

# A Study of Solvent Electron-Pair Donor Ability and Lewis Basicity Scales

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Sandström, M., Persson, I. and Persson, P., 1990. A Study of Solvent Electron-Pair Donor Ability and Lewis Basicity Scales. – Acta Chem. Scand. 44: 653–675.

Comparisons are made of some parameter-based relative scales for Lewis basicity of solvents which give a qualitative measure of the electron-pair donating properties of solvent molecules towards different types of solutes. These scales have been deduced from measured effects of donor–acceptor reactions at the solvation of a reference electron-pair acceptor. The effects are discussed in terms of the intermolecular energies involved in the interaction. Special attention has been paid to scales claimed to represent donor properties of soft solvents, and further measurements have been made in some cases. The donor strength scale  $D_s$ , which is based on the change in the stretching vibration frequency of the  $\text{HgBr}_2$  complex in solution, has been enlarged with 18 new solvents and now includes a total of 80 solvents ranging from weak to very strong Lewis bases. The basicity order of the ethylamines in the neat solvents is found to be in the order ammonia > ethylamine > diethylamine > triethylamine, and the relation found with their molecular dipole moments is discussed. An attempt to enlarge the Cu  $\lambda_{\text{max}}$  scale, based on the solvatochromic changes of the solvated copper(II) complex,  $\text{Cu}(\text{tmen})(\text{acac})^+$ , to encompass strong donor solvents failed owing to the insufficient stability of the acceptor. The proton NMR shift of chloroform,  $\Delta\delta$ , which previously had been measured in 27 solvents and proposed as a suitable complement to the donor number,  $D_N$ , scale of Gutmann for hydrogen-bonding solvents, was extended here to 45 solvents, but a poor correlation was found with the scales mentioned above outside very restricted groups of solvents. Discussions of the relative merits and suitable ranges of applications of a number of solvent basicity scales are made. The proposed ability of some statistically averaged multiparameter scales to describe soft–soft donor–acceptor interactions is critically examined. For correlations and predictions of solvent effects on a chemical system it is recommended to use a basicity scale preferably based on a single selected reference acceptor with similar properties as the Lewis acceptor to be studied.

## Introduction

*Solvent effects.* It has long been known that the solvent can influence the physical properties and chemical reactivity of solutes.<sup>1</sup> Solubilities, redox and distribution equilibria, stability of complexes, reaction rates and mechanisms, spectroscopic and structural properties, etc. are influenced by solvation.<sup>1–4</sup> The overall solvation ability is often called the polarity of the solvent, and depends on the action of all, specific and non-directional, intermolecular forces between the solute and the solvent molecules.<sup>1</sup> Attempts to connect the solvent polarity to single macroscopic or molecular properties such as the dipole moment, dielectric constant, polarizability and measures of acidity and basicity of the solvent have been made, but such relations can only in very restricted cases account for changes in the complicated and often interrelated solvation effects at a microscopic level.<sup>5</sup> A large number of empirical solvent polarity scales, based on measured effects of selected solvation processes, have been proposed in order to systemize and correlate observed

solvation effects, although only a few have gained widespread use. An excellent well referenced review covering this area has recently been given by Reichardt.<sup>1</sup>

In organic chemistry, solvent effects are of great importance for discussions of e.g. reactivity and reaction rates, and most polarity scales have been introduced for such correlations.<sup>1,4</sup> For studies of the solvation of cations and metal complexes acting as Lewis acids the electron-pair donating ability (Lewis basicity) of the solvents is of special interest. In inorganic chemistry the majority of reactions takes place in coordinating solvents, and in the last decades a large number of stability constants have been derived and compiled for complex formation involving ions and/or molecules, also in non-aqueous solvents.<sup>6</sup> The conclusions made on the stoichiometry of the complex species formed are mainly based on activity-dependent thermodynamical measurements, in which the coordinative role of the solvent molecules and the influence of the ionic medium can be difficult to establish. Interpretations of thermodynamic, kinetic or structural properties of complex species, reaction mechanisms, etc., make it necessary to consider the solvent molecules as ligands which actively participate in the reac-

