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Grant N00014-93-1-0351

R & T Code 4133020 - -09

Technical Report No. 8

Solvent Acidity and Basicity in Polar Media and Their Role in Solvation

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by

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Prepared for Publication

in

Theoretical and Computational Chemistry: Solute/Solvent Interactions

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April 20, 1994

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 20, 1994	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE Solvent Acidity and Basicity in Polar Media and Their Role in Solvation			5. FUNDING NUMBERS N00014-93-1-0351	
6. AUTHOR(S) W. Ronald Fawcett				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of California Davis, CA 95616			8. PERFORMING ORGANIZATION REPORT NUMBER No. 8	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Arlington, VA 22217-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared for publication in Theoretical and Computational Chemistry: Solute/Solvent Interactions.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unclassified			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The acidic and basic properties of polar solvents are reviewed with attention focussed on appropriate scales for estimating these important solvent parameters. It is shown that acidity and basicity scales can be related to the parameters arising in the mean spherical approximation for the Gibbs solvation energy of monoatomic cations and anions in polar solvents. Linear solvation energy relationships are used to analyze data for the Gibbs solvation energy of 1-1 electrolytes, the standard potentials of simple electrode reactions, and the solvent induced frequency shifts in the vibrational spectra of polar solutes. It is shown that, not only are solvent acidity and basicity important, but that macroscopic properties based on the solvents permittivity and refractive index also play a role in determining solvent effects.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT unclassified	

Solvent Acidity and Basicity in Polar Media and Their Role in Solvation

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1. INTRODUCTION

The solvation of ions and molecules in polar solvents has been the subject of considerable interest during the past 70 years [1-4]. The early work of Born [5] on ion solvation relied upon continuum concepts in which the solvent was represented as a dielectric with a uniform permittivity. However, it rapidly became apparent that this model overestimates the thermodynamic solvation properties of simple ions because it ignores the local chemical interactions between the ion and individual solvent molecules. Various other models for ionic solvation which are based on continuum concepts have been presented [6], but they are not popular because they neglect the molecular nature of the solvent and the specific way it interacts with cations and anions.

As far as neutral solutes are concerned, the solvation of the noble gases in polar solvents has been studied in some detail [7]. In this case, the solvation parameters are estimated on the basis of the molecular properties of individual solvent molecules including molecular polarizability, magnetic susceptibility, and diameter. In the case of a polyatomic solute with a dipole moment, the description of solvation is more complex, and includes consideration of dipole-dipole interactions induced dipole-dipole interactions and interactions involving multipoles. Thus, the description of solute-solvent interactions on the basis of a hard sphere model becomes increasingly more difficult as the electrostatic description of the components becomes more complex. Moreover, these models neglect chemical interactions such as hydrogen bonding, which are often important in determining the properties of the system. In order to include these, one must consider the quantum mechanical description of the system.

A quite different approach to describing the solvation of polar molecules and ions is based upon the Lewis acidic and basic properties of the solvent [3,4]. Accordingly, the ability of a solvent to solvate a cation depends on its donicity, that is, its ability to donate a pair of electrons or to act as a Lewis base. On the other hand, the solvation of anions depends upon the solvent's ability to act as a Lewis acid, that is, to accept a pair of electrons. Empirical scales measuring solvent acidity and basicity have

been developed [3,4] and can be used to assess the change in experimental quantities related to solvation with the nature of the solvent. When solvent acidity and basicity are the dominant features leading to the change in an experimental parameter Q with solvent nature, these changes can be expressed using the simple linear relationship [8]

$$Q = Q_0 + \alpha A + \beta B \quad (1)$$

where A is the parameter measuring solvent acidity, B , that measuring basicity, α and β , the corresponding response factors, and Q_0 , the value of Q when A and B are both zero. By analyzing experimental data on the basis of this relationship one may assess the relative roles of solvent acidity and basicity in solvation, and rationalize the variation in solubility, ion pairing and other phenomena with the nature of the solvent.

Quite recently [9], a connection between the fundamental theoretical approach to ion solvation and that based on linear solvation energy relationships (LSER) was demonstrated on the basis of a non-primitive statistical mechanical model of the solution. This model which uses the mean spherical approximation (MSA) is derived from the integral equation approach to estimate the thermodynamic properties of electrolyte solutions. Accordingly, the system is described as a collection of hard spheres with point dipoles corresponding to the solvent molecules, and hard spheres with point charges for the ions. The resulting expression for the Gibbs solvation energy is similar to that derived by Born [5] on the basis of the primitive model, but with the important difference that the ionic radius is corrected by a quantity which depends on the nature of the solvent and whether the ion is a cation or an anion. This feature of the MSA result is the same as that found much earlier on an empirical basis by Latimer, Pitzer, and Slansky [10]. Moreover, the reciprocal of the correction term, which is called the polarization parameter, measured in various solvents is linearly related to empirical measures of solvent acidity in the case of anions, and to solvent basicity in the case of cations [9]. These relationships provide the connection between fundamental theory and the empirical description of two important chemical properties relevant to solvation.

In the present review, the appropriate parameters for solvent acidity and basicity are considered for electrolyte solutions. Since the discussion is limited to polar solvents, it is appropriate to note that a polar solvent is considered to be one with a relative dielectric permittivity greater than 15. This criterion was chosen on the basis of Bjerrum's model [11] for ion pairing applied to a 0.1M solution of a 1-1 electrolyte. In such a solution the ions are 2 nm apart from one another on the average. The Bjerrum cut off distance for ion pairing in this solution is 2 nm if its relative permittivity is 15. This simple calculation provides a convenient, although somewhat arbitrary, means of defining what dielectric properties are required to consider a solvent as polar.

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This review is organized in the following way. First, the appropriate parameters for solvent acidity and basicity are considered. Other solvent parameters needed to assess solvation are also tabulated. Then, data relevant to ionic solvation are examined using linear solvation energy relationships (LSER). These data include Gibbs transfer energies for 1-1 electrolytes and single ions, and formal potentials for simple redox couples measured as a function of solvent. Finally, spectroscopic data relevant to the solvation of polar molecules are discussed and analyzed with respect to the roles of solvent acidity and basicity.

2. ACIDITY AND BASICITY SCALES FOR POLAR SOLVENTS

Solvent acidity may be viewed as the ability of the solvent to accept a pair of electrons or as its ability to donate a hydrogen bond. In the case of protic solvents, the latter function is generally considered to be more important, protic solvents being strong Lewis acids. Several empirical parameters for measuring solvent acidity have been developed and they are summarized in Table 1.

Mayer et al. [12] formulated the acceptor number AN on the basis of the relative ^{31}P -NMR chemical shifts produced by a given solvent with a strong Lewis base, triethylphosphine oxide. The data were normalized so that the acceptor number of hexane is zero, and that for the 1:1 adduct with the strong Lewis acid SbCl_5 , 100 when dissolved in 1,2-dichloroethane. The attractive feature of this scale is that it varies over a wide range for the polar solvents normally considered, for example, from 10.6 for hexamethylphosphoramide (HMPA) to 54.8 for water (W).

Another acidity scale is based on the Dimroth-Reichardt E_T parameter [3]. This is obtained by measuring the wavelength of the longest wavelength band in the spectrum of a dilute solution of a betaine dye in the given solvent. This dye, namely, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide undergoes a π - π^* transition in the visible region which is accompanied by a large decrease in molecular dipole moment. E_T was developed as a measure of solvent polarity [3] but clearly is also related to solvent acidity. Its variation for the solvents considered is about half of that of AN so that it is statistically less useful in LSERs (see Table 1). A related acidity scale is the Kosower Z which is based on the absorption band associated with an intermolecular electron transfer in an ion-pair complex [13]. However, this parameter is not available for a significant number of polar solvents, and is not considered further.

