; 9, pentan-2-one; 10, cyclopentanol; 11, cyclohexanol; 12, triethylphosphate; 13, 2-methylpropan-1-ol; 14, butan-1-ol; 15, propan-2-ol; 16, acetone; 17, trimethyl phosphate; 18, methanol; 19, acetonitrile; 20, water.

based on the calculations of Hasted et al. [123,124], for a number of models, which showed that the microscopic dielectric constant of water within 1.5 Å of an ion is about 5, but this rises rapidly to the bulk value, 80, around 4 Å from the ion [125]. Similar results for other solvents can be expected, but the microscopic dielectric constant should not fall as low as for water. What has not been recognised is that water is the exception rather than the rule. Most solvent molecules have a molecular diameter of 6 Å or greater and a much lower bulk dielectric constant, and thus non-aqueous solvent molecules contiguous to ions have a dielectric constant essentially that of the bulk value, thereby further confirming the above calculation identifying solvent shared ion pairs. The absence of a zone of disorder around solvated anions in protic solvents, but continuous hydrogen bonding from anions into the bulk solvent, is now proposed [46].

In the solvation of dipoles hardly any reduction in bulk value must apply to the solvating molecules. Thus in our view the concept of a microscopic dielectric constant for a solvent is not relevant, and should not be adduced in explaining chemical reactions. Differences in reactivity between two solvents of the same dielectric constant, but where one is protic and the other aprotic, should be considered in terms of the contribution of the hydrogen bonding energy.

A much greater differentiation between protic and (dipolar) aprotic solvents is observed [122] if solvent polarity parameters are plotted against dipole moment μ. From Fig. 11 we can also conclude a marked difference in

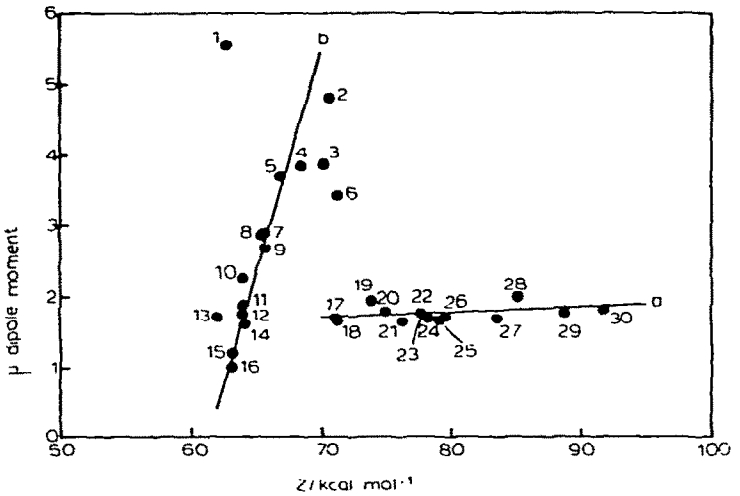


Fig. 11. Variation of Z values with dipole moments: (a) protic solvents, (b) aprotic solvents; 1, hexamethylphosphoramide; 2, sulpholane; 3, dimethyl sulphoxide; 4, dimethylformamide; 5, dimethylacetamide; 6, acetonitrile; 7, hexadeuteroacetone; 8, cyclopropyl methyl ketone; 9, acetone; 10, pyridine; 11, ethyl acetate; 12, tetrahydrofuran; 13, 1,2-dimethoxyethane; 14, dichloromethane; 15, chloroform; 16, deuterochloroform; 17, 2-methylbutan-2-ol; 18, 2-methylpropan-2-ol; 19, 2-methylcyclohexan-1-ol; 20, cyclohexanol; 21, propan-2-ol; 22, 2-methylpropan-1-ol; 23, butan-1-ol; 24, propan-1-ol; 25, acetic acid; 26, ethanol; 27, methanol; 28, 1,2-ethane diol; 29, formic acid; 30, water.

the solvation of the dipolar contact pyridinium iodide ion pair, from which Kosower's Z values are derived. For the protic solvents, largely alcohols, and for which μ is approximately 1.7—1.8, Z decreases as the solvent molecules get larger and the hydroxyl group becomes more sterically restricted. Thus Z decreases as the intermolecular hydrogen bonding decreases. Such a trend would not be expected if there was a structureless region between the solvated dipole and the bulk solvent. Dipolar aprotic solvents, with a small increase in Z (from 64 to 70) with μ increasing from 1 to 5 D, demonstrate clearly the minimal nature of their intermolecular interactions. Dipole—dipole interactions are therefore the major component for the solvation of the contact ion pair. The results of Anderson and Symons [64] suggest that the ion pair formed in each solvent does not necessarily have the iodide ion sited always on the 2,6-protons of the pyridine ring; "above" the nitrogen atom is a possibly more favoured site. We suggest that the scatter around line (b) for dipolar aprotic solvents (Fig. 11) could reflect different positions for iodide in the contact ion pair between these two extreme sites, the position also being influenced by the differing stereochemistries of the solvent molecules.

The nearly vertical and horizontal nature of the correlations in the solvent polarity—dipole moment plot means they can only be used in an indicative, rather than a predictive manner, and they do lend support to our objections to microscopic dielectric constants.