Recently, an acidity scale for polar solvents was introduced on the basis of the MSA expression for the Gibbs solvation energy of a monoatomic monovalent ion [14]. Considering ion-dipole interactions only, the MSA expression for the Gibbs solvation energy of such an ion is

Table 1

Acidity Scales for Polar Solvents

Solvent	AN ^a	E _T ^b	A _p ^c
Protic			
1. water (W)	54.8	63.1	48.0
2. methanol (MeOH)	41.5	55.4	41.0
3. ethanol (EtOH)	37.9	51.9	37.2
4. n-propanol (PrOH)	37.3	50.7	34.7
5. n-butanol (BuOH)	36.8	50.2	34.5
6. formamide (F)	39.8	56.6	34.1
7. N-methylformamide (NMF)	32.1	54.1	31.5
Aprotic			
8. acetone (AC)	12.5	42.2	22.0
9. acetonitrile (AN)	18.9	45.6	24.4
10. benzonitrile (BzN)	15.5	41.5	23.3
11. butyronitrile (BuN)	-	43.1	-
12. dimethylacetamide (DMA)	13.6	43.7	20.1
13. dimethylformamide (DMF)	16.0	43.8	22.2
14. dimethylsulfoxide (DMSO)	19.3	45.1	25.6
15. hexamethylphosphoramide (HMPA)	10.6	40.9	19.2
16. N-methylpyrrolidinone (NMP)	13.3	42.2	22.1
17. nitrobenzene (NB)	14.8	41.2	26.4
18. nitromethane (NM)	20.5	46.3	25.5
19. propylene carbonate (PC)	18.3	46.6	23.9
20. tetramethylene sulphone (TMS)	19.2	44.0	22.0
21. tetramethylurea (TMU)	-	41.0	-

^aGutmann acceptor number [12]

^bDimroth-Reichardt polarity parameter [3]

^cFawcett polar acidity [14]

$$\Delta G_s = - \frac{N_0 e_0^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right) \left(\frac{1}{r_1 + \delta_s}\right) \quad (2)$$

where N_0 is the Avogadro constant, e_0 , the fundamental electronic charge, ϵ_0 , the permittivity of free space, ϵ_s , the relative permittivity of the pure solvent, r_1 , the ionic radius, and δ_s , the MSA distance parameter [9, 14]. The latter quantity depends on the nature of the solvent and also on whether the solvated ion is an anion or cation, reflecting the fact that the mechanism of ion solvation is very different for the two types of ions. It was also found that the reciprocal of δ_s determined in a variety of solvents on the basis of solvation data for the halide ions was linearly related to parameters measuring solvent acidity such as AN and E_T . This suggests that one may define a new acidity scale A_p for polar solvents based on the value of $1/\delta_s$ appropriate for the halide ions in a given solvent. The parameter A_p is defined by the equation

$$\Delta G_s (X^-) = - \frac{N_0 e_0^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right) \left(\frac{A_p}{1 + r_1 A_p}\right) \quad (3)$$

where $\Delta G_s(X^-)$ is the Gibbs solvation energy of the halide ion with radius r_1 in a given solvent. This relationship demonstrates that the Gibbs solvation energy of a monovalent anion is linear in the solvent acidity A_p provided that variation in $(1 - 1/\epsilon_s)$ with solvent is not large, and that the ratio $(1 + r_1 A_p)^{-1}$ is also linear with respect to A_p . A plot of the Gibbs solvation energy of the Cl^- anion in 19 polar solvents against the acidity parameter A_p is shown in Figure 1. A good linear correlation is obtained with a correlation coefficient r of 0.956. The scatter is mainly due to variation in $(1 - 1/\epsilon_s)$ which changes from 0.943 to 0.995 for the solvents considered.

A quite different approach to the assessment of solvent acidity was taken by Taft and Kamlet [15,16]. They defined a hydrogen bond donating ability α on the basis of the solvatochromic comparison method. On this scale, α is only significant for protic solvents and is zero or close to zero for aprotic solvents [16]. In order to account for solvation effects related to solvent polarity, Taft and Kamlet use the solvatochromic parameter π^* . Thus, in order to describe solvent acidity one must use two parameters, namely, α and π^* . Although this separation may be appealing from a fundamental point of view, it is not from a practical one. When one is examining the dependence of a physico-chemical parameter on solvent acidity and basicity on the basis of a LSER, the number of solvents for which data are available is usually limited so that expansion of the description from one involving two independent variables (equation (1)) to one with more independent variables is often unjustified.

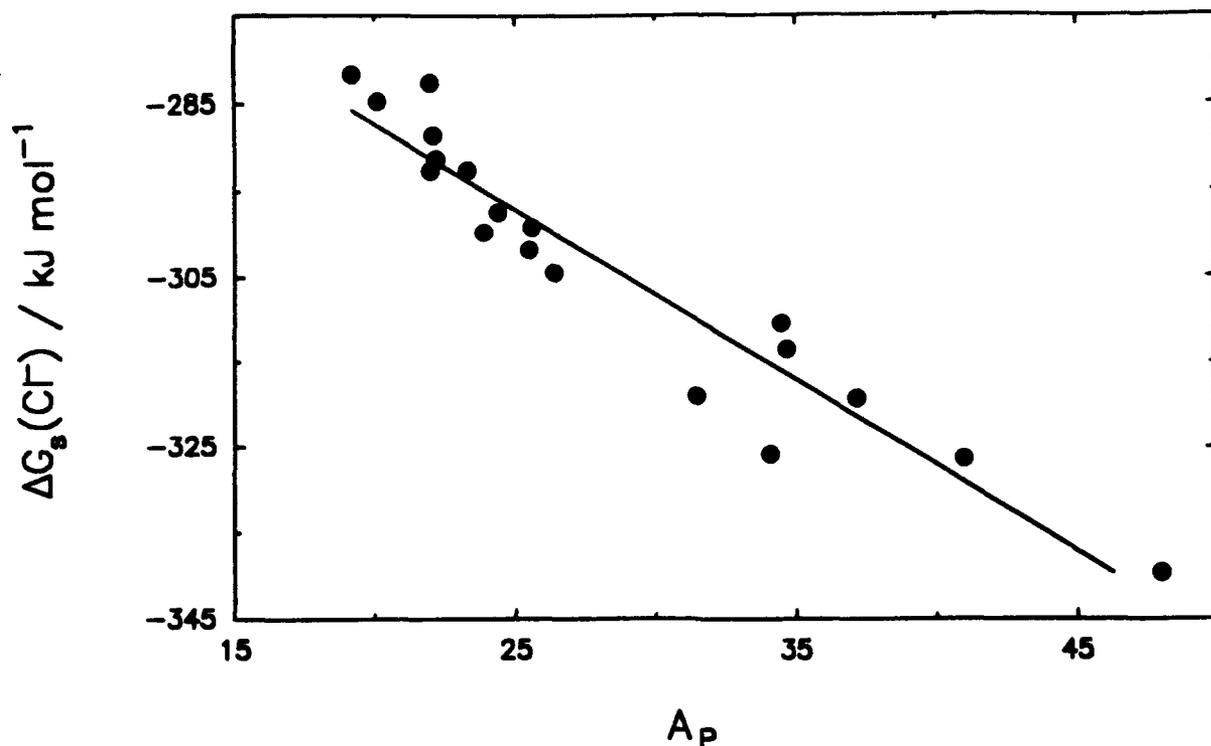


Figure 1. The Gibbs solvation energy of the Cl^- anion as a function of the acidity parameter A_p .

Marcus [17] has analyzed the relationship between the parameters AN and E_T and the Taft-Kamlet parameters α and π^* , and showed that the AN parameter is more sensitive to hydrogen bond donating ability α than the E_T parameter. As pointed out earlier [14] correlations considering a wide range of solvents are greatly influenced by the protic solvents. When only the aprotic solvents were considered it was concluded on the basis of correlations with A_p that both AN and E_T provide acceptable descriptions of solvent acidity in the absence of hydrogen bonding [14]. The correlations between these quantities considering the 19 solvents for which A_p is available are

$$A_p = 13.3 + 0.604 \text{ AN} \quad (r = 0.975) \quad (4)$$

$$\text{and } E_T = 36.0 + 0.467 \text{ AN} \quad (r = 0.964) \quad (5)$$

The fact that A_p is derived from the Gibbs solvation energies of the halide ions, which are very strong Lewis bases, suggests it should be the preferred parameter for estimating solvent acidity for polar solvents. However, the acceptor number AN also performs this function very well, and has the added advantage that it varies over a wide range for the solvents considered here.

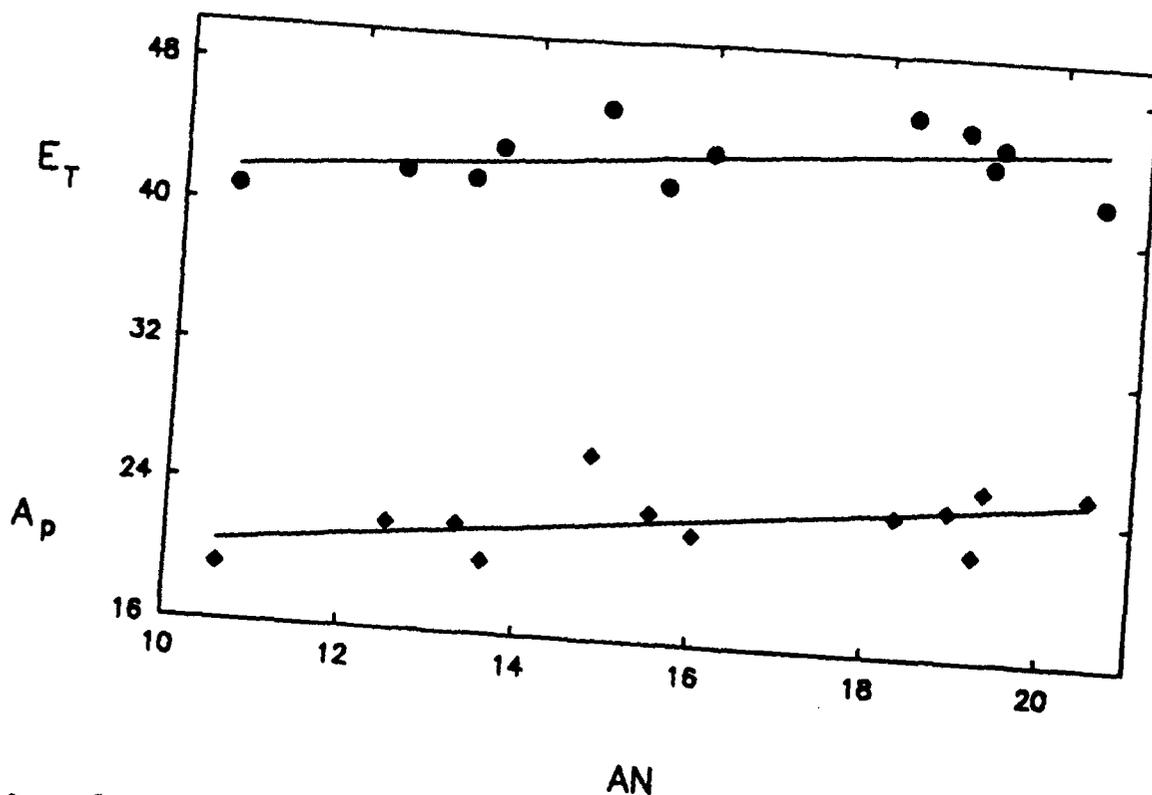


Figure 2. Plot of the acidity parameters E_T (●) and A_p (◆) against the acceptor number AN for the aprotic solvents.

It is important to recognize that the quality of the correlations found between the acceptor number AN and the parameters A_p and E_T is determined to a great extent by the protic solvents which are strongly acidic. However, when the data for the protic solvents are removed quite good correlations are also found between AN and these parameters for the aprotic solvents alone (see Figure 2). These scales distinguish between the acidities of common aprotic solvents such as DMF, DMSO, and HMPA, ordering them $HMPA < DMF < DMSO$ with respect to increasing acidity. On the other hand, the Kamlet-Taft parameter α does not distinguish between the acidities of these solvents. However, their polarity parameter π^* does show that DMSO is a more effective Lewis acid than HMPA or DMF, the relative ordering being $HMPA \sim DMF < DMSO$. All of the above considerations lead to the conclusion that AN is the best parameter for assessing solvent acidity with A_p and E_T being acceptable alternatives.

A number of parameters have been introduced to estimate solvent basicity, the important ones being given in Table 2. These have been compared and analyzed in detail by Persson et al. [18, 19]. The most popular basicity scale is based on the donor number (DN) introduced by Gutmann [20, 21]. This quantity is obtained by measuring the heat of reaction of the solvent with the strong Lewis acid $SbCl_5$ when these reactants are dilute solutes in 1,2-dichloromethane. An important defect of this parameter is that the DN for protic solvents cannot be measured

Table 2

Basicity Scales for Polar Solvents

Solvent	DN ^a	DNs ^b	B _{sc} ^c	B _p ^d
Protic				
1. W	18.0	17	591	12.1
2. MeOH	19.0	18	589	12.1
3. EtOH	19.2 ^e	19	589	11.9
4. PrOH	19.8 ^e	18	-	12.05
5. BuOH	19.5 ^e	18	589	11.3
6. F	24	21	598	12.5
7. NMF	~27	22	604	12.6
Aprotic				
8. AC	17.0	15	569	12.55
9. AN	14.1	12	573	11.47
10. BzN	11.9	12	572	11.2
11. BuN	16.6	13	-	11.7
12. DMA	27.8	24	608	13.5
13. DMF	26.6	24	602	13.2
14. DMSO	29.8	27.5	613	13.3
15. HMPA	38.8	34	633	13.8
16. NMP	27.3	27	-	14.0
17. NB	4.4	9	522	10.6
18. NM	2.7	9	530	10.7
19. PC	15.1	12	554	11.4
20. TMS	14.8	15	562	12.5
21. TMU	31	24	596	14.2

^aGutmann acceptor number [20,21]

^bPersson soft donicity [18,19]

^cPersson solvatochromic basicity [18,19]

^dFawcett polar basicity [14]

^eEstimates by Kanevsky and Zarubin [22]

directly because of the instability of SbCl_5 in these systems. However, values of DN for protic solvents have been estimated by a variety of other techniques [14,22,23], and values are available for all solvents considered here. It is also interesting that values of a bulk DN have been estimated for many solvents [23]. Thus, it was considered that the Lewis basicity of a solvent can be considerably different when the solvent molecules act in concert, rather than when a single molecule is involved as is the case in the Gutmann definition of DN. Significantly higher estimates of the bulk donicity are obtained for protic solvents which are highly structured because of hydrogen bonding. However, on the basis of the polar basicity scale estimated from the Gibbs solvation energies of alkali metal cations, the higher "bulk values" of DN are not relevant for the quantities considered in this review. This may be a reflection of the fact that the structure of protic solvents is very much disrupted near strong Lewis acids such as cations, so that local solvent properties rather than bulk solvent properties are important.

Persson et al. [18] have recently introduced a donor scale for soft acceptors, designated here as DN_s . This scale is defined as the shift in the symmetric stretching frequency in HgBr_2 when it is in the gas phase compared to when it is a solute in a given solvent. These parameters correlate in an approximate way with the Gutmann DN, but deviations from the best linear fit are seen for solvents with soft donating atoms. Persson et al. [18] also devised a scale for hard acceptors based on the Gibbs energy of transfer of the Na^+ ion from water to another solvent [18]. Keeping in mind the fact that the DN is defined with respect to SbCl_5 , an acceptor with properties on the borderline between hard and soft, DN is preferable to the Persson DN_s except in cases where only soft acceptors are considered.

Persson et al. [18,19] also reported values of the maximum wavelength for the absorption band of a solvatochromic Cu^{2+} complex, namely Cu(II) N,N,N',N' -tetramethylethylenediamine acetoacetate. This parameter, which is designated B_{sc} , is especially convenient because it may be measured directly for all the solvents considered here, both protic and aprotic. The relationship between B_{sc} and DN is

$$B_{sc} = 525.2 + 2.89 \text{ DN} \quad (r = 0.942) \quad (6)$$

This relationship may be used to check values of the DN for protic solvents which were obtained by indirect methods. For instance, the DN for *N*-methylformamide, which is given as ~ 27 [24], is estimated to be 27.3 on the basis of the corresponding value of B_{sc} .

The last parameter listed in Table 2 is the polar basicity B_p determined from the Gibbs solvation energies of the alkali metal cations on the basis of the MSA. From the previous discussion and equation (2), one may write

$$\Delta G_s(\text{C}^+) = -\frac{N_0 e_0^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right) \left(\frac{B_p}{1 + r_1 B_p}\right) \quad (7)$$

Values of B_p were extracted from the available data using the procedure described previously [9]. As argued above for the parameter A_p , the Gibbs solvation energy for a given cation should be linear with respect to B_p provided that variation in $(1 - 1/\epsilon_s)$ is not large, and the ratio $(1 + r_1 B_p)^{-1}$ is also linear with respect to B_p . The relationship between ΔG_s and B_p is illustrated in Figure 3. A good linear correlation is found ($r = 0.941$), most of the observed scatter being due to variation in $(1 - 1/\epsilon_s)$. B_p is also linear with respect to the DN, the relationship being

$$B_p = 10.14 + 0.108 \text{ DN} \quad (r = 0.896) \quad (8)$$

The range of variation of B_p for the solvents considered here is much smaller than that of DN so the latter parameter is preferred in LSERs.

Several other basicity scales should be mentioned here. Maria and Gal [25] proposed a donicity scale based on the heat of reaction of BF_3 with a given solvent when these are dilute solutes in dichloromethane. Thus, its basis is very similar to that of DN. The Lewis acid BF_3 and solvent dichloromethane were chosen because there are fewer side reactions with this system than with SbCl_5 and 1,2-dichloroethane [25].