TABLE 7

Compilation of all known measured solvent polarity values

		m.p.	b.p.	Dielectric constant (°C)	Dipole moment (D)	Z	E_T	X_B
1	Acetaldehyde	−124.6	20.8	21.1(21)	2.51			
2	Acetic acid	16.6	118.5	6.2(20)	1.68	79.2		
3	Acetic anhydride	−73.1	136.4	20.7(19)	2.82			
4	Acetone	−95.4	56.2	20.7(25)	2.69	65.7 [b]	42.2	50.1
5	d^6-Acetone				2.9	65.7		
6	Acetonitrile	−45.7	80.1	37.5(20)	3.44	71.3	46.0	53.7
7	Acetophenone	19.7	202	17.4(25)	2.96		41.3	
8	Acetyl chloride	−112	51.5	15.8(22)	2.47			
9	Acetylferrocene							
10	Acrolein	−87.7	53		2.90			
11	Acrylonitrile	−82	77.7	33.0(25)	3.51			
12	Allylamine	−88.2	58		1.31			
13	Ammonia	−77.8	−33.5	16.9(25)	1.40			
14	*i*-Amyl alcohol	−117.2	132	14.7(25)	1.82	77.6 [c]	47.0	
15	*t*-Amyl alcohol	−8.8	103	5.8(25)	1.72	70.7 [c]		
16	Aniline	−6.2	184.3	6.9(20)	6.89		44.3	
17	Anisole	−37.5	153.8	4.3(25)	1.25		37.2	
18	Antimony pentachloride	2.8						
19	Azirane (ethylenimine)		56					
20	Benzaldehyde	−55.9	178.1	17.8(20)	2.77			
21	Benzene	5.5	80.1	2.3(20)	0.0	54.0	34.5	
22	Benzonitrile	−13	190.7	25.2(25)	4.05	65.0	42.0	
23	Benzoyl bromide	−24	219	20.7(20)	3.40			
24	Benzoyl chloride	−1	197.2	23.0(20)	3.26			
25	Benzoyl fluoride	−28.5		22.7(20)				
26	Benzyl alcohol	−15.3	205.4	13.1(20)	1.66		50.8	
27	Benzylamine		185					
28	3,3-Bischloromethyloxetane							
29	Bromobenzene	−30.8	155.9	5.4(25)	1.55		37.5	
30	Bromoform	8.1	149.6	4.4(20)	0.99			

31	2-Bromopyridine		193					
32	3-Bromopyridine	142	183					
33	n-Butanol	−89.8	117.5	17.5(25)	1.75	77.7	50.2	56.8
34	*i*-Butanol	−108	107.7	17.9(25)	1.79	77.7 [c]		
35	*sec*-Butanol	−114.7	99.5	16.6(25)	1.7	75.4 [c]		
36	*t*-Butanol	25.5	82.3	12.5(25)	1.66	71.3	43.9 [p]	
37	2-Butoxyethanol		170.2	9.3(25)	2.08			
38	n-Butyl acetate	−77.9	126.5					
39	n-Butylamine	−50.5	77.8	4.9(20)	1.37			
40	*t*-Butylamine	−67.5	45.2		1.29			
41	Butyl digol	−78	231			75.0		
42	2-n-Butylpyridine							
43	n-Butyl vinyl ether	−92	93.8		1.25			
44	*i*-Butyl vinyl ether	−112	83					
45	n-Butyraldehyde	−96.4	74.8	13.4(26)	2.45			
46	γ-Butyrolactone	−42	206	39.(20)	4.12			
47	*n-Butyronitrile*	−112	118	20.3(21)	3.57	67.8 [c]		
48	*i*-Butyronitrile	−71.5	103.8	20.2(24)	3.61			
49	ε-Caprolactone							
50	Carbon disulphide	−112	45	2.6(20)	0.0		32.6	
51	Carbon tetrachloride	−23.0	76.8	2.2(20)	0.0		32.5	
52	Chlorobenzene	−45	132	5.7(20)	1.54	58.0 [d]	37.5	
53	1-Chloro-2,3-epoxy-propane	−48	116.5	22.6(22)	1.8			
54	Chloroform	−63.5	61.2	4.8(20)	1.15	63.2	39.1	
55	d-Chloroform	−64.1	61.4		1.0	63.2		
56	4-Chloromethyl-1,3-dioxolane							
57	1-Chloropropane	−122.8	46.6	7.7(20)	1.97	37.4		
58	3-Chloropyridine		148	148	2.02			
59	*p*-Chlorotoluene	7.5	162					
60	*m*-Cresol	11.5	202.2					
61	*o*-Cresol	30.94	190.95					
62	Crotonaldehyde	−74	104		3.50			
63	Cumene	−96	153					
64	β-Cyanothyl ethyl ether							
65	Cyclohexane	6.5	80.7	2.0(20)		60.1 [e]	31.2 [q]	
66	Cyclohexene	−103.50	82.98					

TABLE 7 (*Continued*)