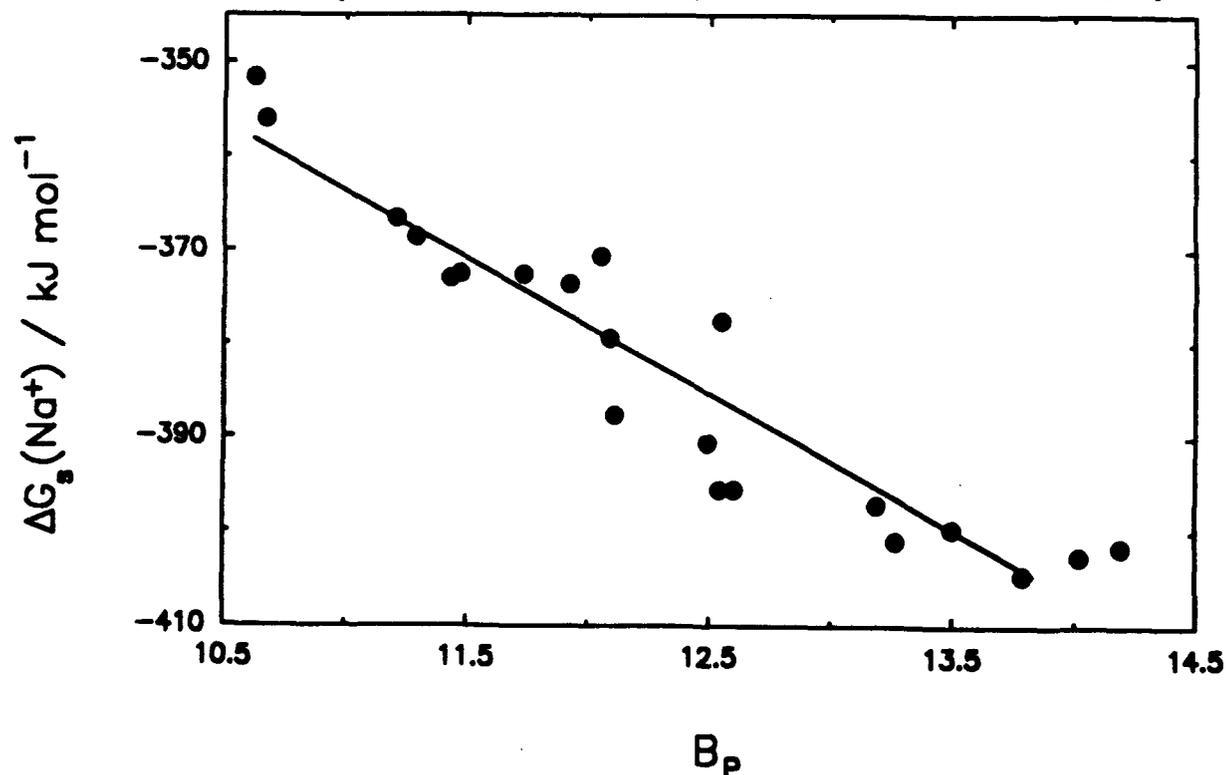


Figure 3. A plot of the Gibbs solvation energy of the Na^+ ion against the basicity parameter B_p .

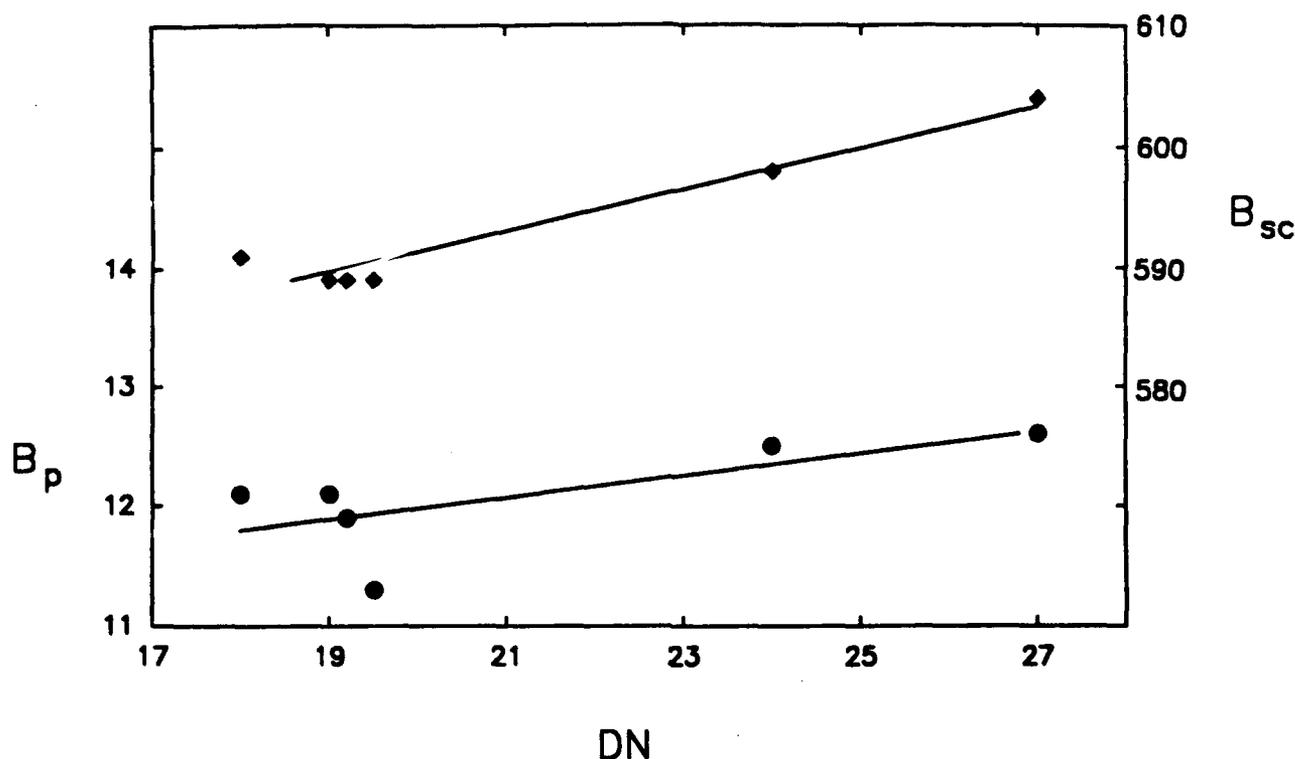


Figure 4. Plot of the basicity parameters B_p (\bullet) and B_{sc} (\blacklozenge) against the donor number DN for the protic solvents only. The left hand ordinate scale is for B_p and the right hand scale for B_{sc} .

However, the Maria-Gal parameter is not available for the protic solvents considered here, and therefore is not considered further. Another parameter B was introduced by Koppel and Palm [26,27] on the basis of the red shift of the O-D stretching vibration for CH_3OD dissolved in a given solvent. The value of B for water is anomalously low on this scale when one compares it with other basicity scales such as DN and B_p [14]. This may be related to problems in resolving overlapping bands in strongly associated media. Finally, Taft and Kamlet [15,16] introduced the basicity parameter β using the solvatochromic comparison method. This parameter was described as less certain for the alcohols and water in [16] but improved values were given later by Marcus et al. [28]. Because the Taft-Kamlet parameters require three independent variables to describe local solvation effects, they are considered to be less practical than other scales as discussed above.

In order to illustrate the question of the donicity of protic solvents, the values of B_p and B_{sc} for six solvents are plotted against estimates of their donor number in Figure 4. First of all, it is clear that the donor number of water is close to 18 on the basis of both the polar basicity B_p and the solvatochromic parameter B_{sc} . The donicity of the alcohols is not much different from that of water on all three scales. The estimates of DN given for formamide and N-methyl formamide [24] appear to be quite reasonable on the basis of Persson's B_{sc} [18, 19]. The excellent

correlation between B_{sc} and DN clearly provides the best method of estimating the DN in protic media.

In conclusion, the best solvent parameters describing acidity and basicity for polar solvents are AN and DN, respectively. This choice is based on the fact that they are available for all solvents considered and vary most widely within this group. Furthermore, values of DN which are unavailable directly for protic solvents, are supported by the values of B_{sc} and B_p obtained by quite different methods. Since the range of variation in the variables used is important in determining the quality of the statistical analysis required to obtain LSERs, it was the overriding consideration in making the present choice. Clearly, scales such as B_{sc} and B_p should be expanded so that this question can be reconsidered.

3. METHOD OF DATA ANALYSIS

In previous analyses of solvent effects [8, 14, 29] attention was focussed on ion-solvent interactions. Under these circumstances local or specific solvation effects dominate and the two parameter LSER involving an acidity and basicity parameter often suffices. However, in general, one should also consider non-specific effects which depend on the bulk dielectric properties of the solvents. Such an approach is originally due to Koppel and Palm [3,27,30]. These authors examined many sets of experimental data [27] using four independent variables with an acidity and basicity parameter for specific effects, and with solvent polarity and polarizability for non-specific effects. Solvent polarity is defined as

$$Y = (\epsilon_s - 1) / (\epsilon_s + 2) \quad (9)$$

and polarizability as

$$P = (\epsilon_{op} - 1) / (\epsilon_{op} + 2) \quad (10)$$

where ϵ_{op} is the solvent's relative permittivity at optical frequencies. The equation describing the solvent effect on quantity Q is then

$$Q = Q_0 + \alpha AN + \beta DN + \gamma Y + \delta P \quad (11)$$

where the coefficients α , β , γ , and δ describe the response of Q to the respective solvent parameter, and Q_0 is the value of Q when AN, DN, Y and P are all zero. Application of this equation to experimental data requires that Q be measured in at least six solvents and that proper statistical analysis be made to test the significance of each of these coefficients.

In order to discuss the application of equation (11) to experimental data it is written in a more general form:

$$Q = Q_0 + \sum_{i=1}^n k_i X_i \quad (12)$$

where X_i is the i th solvent parameter, k_i , the corresponding coefficient and n , the number of independent variables. The coefficients k_i are calculated from the normal equations for linear regression using well known matrix diagonalization techniques [31]. Assessment of the quality of the fit is based on the scatter of the observed values of Q from those calculated on the basis of the fit, and the correlation coefficient R . However, these quantities provide no indication of the importance of an individual solvent parameter X_i or the validity of its inclusion in the analysis of a specific set of data. In order to carry out a complete analysis, one must calculate quantities related to the variance of each independent variable, and the dependent variable, namely

$$v_i = m \sum_{k=1}^m X_k^2 - \left(\sum_{k=1}^m X_k \right)^2 \quad (13)$$

where m is the number of values of Q_i . In addition, the quantities related to the covariance between any two independent variables, or between an independent variable and the observed quantity Q_i are needed:

$$v_{ij} = m \sum_{k=1}^m X_k X_j - \left(\sum_{k=1}^m X_k \right) \left(\sum_{k=1}^m X_j \right) \quad (14)$$

On the basis of the variances one may define partial regression coefficients k'_i which are normalized to remove dependence of k_i on the range of variation of X_i . Thus, the partial regression coefficients are [8,14].

$$k'_i = k_i (v_i / v_Q)^{1/2} \quad (15)$$

An even better way of presenting these coefficients is in terms of relative partial regression coefficients defined as

$$\bar{k}_i = k'_i / \sum_{i=1}^n k'_i \quad (16)$$

A given \bar{k}_i represents the fraction of the explained variation in Q due to the independent variable X_i . The relative partial regression coefficients are much more informative than the normal regression coefficients usually reported, and are given in the tables of results below.

The covariances are also important in assessing the quality of the fit. From these one may calculate the correlation coefficient between any two variables. Thus, the correlation coefficient for variables X_i and X_j is

$$r_{ij} = \frac{v_{ij}}{v_i^{1/2} v_j^{1/2}} \quad (17)$$

When these are independent variables, the value of r_{ij} should be zero or close to zero. This is certainly the case for the variables used in the Koppel-Palm equation, namely, AN, DN, Y and P as applied here. The value r_{ij} depends on the specific solvents used in the experimental study so that the values of r_{ij} should be calculated in each analysis to check for fortuitous correlations. Values of r_{ij} are also calculated for the correlation between the dependent variable and each of the independent variables. In this way, one immediately finds which of the independent variables is most important, and can then perform the analysis adding one independent variable at a time to the LSER in order of increasing importance.

Finally, one needs to calculate the overall correlation coefficient at each stage in the analysis. This is given by [31]

$$R^2 = \sum_{i=1}^n k_i' r_{i0} \quad (18)$$

By comparing the value of R using n independent variables with that for $n-1$ independent variables one may assess the importance of adding the n th variable. Using this criterion and the other usual statistical criteria, one may avoid descriptions of the solvent effect which are unnecessarily detailed.

In order to carry out the analyses presented in the following section, one also needs values of the relative permittivities ϵ_s and ϵ_{op} . These are listed in Table 3 for the 21 solvents considered. Also listed in this table are values of the molecular dipole moment and polarizability. It was shown recently [32] on the basis of the MSA, that the bulk dielectric properties of polar solvents may be derived from their molecular properties provided one includes in the electrostatic description of the system a stickiness parameter which accounts for interactions other than dipole-dipole interactions. An understanding of interactions between solvent molecules at a molecular level is essential to the development of a picture of the mechanism of solvation.

Before presenting the results of analyzing some experimental data, the approach taken here to the LSER is illustrated with the example of infrared data for the solvent induced frequency shift for the $C\equiv N$ stretching vibration in acetonitrile [33]. Studies of this system in both

Table 3

Bulk and Molecular Dielectric Properties for Polar Solvents

Solvent	Relative Permittivity		Dipole Moment p/Debye ^b	Polarizability ^c 10 ³ α/nm ³
	Static ε _s	Optical ^a ε _{op}		
Protic				
1. W	78.3	1.7756	1.83	1.48
2. MeOH	32.7	1.7596	1.66	3.29
3. EtOH	24.6	1.8480	1.66	5.21
4. PrOH	20.3	1.9146	1.66	7.10
5. BuOH	17.5	1.9525	1.66	8.79
6. F	111.0	2.0932	3.82	4.26
7. NMF	182.4	2.0449	3.82	6.20
Aprotic				
8. AC	20.7	1.8387	2.87	6.51
9. AN	37.5	1.7999	3.47	4.48
10. BzN	25.2	2.3284	4.54	13.05
11. BuN	22.7	1.9099	3.50	8.29
12. DMA	37.8	2.0609	3.80	9.91
13. DMF	36.7	2.0398	3.80	8.12
14. DMSO	46.7	2.1824	3.96	8.24
15. HMPA	30.0	2.1228	4.47	19.6
16. NMP	32.2	2.1550	4.09	11.0
17. NB	34.8	2.4025	4.28	13.5
18. NM	35.8	1.9033	3.46	5.04
19. PC	66.1	2.0190	4.98	8.80
20. TMS	43.3	2.1963	4.81	11.2
21. TMU	23.1	2.1005	3.40	13.1

^aThe square of the refractive index measured at the sodium D line.

^b1 Debye is equal to 3.335 x 10⁻³⁰ Cm.

^cCalculated on the basis of the MSA as described in [32]

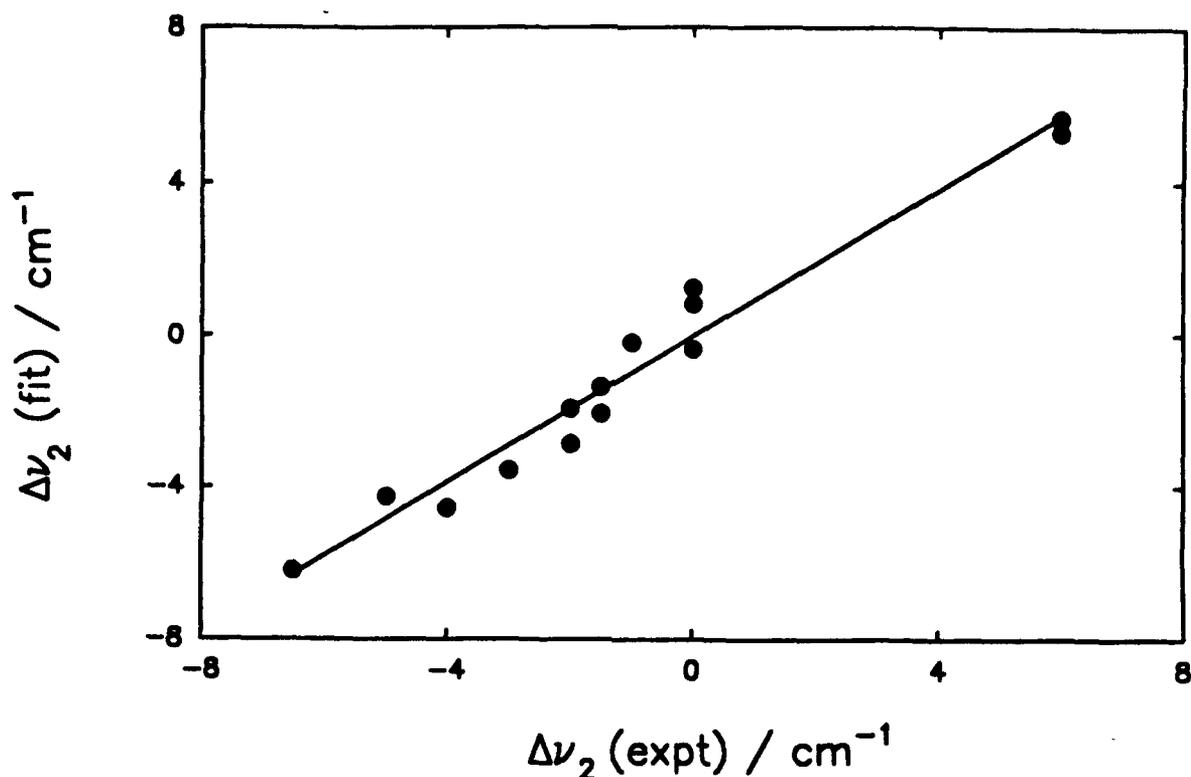


Figure 5. The frequency shift for the C≡N stretching mode in d-acetonitrile calculated by the Koppel-Palm equation (see text) plotted against the experimentally observed value.

polar and non-polar solvents have shown that the ν_2 band is blue shifted when the solvent is a stronger Lewis acid than acetonitrile, and red shifted when it is a stronger Lewis base. When the LSER analysis is applied to data obtained in 14 polar solvents from those listed in Tables 1-3, the strongest correlation is with the acceptor number ($R = 0.746$), correlations with each of the other three parameters being much weaker. The standard deviation for this simple linear fit is 2.5 cm^{-1} . Considering the fact that the correlation with AN is not very good, addition of a second parameter is expected to improve the description of the solvent effect.