		m.p.	b.p.	Dielectric constant (°C)	Dipole moment (D)	Z	E_T	χ_B
67	Cyclohexanol	25.2	161.1	15.0(25)	1.8	75.0[f]		
68	Cyclohexanone	−32.1	155.7	18.3(20)	3.01		40.8	
69	Cyclopropylamine							
70	Cyclopropyl methyl ketone	−68.4	114		2.87	65.4		
71	*p*-Cymene	−67.94	177.1					
72	Decalin	−43.01	195.65					
73	1-Decanol	7	229	7.7(25)		73.3[g]		
74	Diallyl ether		94					
75	1,2-Diaminoethane	8.5	116.5					
76	Dibenzyl ether	3.6	298					
77	Dibromomethane	−52	97			62.8[e]		
78	Di-n-butyl ether	−97.9	142	3.1(20)	1.18	64.0[e]		
79	Di-*t*-butyl ether							
80	Di-n-butyl sulphone	46			4.46	67.4[h]		
81	1,2-Dichlorobenzene	−16.7	180.3	9.8(20)	2.27	60.0[d]		
82	1,3-Dichlorobenzene	−24.8	173.0	5.0(25)	1.38			
83	1,1-Dichloroethane	−96.6	57.3	10.0(18)	1.97	62.1[g]		
84	1,2-Dichloroethane	−35.9	83.5	10.7(20)	1.75	63.4[g]	41.9	
85	*cis*-Dichloroethylene	−82	60.3	9.2(25)	1.76	63.9[d]		
86	Dichloroethylene carbonate							
87	Dichloromethane	−97	39.8	8.9(25)	1.55	64.2[i]	41.1	47.5
88	3,5-Dichloropyridine							
89	*N,N*-Diethylacetamide		186		3.75			
90	Diethylamine	−48	56.3	3.6(21)				
91	Diethylenetriamine	−39	208					
92	Diethyl ether	−116.2	34.6	4.3(20)	1.15		34.6	
93	*N,N*-Diethylformamide		178					
94	Diethyl ketone	−39.0	102.0	17.0(20)	2.82			
95	Diethyl maleate	−8.8	223					
96	Diethyl phthalate		298					
97	Diiodomethane	6.1	182d	5.3(25)	1.08			
98	1,2-Dimethoxyethane	−58	93.0	72.0(25)	1.71	61.2[j]	38.2	

99	*N,N*-Dimethylacetamide	−20.0	165.0	37.8(25)	3.72	66.9	43.7	
100	*p*-Dimethylaminobenzonitrile							
101	4-Dimethylaminopyridine							
102	*N,N*-Dimethylaniline	2.5	194.2					
103	*N,N*-Dimethylbenzamide							
104	*N,N*-Dimethylbenzylamine							
105	Dimethyl carbonate	1	90		1.0	64.7 [e]		
106	*N,N*-Dimethylchloro-acetamide							
107	*N,N*-Dimethylcyclohexyl-amine							
108	Dimethyl digol		159.8d		1.97	61.5 [e]		
109	*N,N*-Dimethylformamide	−61.0	153.0	38.3(20)	3.86	68.5 [k]	43.8	51.5
110	*N,N*-Dimethyl-*p*-nitrobenzamide							
111	2,6-Dimethylphenol	49	212		1.41		47.2 [r]	
112	*N,N*-Dimethyl-n-propyl-amine							
113	2,6-Dimethylpyridine	6.1	143		1.66		37.0	43.2
114	2,6-Dimethyl-γ-pyrone							
115	Dimethyl sulphide							
116	Dimethyl sulphone	109	234		4.25	74.3 [l]		
117	Dimethyl sulphoxide	18.5	189.0	46.4(23)	4.3	70.2 [e]	45.0	
118	d^6-Dimethyl sulphoxide				4.3	71.1		
119	1,4-Dioxan	11.8	101	2.2(25)	0.45	64.55 [e]	36.0	
120	1,3-Dioxolane	−95	78		1.47			
121	Diphenyl ether	26.9	258.3	3.7(30)	1.17		35.3 [p]	
122	Diphenyl methane	25.35	264.3					
123	Diphenyl phosphonic chloride							
124	Diphenyl sulphoxide							
125	Di-n-propylamine	−63	109.2	3.1(20)	1.03			
126	Di-n-propyl ether	−123.2	89.6	3.4(26)	1.32			
127	Di-*i*-propyl ether	−85.5	68.3	3.9(25)	1.22			
128	1,2-Ethane diol	−13.2	198	40.8(25)	2.3	85.1	56.3 [s]	
129	Ethanol	−117.3	78.5	34.6(25)	1.66	79.6	51.9	60.4
130	2-Ethoxyethanol		135.6	29.6(24)	2.10	77.1 [e]		
131	Ethyl acetate	−85.6	77.1	6.0(25)	1.88	64.0 [e]	38.1	
132	Ethyl acrylate	−71.2	99.8					

TABLE 7 (*Continued*)

		m.p.	b.p.	Dielectric constant (°C)	Dipole moment (D)	Z	E_T	X_B
133	Ethylamine	−84	16.6	6.9(10)				
134	Ethylbenzene	−95.0	136.2	2.4(20)	0.37			
135	Ethyl-n-butyl ether	−124	92					
136	Ethyl-*N*,*N*-dibutyl-carbamate							
137	Ethylene carbonate	36.4	238	89.6(40)	4.87			
138	Ethylene oxide							
139	Ethylene sulphite			41.0(20)	3.68			
140	Ethyl carbonate							
141	Ethyl nitrate							
142	Ethyl propionate	−73.9	99.1	5.7(19)	1.74			
143	3-Ethylpyridine	−76.9	165		2.41			
144	4-Ethylpyridine	−10.5	165		2.65			
145	Ethyl trifluoroacetate							
146	Ethyl vinyl ether	−115.8	36		1.26			
147	Flavone	100						
148	Fluorobenzene	−42.2	84.7	5.4(25)	1.47	60.2 [d]	38.1	
149	1-Fluorohexane	−103	91.5					
150	Formamide	2.5	193.0	111.0(20)	3.37	83.3	56.6	
151	Formic acid	8.4	100.8	57.0(20)	1.5			
152	Furan	−85.6	32	2.9(25)	0.71			
153	Glycerol	18.6	290d	42.5(25)	2.6	82.7 [c]		
154	n-Heptane	−91	98.4	1.9(20)	0			
155	Hexamethylphosphoramide	7.2		29.6(30)	5.54	62.8	40.9	
156	n-Hexane	−95	68	1.9(20)	0		30.9	
157	1-Hexanol	−46.7	157.5	12.5(25)		76.5 [c]		
158	Hydrazine	1.4	113.5	51.7(25)				
159	Iodobenzene	−31.4	189	4.6(20)	1.26		37.9	
160	Mesitylene	−44.7	164.7	2.3(20)	0			
161	Methane sulphonyl fluoride							
162	Methanol	−97.8	65.0	33.6(20)	1.66	83.6	55.5	63.0
163	*p*-Methoxyacetophenone	38	258					

164	*p*-Methoxybenzaldehyde	0	249.5				
165	*p*-Methoxybenzonitrile	61	257				
166	2-Methoxyethanol	−85.1	124.6	16.9(25)	2.04	78.5 [e]	52.3
167	4-Methoxypyridine		191				
168	*N*-Methylacetamide	29.5	206	186(25)	4.4	77.9	52.0 [p]
169	Methyl acetate	−98.1	57	6.7(25)	1.61		
170	Methyl acrylate		80				
171	*N*-Methylaniline	−57	196.3				
172	Methyl benzoate	−12.3	199.6				
173	Methyl-*i*-butyrate	−84.7	92.3				
174	*N*-Methyl-ε-caprolactam						
175	Methyl chloroacetate	−32.1	129.8			66.4 [e]	
176	Methylcyclohexane	−126.59	100.9				
177	2-Methylcyclohexanol	−9.5	165	13.3(20)	1.95	73.8 [e]	
178	Methyl dichloroacetate	−51.9	142.8				
179	2-Methyl-1,3-dioxolane		82				
180	4-Methyl-1,3-dioxolane						
181	Methyl ethyl ketone	−87	79.6	18.5(20)	2.77	64.0 [e]	
182	N-Methylformamide	−3.8	185	200.1(15)	3.86		54.1
183	Methyl formate	−99	31.5	8.5(20)	1.77	71.6 [l]	
184	Methyl iodide	−66.5	42.4		1.48		
185	Methyl methacrylate	−48.2	100.3	2.9(20)	1.68		
186	2-Methylpentan-2,4-diol		197	24.4(30)	2.9	76.7 [e]	
187	3-Methyl pentane		63.28				
188	Methyl-n-pentyl ketone	−35.5	151.5	12.0(20)	2.61	65.2 [e]	
189	Methyl propionate	−87.5	78.7				
190	Methyl-n-propyl ketone	−77.8	102	15.5(20)	2.72	63.3 [e]	
191	*N*-Methyl-2-pyrrolidone						
192	α-Methyl styrene	24.5	162				
193	*p*-Methyl styrene						
194	Methyl vinyl ketone						
195	Nitrobenzene	5.7	210.8	34.8(25)	4.03		42.0
196	Nitroethane	−90	115	27.4(35)	3.60		43.6
197	Nitromethane	−28.5	100.8	35.9(25)	3.56	71.2 [m]	46.3
198	*p*-Nitrophenyl methyl sulphoxide						
199	1-Nitropropane	−108	131	22.7(35)	3.59		
200	Nitrosyl chloride	−61	−5	18.2(12)	1.84		

TABLE 7 (*Continued*)

		m.p.	b.p.	Dielectric constant (°C)	Dipole moment (D)	Z	E_T	X_B
201	2,2,3,3,4,4,5,5,-Octa-fluoropentan-1-ol				2.88	84.8 [f]		
202	*i*-Octane			1.9(20)		60.1		
203	1-Octanol	−15.0	195.2	10.3(20)	1.76			
204	Octan-2-one	−20.9	173	10.4(20)	2.72			
205	*t*-Pentanol	−8.8	102	5.8(25)	1.7	71.2 [f]		
206	*i*-Pentyl nitrite							
207	Perfluoro-octane							
208	Phenetole	−30	172	4.2(20)	1.36	58.9 [m]		
209	Phenylacetonitrile	−23.8	234	18.7(27)	3.47			
210	*N*-Phenylazirane							
211	2-Phenyl-1,3-dioxolane							
212	Phenyl methyl sulphoxide							
213	Phenyl phosphonic dichloride	3	258	26.0(20)				
214	Phenyl phosphonic difluoride			27.9(20)				
215	Phosgene	−128	8	4.3(22)	1.1			
216	Phosphorus oxychloride	1.3	108	13.3(22)	2.41			
217	α-Picoline	−66.8	128.8	9.8(20)	1.88		38.3	
218	β-Picoline	−18.3	144		2.40			
219	γ-Picoline	3.6	143.1		2.60			
220	Piperidine	−9	106.0	5.8(20)	1.19		35.5	
221	Propan-1,2-diol	−60	187.6	32.0(20)	2.25	80.3 [e]		
222	n-Propanol	−127	97.1	20.3(25)	1.7	78.3	50.7	
223	*i*-Propanol	−89.5	82.4	19.9(25)	1.66	76.3	48.6	56.1
224	Propargyl alcohol	−48	113.6					
225	Propargylamine							
226	β-Propiolactone	−33.4	155d					
227	Propionaldehyde	−80	48.0	18.5(17)	2.54			
228	Propionitrile	−91.9	97.2	27.2(20)	3.57			
229	n-Propylamine	−83.0	48.5	5.3(20)	1.33			