Each of the remaining three parameters is now added as a second parameter in a least squares fit, the best results being obtained with solvent polarity Y . The correlation coefficient increases significantly to 0.905 and the standard deviation drops to 1.6 cm^{-1} . The next parameter in order of importance is the donor number DN. When this is added in a least squares fit involving three independent variables the correlation coefficient increases to 0.968 and the standard deviation decreases to 1.0 cm^{-1} . Finally, addition of solvent polarizability P in a least squares fit with four independent variables results in a correlation coefficient of 0.981 with a standard deviation of 0.8 cm^{-1} . It is clear that all four independent parameters are significant in the description of the solvent effect. The quality of the fit obtained is illustrated in Figure 5 where the value of the C≡N stretching frequency shift calculated by the four

parameter least squares analysis is plotted against the experimentally observed value. The level of error estimated by the least squares fit corresponds rather well with the precision with which the frequency shift can be determined (0.5 cm^{-1}).

If during the course of the analysis the correlation coefficient does not increase significantly or the standard deviation remains constant or increases, then one has a clear indication that addition of the next parameter is not justified. As will be seen below, this is often the case. Thus, the statistical analysis should be performed in a sequential fashion in order to avoid addition of meaningless correlations in the multiparameter fit.

4. ANALYSIS OF EXPERIMENTAL DATA

4.1 The Gibbs Energy of Transfer of 1-1 Electrolytes

The standard Gibbs energy of transfer between water and a non-aqueous solvent has been measured for a number of 1-1 electrolytes [34-41]. These data have then been used to extract values for single ion Gibbs energies of transfer on the basis of the equality of solvation of two very large ions, namely, the tetraphenylarsonium cation and the tetraphenylborate anion (TATB assumption) [4,42]. Analysis of the data for transfer of the whole electrolyte on the basis of equation (11) provides an opportunity to assess the relative importance of cationic and anionic solvation, and specific and non-specific solvation for several simple electrolytes.

Examination of the data in Table 4 reveals that very good fits to the Koppel-Palm LSER are obtained for all electrolytes considered. In three cases, the contribution from solvent polarizability is negligible, and in one case, that from solvent basicity is unimportant. Under these circumstances, the parameters quoted are those from a fit with three independent variables.

In the case of the alkali metal halides, solvent acidity is the most important parameter when ionic size is small. As ion size increases, solvent acidity becomes less important, whereas solvent polarity becomes more important. For the perchlorate salts, solvent polarity is the dominant factor. In the case of the tetraalkylammonium and tetraphenylarsonium salts, the relative importance of specific and non-specific effects varies from one system to another, no particular trend being apparent.

It was pointed out previously [14] that the analysis of the data for tetraphenylarsonium tetraphenylborate is especially significant with respect to the TATB assumption used to separate the cationic and anionic contributions for thermodynamic transfer properties [42]. If this

Table 4

LSE Analysis of Data for Gibbs Energy of Transfer of 1-1 Electrolytes

Electrolyte	Number of Solvents	Relative Partial Regression Coefficients				stand. Dev. kJmol^{-1}	R
		$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$	$\bar{\delta}$		
LiCl	9	0.53	0.44	0.03	-	2.5	0.997
NaCl	10	0.58	0.32	0.04	0.06	1.3	0.999
KCl	8	0.55	0.30	0.12	0.03	1.7	0.999
KBr	10	0.38	0.43	0.19	-	4.4	0.984
CsBr	10	0.20	0.32	0.32	0.16	6.6	0.967
KClO ₄	10	0.19	0.25	0.40	0.16	3.9	0.977
RbClO ₄	10	0.22	0.22	0.40	0.16	4.4	0.967
(CH ₃) ₄ NC10 ₄	8	0.33	0.04	0.43	0.20	4.2	0.950
(C ₂ H ₅) ₄ NI	10	0.04	-	0.70	0.26	2.3	0.968
(C ₆ H ₅) ₄ As(C ₆ H ₅) ₄ B	12	0.87	0.12	0.01	-	7.3	0.959

assumption is correct, the values of $\bar{\alpha}$ and $\bar{\beta}$ for this salt should be equal. Since they are clearly not equal, the TATB assumption can be questioned. On the other hand, if one removes the data for the protic solvents namely, water, methanol and formamide, and performs the analysis using the data for aprotic solvents alone, the values of $\bar{\alpha}$ and $\bar{\beta}$ are equal [14]. This suggests that the TATB assumption is valid only in the absence of hydrogen bonding. It is clear that the TATB assumption needs to be reexamined and a better reference solvent other than water be used to tabulate thermodynamic transfer quantities.

A large body of data is also available for the enthalpy of transfer of simple 1-1 electrolytes from water to non-aqueous solvents [34-36, 38, 43-47]. When these are combined with results for the Gibbs energy of transfer for the same system, one may calculate the entropy of transfer. The present analysis was applied to the enthalpic data for 12 electrolytes including seven alkali metal halides, three alkali metal perchlorates, and two tetraalkylammonium bromides. In the case of the alkali metal salts, successful fits of the Koppel-Palm equation were obtained in all cases with correlation coefficients greater than 0.9 for data sets containing not less than 9 points. The standard deviation of the fits was approximately 6 kJmol^{-1} , that is, somewhat poorer than the corresponding fits for the Gibbs energy of transfer (Table 4). However, in the case of the

tetraalkylammonium salts, the data could not be fitted to the LSER used here.

According to the Born [5, 6] model or MSA model [9, 48], the enthalpy of transfer depends on the temperature coefficients of the solvent permittivity and in the latter case on the temperature coefficients of the MSA distance parameter δ . This follows from the fact that ΔH_{tr} is calculated by adding $T\Delta S_{tr}$ to ΔG_{tr} . The parameters used in the present analysis are all temperature dependent and there is no reason to expect the LSER to follow the solvent dependence of a temperature coefficient such as ΔS_{tr} . Thus, if the entropic contribution to ΔH_{tr} is small, one can still obtain an acceptable fit to the solvent dependence of ΔH_{tr} because one is really following the corresponding solvent dependence of ΔG_{tr} . On the other hand, when the entropic contribution is large as in the case for tetraalkylammonium salts [38], the present LSER fails.

The above analysis suggests on the basis of theory and available experimental data that one should not apply the Koppel-Palm equation to analyzing thermodynamic data for enthalpy changes. A proper analysis of such data should consider both the specific and non-specific parameters discussed here, as well as their temperature coefficients.

4.2 Standard Potentials of Simple Electrode Reactions

The simplest systems which can be examined in terms of the acid/base properties of the solvent are redox reactions involving the one-electron reduction or oxidation of an organic molecule to form the corresponding anion or cation radical. Data from the literature for eight systems [49-53] are summarized in Table 5. Very good to excellent fits to the Koppel-Palm equation are obtained in all cases, some of the relative partial regression coefficients being negligibly small. When cation radicals are formed in an oxidation reaction (1,4-diaminobenzene and phenothiazene), solvent basicity is the most important parameter. On the other hand, when the molecule is reduced to form an anion radical as in the case for the other six systems, solvent acidity plays the most important role. The importance of the remaining parameters varies from system to system. In two cases, namely, 1,4-benzoquinone and phenazine, only solvent acidity is important in determining the variation in standard potential with solvent.

Another group of electrode reactions for which solvent effects have been studied involve the reduction of various cations at a dropping mercury electrode. Gritzner [54,55] has reported half-wave potentials for a number of metal cations in a wide variety of solvents. The results of applying the Koppel-Palm analysis to data for the monovalent cations in the solvents considered in this review are summarized in Table 6. As one would expect, solvent basicity plays the predominant role. As the size of the cation increases in the alkali metal cation series, the relative importance of this factor decreases, and that of solvent acidity increases.