230	*i*-Propylamine	−101	33.0	5.5(20)				
231	Propylene carbonate	−49.2	241.7	70(20)	4.98		46.6	
232	Propylene oxide	−111.9	35	2.00				
233	Pyridine	−42	115.5	12.0(25)	2.25	64.0	40.2	50.0
234	Pyrimidine	22	124					
235	Pyrrole	−23.4	131	8.1(25)	1.80			
236	Quinoline	−14.9	237.1	9.0(25)	2.18		39.4	
237	Selenyl chloride	10	178	46.2(20)	2.64			
238	Silica gel					88 [n]		
239	Styrene	−33	146	2.4(20)	0.13			
240	Styrene oxide		192					
241	Sulpholane	28	284	43.3(30)	4.81	70.6 [c]	44.0	
242	Sulphuryl chloride	−54	70	9.1(20)	1.65			
243	1,1,2,2-Tetrachloroethane	−43.8	146.2	8.2(20)	1.71	64.3 [g]		
244	Tetrachloroethylene	−22.4	121.2	2.3(25)	0.0			
245	Tetrachloroethylene carbonate							
246	2,2,3,3-Tetrafluoropropan-1-ol					86.3 [f]		
247	Tetrahydrofuran	−108.5	65	7.6(25)	1.75	58.8 [m,o]	37.4	
248	Tetrahydropyran	−45	88	5.6(25)	1.55			
249	Tetramethylurea	−1.2	175.2	23.1(20)	3.47		41.0	
250	Thionyl chloride	−104	76	9.3(20)	1.61			
251	Thiophene	−38.25	84.16					
252	Toluene	−95	110.6	2.4(25)	0.39		33.9	41.7
253	*o*-Toluidine	−27.7	199.7	6.3(18)	1.60			
254	Triallylamine		156					
255	Tri-n-butylamine		213					
256	Tri-n-butyl phosphate	−80.0	289.0	8.0(30)	3.07	61.3 [c]		
257	Trichloroacetonitrile	−42	84.6					
258	Triethylamine	−114.7	89.5	2.4(25)	0.87		33.3	
259	Triethylene glycol	−4.3	288.0	23.7(20)	2.99		53.5	
260	β,β,β-Trifluoroethylamine							
261	Trimethylacetonitrile	15	106		3.65	63.1 [c]		
262	3,5,5-Trimethylhexanol					75.7 [c]		
263	Trimethyl phosphate	−46.1	197.2	20.6(20)	3.02	70.4 [c]		

TABLE 7 (*Continued*)

		m.p.	b.p.	Dielectric constant (°C)	Dipole moment (D)	Z	E_T	X_B
264	Triphenyl phosphine	80	>360					
265	Triphenyl phosphine oxide	157	>360					
266	Vinyl acetate	−92.8			1.79			
267	4-Vinyl pyridine							
268	Water	0.0	100.0	80.4(20)	1.84	See text	63.1	68.9
269	Deuterium oxide	3.8	101.4	79.8(20)	1.9			
270	*m*-Xylene			2.4(20)	0.37			
271	*o*-Xylene			2.6(20)	0.62			
272	*p*-Xylene			2.3(20)	0.0			
273	Zinc chloride	283	732					

No.	X_R	F	$\Delta\nu_D$	$\Delta\nu_A$	G	$\Delta\nu_{PFP}$	DN	Q_m	PA	HCl_{sol}
1			79							
2									188	0.195
3							10.5			
4	45.7						17.0		202	
5										
6	45.7	0.16	49	1.9	93		14.1			
7			56							
8							0.7 [u]			
9										
10			122							
11			37	2.2						
12										
13							55 [v]			
14										
15										
16	41.1		158							
17			26	1.4						
18				125.2						
19			237							

20			53							
21	46.9	−0.05	0	0	80	49	0.1	90	178.0 [x]	
22	43.3		38				11.9	297		
23							2.5			
24							2.3			
25							2.0			
26										0.812
27										
28			78	0.8						
29	44.6		−1	0.7						
30					118					
31										
32										0.956
33	44.5									0.971
34										
35									198	1.115
36		0.17								
37	44.8									
38	47.5									
39										
40							57.5 [y]			
41										
42										
43			33							
44			33							
45			83							
46	42.6		66							
47	45.4						16.6			
48							15.4			
49			82							
50					74					
51	48.7		−21	−0.8	69			55		
52	45.2		−2	0.9						
53			45	3.2						
54	44.2	0.08	−17		106			0		
55										
56			43							
57										

TABLE 7 (*Continued*)

No.	χ_R	F	$\Delta\nu_D$	$\Delta\nu_A$	G	$\Delta\nu_{PFP}$	DN	Q_m	PA	HCl_{sol}
58										
59	45.6									
60	33.6 [t]									
61	35.5 [t]									
62			75							
63	47.6									
64										
65	50.0	−0.01			49					
66										
67										1.031
68	44.3		66			229		618		
69										
70										
71	48.0									
72										
73										
74			66							
75							55 [v]			
76										
77					108					
78	48.6				61					
79										
80										
81			−11	2.8						
82			−15	1.7						
83			−12							
84			2		95		0.1			
85										
86							3.2			
87	44.9		−12		100					
88										
89										
90										
91										

92	48.3	0.07	78	−3.4	64	285	19.2	700	205	0.892
93							30.9			
94			56							
95										
96	44.3									
97										
98			71	−1.5						
99	43.0		113			356	27.8	920		
100										
101										
102			148							
103										
104										
105										
106										
107										
108										
109	43.7	0.09	107			308	27.0			
110										
111										
112										
113	44.7									
114										
115										
116										
117	42.0		141	8.2		367	29.8	657		
118										
119	48.4	0.10	77	0.2	86	252	453			1.046
120			58							
121										
122										
123										
124										
125			242							
126	48.6		73							
127			75	−4.0						
128	40.4									
129	43.9	0.25							187	0.943
130	44.1									