Table 5

LSER Analysis of Data for the Standard Potential for Simple Redox Reactions Involving Organic Molecules

Reactant	Number of Solvents	Relative Partial Regression Coefficients				stand. dev. mV	R
		$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$	$\bar{\delta}$		
9,10-anthraquinone (0/-)	7	.50	.17	.09	.24	8	.998
benzophenone (0/-)	7	.47	.26	.08	.19	14	.988
1,4-benzoquinone (0/-)	6	1.00	-	-	-	9	.998
1,4-diaminobenzene (0/+)	9	.08	.63	.13	.16	46	.972
1,4-naphthoquinone (0/-)	6	.89	-	.11	-	4	.999
9,10-phenanthrene-quinone (0/-)	7	.49	.24	-	.27	5	.999
phenazine (0/-)	8	1.00	-	-	-	10	.993
phenothiazene (0/+)	11	.04	.77	.14	.05	15	.982

Table 6

LSER Analysis of Data for the Polarographic Half-Wave Potential for Reduction of Monovalent Metal Ions at Mercury

Reactant	Number of Solvents	Relative Partial Regression Coefficients				stand. dev. mV	R
		$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$	$\bar{\delta}$		
Li ⁺	12	.08	.84	.08	-	43	.988
Na ⁺	14	-	.96	.04	-	48	.955
K ⁺	13	.21	.72	.08	-	44	.920
Rb ⁺	13	.26	.60	.14	-	33	.926
Cs ⁺	13	.31	.58	.12	-	29	.936
Tl ⁺	17	.13	.83	.04	-	41	.962

Solvent polarity plays a minor role, but in no case is there a significant contribution from solvent polarizability. The role of solvent acidity in the solvent effect is difficult to rationalize but it may be connected with ion pairing which depends on both solvent acidity and basicity. It should also be noted that the level of error in fitting these data is significantly higher than that for the redox reactions of organic molecules. This is

undoubtedly because the half-wave potential is often not simply related to the standard potential for the corresponding electrode reaction. In some cases, the polarographic current-potential dependence does not correspond to a reversible (fast) electrode reaction so that the half-wave potential reflects not only the thermodynamics of the process but also its kinetics. Nevertheless, the correlation between the half-wave potential and solvent basicity is very strong.

Other systems which have been considered involve transition metal complexes which are often highly charged ions [14,56]. These systems are usually cationic so that solvent basicity plays a predominant role. When anions are involved, solvent acidity predominates. Transition metal ion redox potentials are undoubtedly complicated by ion pairing especially when the ions are highly charged. In the analyses reported previously, at least three parameters are involved in the LSER, namely, solvent acidity and basicity, and either solvent polarity or polarizability [14]. The quality of the fit to the experimental data using the Koppel-Palm equation was better than that obtained by Lay et al. [56] on the basis of Kamlet-Taft parameters. This not only reflects the fact that the Kamlet-Taft parameters are often poorly defined for some of the polar solvents used in electrochemical studies but also that the hydrogen bond donating ability of the solvent was not considered in their analysis.

All of the electrochemical data analyzed here involve an extrathermodynamic assumption. More specifically, the electrode potentials are reported with respect to either the ferrocenium^{+/0} or bis(biphenyl) chromium^{+1/0} redox couples [57] in the same solvent. In this way, problems with changing liquid junction potentials were avoided. The assumption made is that the standard potential of the reference couple is independent of solvent. If the assumption is not valid, there should be some contribution to the correlation with solvent basicity. On the basis of the data presented in Table 5 this cannot be very important since in three cases involving reduction reactions, no contribution from solvent basicity was found.

In conclusion, the electrochemical data for standard potentials are especially interesting for assessing the role of solvent acidity and basicity in solvation. However, ideally these data should be obtained at zero ionic strength in order to avoid problems associated with ion pairing. Unfortunately, all available data were obtained in the presence of an inert electrolyte so that ion pairing effects are undoubtedly present.

4.3 Solvent Induced Frequency Shifts for Polar Solutes

A particularly interesting subject is the role of solvent acidity and basicity in the solvation of polar solutes. Since these molecules are dipolar one might expect the solvent to be involved both as an acid and a base at the negative and positive ends of the molecular dipole, respectively. Usually polar molecules have a characteristic vibrational frequency associated with the electronegative end of the molecular dipole. Interaction of a Lewis acid with this part of the molecule results in a shift

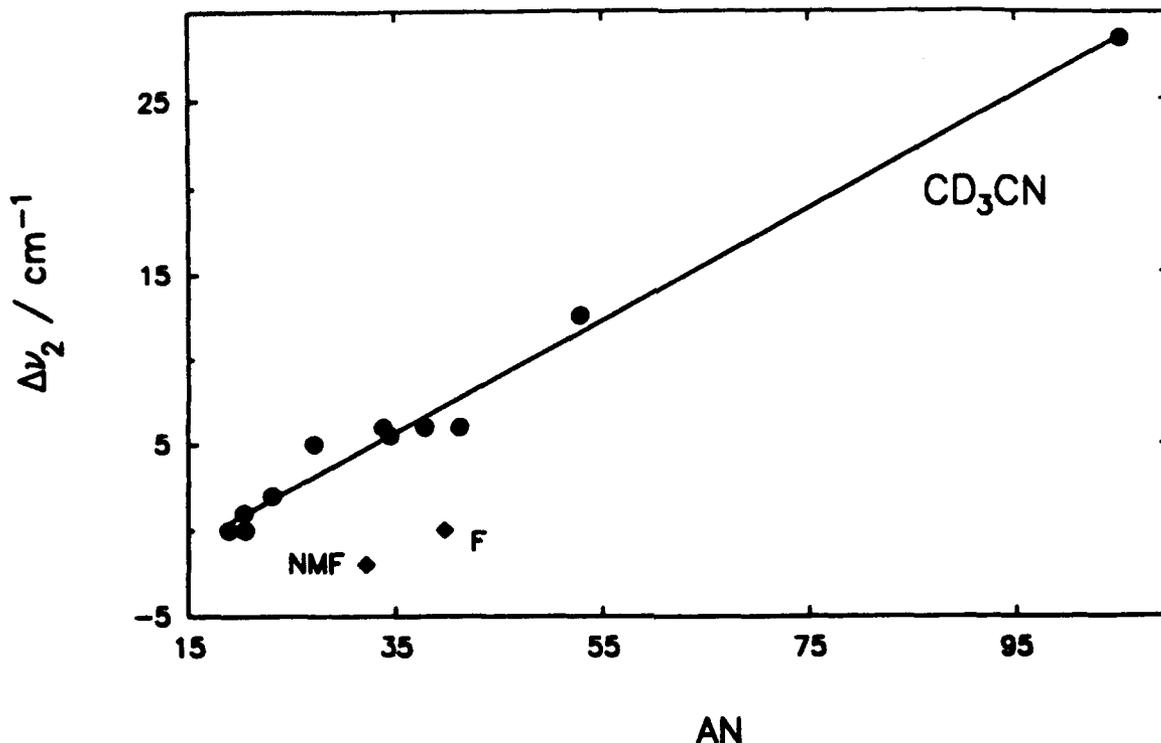


Figure 6. The shift in the C≡N stretching frequency for d-acetonitrile, $\Delta\nu_2$ in solvents which are more acidic plotted against the solvent's acceptor number AN. The data for formamide and N-methyl formamide (♦) were not included in the linear correlation (see text).

in the frequency of the associated infrared band which can be seen using IR spectroscopy. Thus, in ketones such as acetone one can follow the change in C=O stretching frequency with nature of the Lewis acid, and with acetonitrile, the change in the C≡N stretching frequency. These frequency shifts have been used effectively to study cation solvation in a number of aprotic solvents [58-61].

In the experiments discussed here the polar molecule, which is often used as a solvent, is a dilute solute in other solvents both polar and non-polar. The system which has been studied most extensively is acetonitrile [33, 62]. By using deuterated acetonitrile, the effect of the medium on the CD₃ symmetrical and asymmetrical stretching modes could be examined as well as the frequency shift for the C≡N stretching mode [33]. In solvents which are more acidic than acetonitrile itself, the C≡N stretching frequency is shifted in the blue direction by an amount which depends on the acceptor number of the solvent (Figure 5). This clearly shows that solvent acidity plays a major role in determining solvation of the electronegative end of the molecular dipole. The correlation shown in Figure 6 does not include formamide and N-methylformamide. These solvents are moderately strong as both a Lewis acid and base. As a result, the solvent induced frequency shift does not