TABLE 7 (*Continued*)

No.	χ_R	F	$\Delta\nu_D$	$\Delta\nu_A$	G	$\Delta\nu_{PFP}$	DN	Q_m	PA	HCl_{sol}
131	47.2		39			199	17.1	463	205	0.659
132			33							
133			233				55.5 [v]		221 [y]	
134			4							
135			77	−3.3						
136	46.0									
137							16.4			
138										
139							15.3			
140								523		
141										
142			32							
143										
144			179							
145										
146			31	−0.2						
147										
148										
149										
150										
151									175	0.078
152			4							
153										
154	50.9		0							
155			180			479	38.8			
156	50.9	0.0	1		44					
157										
158							44 [v]			
159										
160	47.5				76			216		
161										
162	43.1	0.34					19.0		182	0.857
163										
164										

165									
166	43.5								
167									
168									
169			36			16.5	370	202	0.612
170			30						
171			151						
172									0.445
173			32						
174						27.1			
175			27						
176	50.1								
177									
178			23						
179			61						
180			56						
181	45.4		57						
182									
183									
184					89				
185			37						
186									
187									
188									
189			33						
190									
191						27.3			
192			4						
193			2						
194			89						
195	42.6		21	9.0		4.4	188		
196			8	3.6					
197	44.0		6	4.8	99	2.7	0		
198									
199									
200						0			
201									
202	50.9	0.03							

TABLE 7 (*Continued*)

No.	X_R	F	$\Delta\nu_D$	$\Delta\nu_A$	G	$\Delta\nu_{PFP}$	DN	Q_m	PA	HCl_{sol}
203	45.4									
204	45.8									
205										
206										
207					36					
208			25							
209							15.1			
210			186							
211			56							
212										
213							18.5			
214							16.4			
215							0			
216							11.7			
217			183							
218										
219			160							
220			240							
221										
222	44.1								189	0.957
223	44.5								193	1.029
224	38.9									
225										
226			34							
227			85							
228			52				16.1			
229			230							
230							57.5 [v]			
231							15.1			
232			59	−0.6						
233	43.9		168		94	485	33.1 [v]			
234										
235										
236										

237						12.2			
238									
239		2	1.0						
240		51							
241						14.8			
242						0.4 w			
243									
244				64					
245						0.8			
246									
247	46.6	90	0.2		292	20.0	677		1.38
248		93	−5.9						
249									
250						0.1 w			
251									
252	47.2	2	−0.9	74	57		157	184.4 x	
253		145							
254									
255									
256						23.7			
257									
258	49.3	238	−4.8	62				229 y	
259									
260									
261									
262									
263						23.0			
264									
265									
266		21							
267		193							
268						18.0		165	
269									
270	47.8								
271	47.3							188 x	
272	47.7								
273			72.2						

TABLE 7 (*Continued*)

No.	ΔR	δ_0 ^{23}Na	δ ^{7}Li	P	Δppm	Δ^{19}F	AN	Y
1								
2	59.0	5.4	0.03	1.60				−1.639
3		9.9		2.15				
4		5.8	−1.34	1.45			12.5	
5	75.5							
6	53.5	6.4	2.80	2.30	1.88		18.9	
7				1.95	1.92			
8								
9								
10					2.15			
11								
12								
13								
14								
15								
16								
17				1.50				
18								
19								
20		4.3			1.70			
21				0.80			8.2	
22				2.20	1.71		15.5	
23								
24								
25								
26								
27					2.40			
28								
29				1.55				
30								
31					2.07			
32					1.99			
33								
34								

35				
36	70.4	1.60		−3.26
37				
38				
39				
40				
41				
42			2.52	
43				
44				
45				
46		2.35		
47				
48				
49				
50				
51		0.50		8.6
52		1.50		
53				
54		2.30		23.1
55	87.1			
56				
57				
58				
59				
60				
61				
62				
63				
64			1.88	
65		0.00 [z]		
66				
67				
68			2.12	
69			2.29	
70				
71				

TABLE 7 (*Continued*)

No.	ΔR	$\delta_0{}^{23}Na$	$\delta{}^{7}Li$	P	Δppm	$\Delta^{19}F$	AN	Y
72				0.15				
73								
74								
75								
76					1.70			
77								
78								
79					2.01			
80								
81				1.80				
82				1.35				
83								
84	80.2			2.20			16.7	
85								
86								
87	80.3			2.30			20.4	
88					1.62			
89								
90								
91								
92				0.90	1.88		3.9	
93								
94								
95				2.00				
96								
97				2.35				
98								
99					2.86		13.6	
100					2.16			
101					3.37			
102					1.75			
103					2.96			
104					2.33			
105								

106					2.41		
107					2.71		
108							
109		4.5	−0.45	2.25	2.72	16.0	
110					2.23		
111							
112					2.54		
113							
114					2.98		
115				1.30			
116							
117		0	1.01	2.60	2.71	19.3	
118							
119				1.25	1.45	10.8	
120							
121				1.25			
122							
123							
124					2.70		
125							
126							
127							
128							
129	60.3			1.70		37.1	−2.033
130							
131		−3.5		1.45	1.85		
132							
133							
134							
135							
136							
137							
138				1.75			
139							
140							
141				1.90			
142							
143							

TABLE 7 (*Continued*)

No.	ΔR	$\delta_0{}^{23}$Na	δ^7Li	P	Δppm	Δ^{19}F	AN	Y
144								
145				1.55 [aa]				
146								
147					2.45			
148								
149				1.05				
150							39.8	0.604
151	47.9							2.054
152								
153								
154				−0.10				
155					3.71		10.6	
156							0.0 [z]	
157								
158								
159				1.90				
160								
161				2.50				
162	54.4		0.54	1.85			41.3	−1.090
163					2.10			
164					1.90			
165					1.83			
166								
167					2.77			
168								
169								
170								
171								
172								
173								
174								
175								
176								
177								

178				
179				
180				
181			2.02	
182			2.15	32.1
183		1.85		
184				
185				
186				
187		−0.40		
188				
189				
190				
191				
192				
193				
194				
195		2.25		14.8
196				
197	0.36	2.40		20.5
198			2.32	
199				
200				
201				
202				
203				
204				
205				
206		1.35		
207				
208				
209				
210				
211				
212			2.67	
213				
214				
215				

TABLE 7 (*Continued*)

No.	ΔR	$\delta_0{}^{23}$Na	δ^7Li	P	Δppm	Δ^{19}F	ΔN	Y
216								
217								
218								
219					2.70			
220								
221								
222	63.3							
223	65.0						33.5	−2.73
224								
225					2.16			
226								
227								
228								
229								
230								
231			0.61				18.3	
232								
233		−6.6	−2.54	2.05	2.49			
234					1.84			
235							14.2	
236					2.40			
237								
238								
239								
240								
241				2.70				
242								
243								
244								
245								
246								
247		−5.5	0.60	1.45	2.00		8.0	
248								
249					3.00			

250								
251				1.30				
252				0.55				
253								
254					2.22			
255					2.50			
256								
257				1.55				
258				0.20	2.66			
259								
260					1.45			
261								
262								
263					2.74			
264								
265					3.58			
266								
267								
268		0.0				54.8	3.493	
269	47.3							
270								
271								
272								
273								

No.	$\log k_{ion}$	X	Ω	$\log k$	S	δ [bb]	D(II,I)	D(II,I) [a]
1								
2	−2.772	0.0	0.823		0.0050		3.69	3.8
3	−4.467							
4	−5.067		0.619 [p]		−0.1748	9.66		2.4
5								
6	−4.221	0.04			−0.1039	11.8	2.60	2.6
7						10.4		
8								
9								
10								
11								

TABLE 7 (*Continued*)

No.	$\log k_{ion}$	X	Ω	$\log k$	S	δ [bb]	D(II,I)	D(II,I) [a]
12								4.8
13							4.62	4.1
14							3.8	4.2
15								
16					−0.001			3.3
17					−0.214			
18								
19								
20								
21				4.332	−0.215	9.15	1.58	1.85
22								
23								
24								
25								
26								
27								
28								
29					−0.164			
30					−0.042	10.6		
31								
32								
33					−0.0240	10.7	4.1	4.25
34								
35								
36					−0.1047	10.5		4.1
37								
38								
39								4.45
40								4.0
41								
42								
43								
44								

45						
46						
47						
48						
49						
50			−0.240	10.0	1.58	1.95
51	−4.8	3.784	−0.245	8.58	1.07	2.0
52	−1.9	4.612	−0.182	9.50		1.85
53						
54		4.655	−0.200	9.24	1.94	1.95
55						
56						
57						
58						4.3
59		4.599				
60						
61						
62						
63		4.179	−0.245			
64						
65		3.324	−0.324	8.18		
66		3.579				
67						
68						
69						
70			−0.1788			
71		4.068				
72						
73						
74						
75						
76						
77			−0.095	10.7		
78		3.846	−0.286			
79						
80						
81						
82						

TABLE 7 (*Continued*)

No.	log k_{ion}	X	Ω	log k	S	δ [bb]	D(II,I)	D(II,I) [a]
83								
84			0.600		−0.151	9.91		
85								
86								
87				4.839	−0.1890	9.88		
88								
89								
90								4.0
91								4.0
92					−0.277	7.74		
93								
94								
95								
96								
97					−0.043	11.8		
98								
99								
100								
101								
102								
103								
104								
105								
106								
107								
108								
109	−4.298	0.8	0.620		−0.1416		3.94	4.1
110								
111								
112								
113								
114								
115								

116								
117	−3.738	1.6					4.18	3.8
118								
119				4.362	−0.179	9.73	4.02	3.2
120								
121								
122				4.569				
123								
124								
125								
126								
127					−0.229	7.14		
128					+0.0679	14.5		
129	−3.204		0.718		0.0 [illegible]	12.9	4.26	4.5
130								
131	−5.947				−0.210	9.04		
132								
133							4.73	4.5
134								
135								
136								
137								
138								
139								
140								
141								
142								
143								4.4
144								4.2
145								
146								
147								
148								
149								
150					0.0463		5.15	
151	−0.929				0.1139		3.25	
152								
153								

TABLE 7 (*Continued*)

No.	$\log k_{ion}$	X	Ω	$\log k$	S	δ [bb]	D(II,I)	D(II,I) [a]
154				3.182	−0.337	7.42		
155								3.6
156					−0.337	7.24		
157								
158								
159								
160					−0.217	8.8		
161								
162	−2.796	0.91	0.845		0.0499	14.45	4.42	4.7
163								
164								
165								
166								
167								
168								
169								
170								
171								
172								
173								
174								
175								
176								
177								
178								
179								
180								
181								
182								4.55
183								
184					−0.170	9.9		
185								
186								
187								