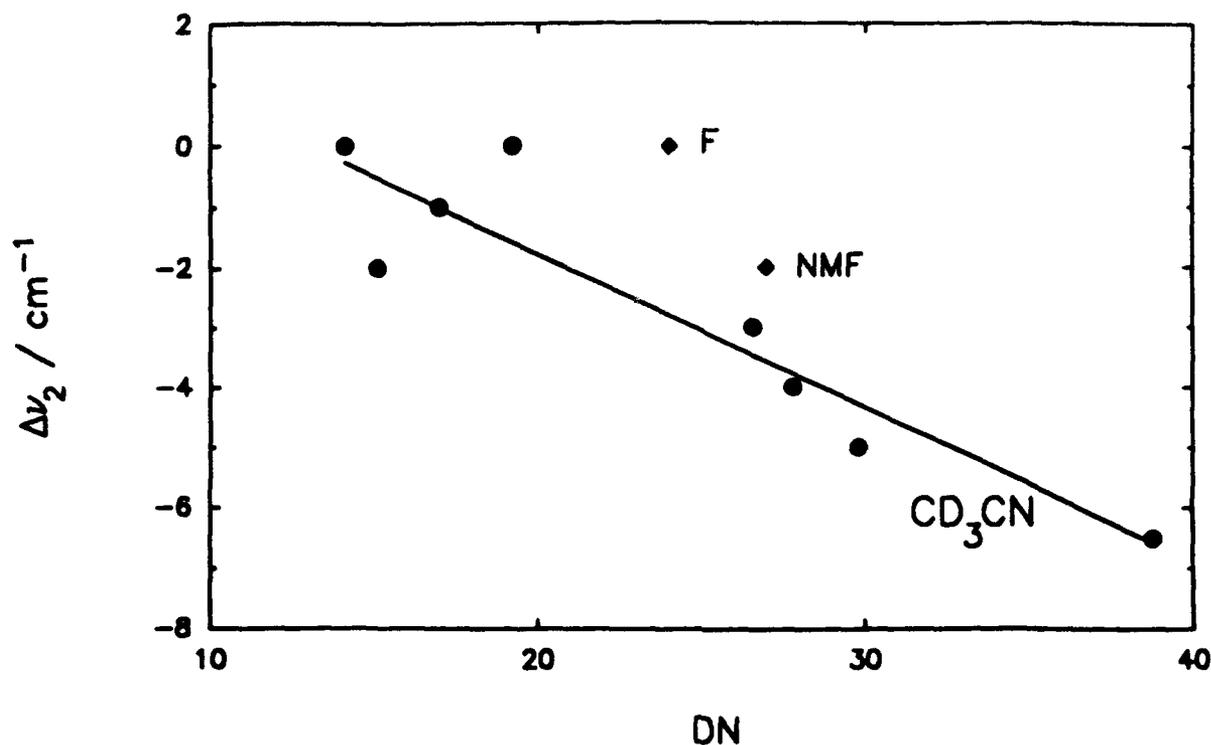


Figure 7. The shift in the C≡N stretching frequency for d-acetonitrile, $\Delta\nu_2$, in solvents which are more basic plotted against the solvent's donor number DN. The data for formamide and N-methylformamide (◆) were not included in the linear correlation (see text).

correlate with those of the other solvents which are stronger acids than acetonitrile but whose basicity is approximately the same or less.

In the case of solvents which are more basic than acetonitrile, the C≡N stretching frequency is shifted in the red direction to an extent which depends on solvent donicity (Figure 7). These observations were rationalized as involving interaction of the electronegative end of the solvent molecule with the CD₃ group in d-acetonitrile, which in turn affects the C≡N stretching frequency by weakening this bond. This explanation is supported by the observation that the symmetrical and asymmetrical stretching frequencies for the CD₃ group are also shifted in the same direction [33].

The LSER analysis based on the Koppel-Palm equation was applied to the acetonitrile data and data for six other polar solutes [62-68]. The solvents included both polar and non-polar liquids with the polar media being limited to those considered above. In the case of acetonitrile, the dominant parameter is solvent acidity which accounts for 42 percent of the explained frequency shift for the C≡N stretching frequency using data for 22 different solvents (Table 7). The second parameter in order of importance is solvent polarity, a non-specific parameter. The quality of the fit is quite good with an overall correlation coefficient of 0.950. If the correlation is limited to the polar solvents considered in this review

(Tables 1-3), the fit improves considerably with a correlation coefficient of 0.987 and standard deviation of 0.8 cm^{-1} for 14 solvents. However, the relative importance of the four solvent parameters remains approximately the same.

A related solvent for which shifts in the $\text{C}\equiv\text{N}$ stretching frequency have been studied is benzonitrile [62]. For this system, the dominant parameter in explaining the observed frequency shifts is solvent polarizability, which accounts for 32 percent of the explained variation. The remaining parameters are of approximately equal importance. The changes observed from acetonitrile to benzonitrile undoubtedly reflect the presence of the phenyl ring with its very polarizable electron density.

Another group of molecules including acetone [64] cyclopentanone [65] and tetramethylurea [63] contain the $\text{C}=\text{O}$ group whose stretching frequency depends on the nature of the solvent. These systems are moderately strong to strong bases. As a result, solvent acidity plays a dominant role in accounting for the observed frequency shifts. For each of these systems, one of the remaining three parameters is of negligible importance. Obviously, the details of molecular structure are important in determining the relative roles of the other parameters.

The remaining molecules considered here are the nitro compounds, nitromethane and nitrobenzene. Both are very weak bases and not very strong acids. The medium effect may be examined by studying the vibrational modes of the NO_2 group [67]. On the basis of the asymmetric stretching frequency for this group in nitromethane, the predominant factor in solvation of this molecule is the solvent's basicity. In fact, most solvents considered in the study carried out by Nyquist [67] are stronger Lewis bases than nitromethane itself. Thus, it is not at all surprising that no significant correlation with the acceptor number alone was found in his study [67]. The parameter of second importance is solvent polarity, indicating that non-specific effects are important for this system. When nitrobenzene is considered, the relative importance of the solvent parameters changes considerably. Because of the polarizable electron density associated with the phenyl ring, solvent polarizability predominates. Solvent polarity is also important, and solvent acidity plays a negligible role.

The data summarized in Table 7 confirm that one needs to consider both specific and non-specific effects in order to understand the solvation of polar molecules. It is particularly striking that solvent acidity or basicity often plays the major role. The vibrational spectroscopic data allow one to examine the electronegative end of the molecular dipole for most polar molecules, and in some cases the electropositive end. Since many polar organic solvents contain methyl or phenyl groups, it is helpful to use the deuterated solute so that the solute's vibrational modes associated with these groups may be distinguished from those of the solvent.

Table 7

LSER Analysis of Data for the Solvent Induced Frequency Shift of the Band Associated with the Electronegative Group in Polar Molecules

Solute	Vibrational Band	Number of Solvents	Relative Partial Regression Coefficients					stand. Dev./ln V	R
			α	β	γ	δ			
AC	C=O stretch	10	0.73	0.10	-	0.17	1.6	0.980	
AN	C≡N stretch	22	0.42	0.17	0.24	0.17	1.4	0.950	
BzN	C≡N stretch	11	0.22	0.24	0.22	0.32	0.9	0.914	
CPNa	C=O stretch	13	0.52	-	0.25	0.23	2.5	0.924	
NB	asym. NO ₂ stretch	10	0.11	-	0.39	0.50	1.4	0.932	
NM	asym. NO ₂ stretch	10	0.16	0.47	-	0.37	2.2	0.891	
TMU	C=O stretch	14	0.72	0.12	0.17	-	2.4	0.981	

^aCPN = cyclopentanone.

Most of the previous studies [62-68] focused on the role of solvent acidity in determining the frequency shift. For this reason, the solvents chosen in this work covered a wide range of acidities. However, there are a significant number of other polar and non-polar solvents which could be included. Extension of the number of solvents for systems such as benzonitrile and the nitrocompounds would undoubtedly improve the correlations observed for these systems and clarify the role of the less important parameters in the LSER.

5. CONCLUSION

The important conclusion of the studies reviewed here is that one must consider both specific and non-specific solvation effects in order to understand the related physical characteristics. Attempts to rationalize solvation on the basis of the continuum dielectric properties of the solvent can only be partially successful because they do not recognize the chemical interactions due to the specific composition of the solute and solvent. Solvent acidity and basicity estimated through empirical parameters provide a very effective way of evaluating specific effects.

The analysis presented in this review emphasizes the relative importance of four solvent parameters namely solvent acidity, basicity, polarity and polarizability. Rather than reporting regression coefficients, only relative partial regression coefficients are given in the tables. This approach is quite different from that usually taken in reporting linear free energy relationships and is meant to emphasize that the main purpose of the analysis is to assess the relative importance of the independent variables rather than to predict a value for the quantity under investigation for an unstudied solvent. When a sufficient number of solvents are included in the analysis, the relative partial regression coefficients do not change significantly. In the absence of this information, one has no reliable way of assessing the relative importance of each parameter on the basis of the overall fit. This follows from the fact that the range of variation of each parameter is not the same.

As far as solvent acidity and basicity are concerned, the parameters developed by Gutmann [24] appear to be the best. This is largely due to the fact that they change over a wide range and are available for most polar solvents. Strong support for these parameters is obtained from analyzing thermodynamic data for the Gibbs solvation energy of simple monoatomic monovalent cations and anions [9, 14]. The fact that the donor number cannot be measured for protic solvents is then circumvented by estimating it using the value of B_p calculated from the Gibbs solvation energy of the alkali metal cations, or B_{sc} estimated from Persson's solvatochromic parameter.

In conclusion, much can be learnt about the mechanism of solvation of both ionic and polar solutes by applying the above analysis provided data are available in a sufficiently large number of solvents. Since application of the Koppel-Palm requires estimation of five parameters, the experimental

study must involve at least six solvents, and preferably, at least ten. This limitation often prevents analysis of existing data in the literature for which only a few solvents have been involved in the study. Considering the importance of solvation to reactions in solution, further experimental work to study solvation as a function of solvent nature seems well worthwhile.

ACKNOWLEDGMENT

Recent work from this laboratory discussed in this review was supported by the Office of Naval Research, Washington and by the National Science Foundation, Washington (Grant No. CHE 9008171).

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