188							
189							
190							
191							
192							
193							
194							
195	−0.218		5.326		10.4	1.95	2.25
196							
197	−3.921	0.680	5.223	−0.134	12.6	2.26	
198							
199							
200							
201							
202					6.85		
203							
204							
205							
206							
207							
208							
209							
210							
211							
212							
213							
214							
215							
216							
217							4.2
218							4.3
219							4.25
220						4.02	
221							
222				−0.0158	12.0		4.3
223				−0.0413	11.5		
224							
225							

TABLE 7 (*Continued*)

No.	$\log k_{ion}$	X	Ω	$\log k$	S	δ [b,b]	D(II,I)	D(II,I) [a]
226								
227								
228								
229							4.31	
230								4.05
231								3.4
232								
233	−4.670		0.595		−0.1970	10.6	4.39	4.3
234								
235					0.012			
236							4.21	
237								
238								
239				4.519				
240								
241								
242								
243					−0.083			
244					−0.263	9.3		
245								
246								
247	−6.073			4.489		9.32	3.18	3.4
248								
249								
250								
251								
252				4.248	−0.237	8.91	1.55	1.8
253								
254								

255							
256							
257							
258		0.445	−0.285				
259							
260							
261							
262							
263							
264							2.0
265							
266							
267							
268	−1.180		0.1540	23.4	5.49		5.4
269							
270					1.50		
271							
272		4.137					
273							

[a] Values obtained from C.M. Guzy, J.B. Raynor and M.C.R. Symons, J. Chem. Soc., (1969) 2791. Only one of their values is identical with those measured in ref. 108 (preceding column). It is not therefore recommended that these two columns be combined, but that they should be treated as two separate scales. [b] Also reported as 65.5 (E.M. Kosower and M. Mohammad, J. Am. Chem. Soc., 90 (1968) 3271). [c] This work; 77.5 reported as a private communication from D. Hart to R.S. Drago and K.F. Purcell, in T.C. Waddington (Ed.), Non-Aqueous Solutions, (Academic Press, London, 1965) p. 246. [d] C. Walling and P.J. Wagner, J. Am. Chem. Soc., 86 (1964) 3368. [e] [5]. [f] [122]. [g] P.M. Emslie and R. Foster, Rec. Trav. Chim. Pays-Bas Belg., 84 (1965) 255. [h] This work, 59°C. [i] Also reported as 64.7 (see footnote (b)). [j] [95]. [k] Also reported as 68.4 (see footnote (b)). [l] This work, 125°C. [m] J.F. King and R.G. Pews, Can. J. Chem., 43 (1965) 847. [n] P.A. Leermakers, H.T. Thomas, L.D. Weis and F.C. James, J. Am. Chem. Soc., 88 (1966) 5075. [o] Also reported as 64.0 (M.J. Blandamer, T.E. Gough and M.C.R. Symons, Trans. Faraday Soc., 62 (1966) 286). [p] 30°C. [q] K.M.C. Davis, in R. Foster (Ed.), Molecular Association, Vol. I, Academic Press, London, p. 168. [r] 55°C. [s] Also reported as 53.8 in ref. 5. [t] Calculated by extrapolation in ref. 58. [u] In ref. 16 Gutmann also uses the values 1.0 and 2.0, but we consider the number here correct. [v] [97]. [w] See text. [x] S.L. Chong and J.L. Franklin, J. Am. Chem. Soc., 94 (1972) 6630. [y] D.H. Aue, H.M. Webb and M.T. Bowers, J. Am. Chem. Soc., 94 (1972) 4726. [z] Reference value. [aa] 1.4 also given in refs. 52 and 53. [bb] [103].

We finally note in this section that those solvent polarity scales which are based on a specific 1 : 1 solute—solvent interaction, e.g., $\Delta\nu_D$ and Gutmann's donor numbers, do not correlate when plotted against dielectric constant. This is not really surprising, and neither do these scales correlate with the more general Z, Y and E_T scales.

K. SUMMARY AND APPLICATIONS

We have listed in Table 7 all the published solvent polarity data of which we are aware, plus some of our own unpublished measurements, for some 273 solvents and 29 scales. If, therefore, information is required regarding a particular compound the extent and values of the measured polarity data are readily determined. If information concerning a particular scale is desired, say its Z value, then reference to Table 3 reveals those scales which have a linear relationship with the Z scale, and generally on one or more of these scales the value has been measured for the solvent in question. The accompanying correlation coefficient indicates the precision of the Z value subsequently calculated.

Alternatively, if the identity was required of a solvent having a solvent polarity value close to a particular value, say a Z value of 60, then scanning the Z scale column vertically will ascertain those solvents. In addition, if horizontal scanning is also employed for these solvents, then the equivalent values on other scales can be obtained, and scanning these scales vertically will in principle identify many more such solvents.

We could have filled in the majority of the blanks in Table 7 using the equations of the correlations in Table 3, and giving mean values where several values are determinable. However we judged it better not to do so, to avoid uncritical use of Table 7. We therefore hope that our readers will calculate those values they require (and enter them into the compilation) while also having due regard for the footnotes in Table 7 and the above discussion on the various solvent polarity scales they employ.

We welcome any information on solvent polarity scales we may have overlooked, and being informed of new scales as they are published.

ACKNOWLEDGEMENTS

We thank the Science Research Council for the provision of an Applied Physics Cary 14H spectrophotometer and the University of Leeds for a University Demonstratorship to D.C.P. Valued discussions with Dr. R.H. Wijayanayake and Professor M.C.R. Symons are also acknowledged.

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