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tions. In order to learn more about the coordinative role of the solvent molecules and intermolecular forces in solution from thermodynamic data, it is important to evaluate all the thermodynamical quantities for the reaction and not only the stability constants. The stabilities of e.g., the mercury(II) halide systems in several solvents with different donor properties, viz. water,<sup>6-8</sup> dimethyl sulfoxide,<sup>9</sup> pyridine<sup>10</sup> and acetonitrile,<sup>11</sup> can be of the same order of magnitude, in spite of large differences in the enthalpy and entropy terms. A solvent scale allowing a relative comparison of the Lewis basicity of different solvents is therefore often of interest also in inorganic and organometallic chemistry.

*Donor-acceptor complexes.* Complex formation with coordinative bonds in solution can often be described in Lewis' acid-base terminology. The solute is a Lewis acid acting as an electron-pair acceptor, and the ligands are Lewis bases (electron-pair donors), and bonds with some amount of charge-transfer are formed.<sup>12</sup> As described in a review by Jensen on general Lewis acid-base definitions,<sup>12</sup> which gives an account of the historical development of the concept, the closed shell donor-acceptor interactions can vary considerably in strength, from weak intermolecular forces over partial charge-transfer and coordinative bond formations to complete electron transfer, leading to redox reactions and ionization. This has led to several classification schemes which can be used for qualitative predictions of the interaction strength. For the special case of metal ions, Ahrland *et al.* distinguished between class *a* and *b* acceptors on the basis of the relative stabilities of the complexes formed with different types of donor atoms.<sup>12,13</sup> This classification was generalised by Pearson, and the hard-soft terminology was introduced with the simple rules that hard acids with low polarizability prefer to bind to hard bases, and soft acids with high polarizability to soft bases, forming bonds with more covalent character.<sup>14-16</sup> These principles, which are very useful for comparisons of different types of solvent-solute interactions, have gradually been developed and theoretically related to atomic and molecular properties.<sup>15,17</sup> However, the theoretically derived parameters refer to overall molecular quantities in the gas phase and cannot yet be used for more quantitative descriptions of specific and localized Lewis acid-base interactions in solution. Nevertheless, even the qualitative hard-soft classifications of solvents and acceptor acids are very useful for this discussion of solute-solvent interactions, and will frequently be used in the following.

Following Mulliken's classical theoretical study on donor-acceptor complexes the common types of donors can be divided into  $n$  (lone-pair) and  $\pi$  (bonding  $\pi$ -orbital), and the acceptors as  $\sigma$  (vacant orbital),  $\pi^*$  (antibonding  $\pi$ -orbital) and  $\sigma^*$  (antibonding  $\sigma$ -orbital).<sup>18</sup> This classification is of interest for a better understanding of the properties of the reference acceptors used for the basicity scales discussed in this paper. Many  $n$ -donor solvents coordinate strongly to cations and are thus good solvents for electrolytes and inorganic compounds. The special effects some-

times caused by the formation of  $\pi$ -bonds, often by a participation of  $d$ -orbitals on the acceptor to donate or accept electrons from the solvent molecule, are also related to the polarizability of the interacting species. This effect is partly responsible for the softness of donors and acceptors mentioned above, and can hardly be described quantitatively in soft-soft interactions without detailed theoretical calculations of the electron distribution in the specific cases.

*Principles of basicity scales.* The Lewis basicity of solvents is often characterized by measuring the effect of a solvent, in most cases spectroscopically or thermodynamically, on a convenient solvent-sensitive reference reaction. However, the parameters or solvent index obtained from the measurements reflect the contributions from *all* interactions influencing the measured quantity. A necessary condition for a solvent index to be a good relative measure of the solvent basicity is that the effect of the donor-acceptor reaction provides a major contribution to the derived index or relation. A careful choice of a suitable acceptor or Lewis acid is therefore essential for the properties of the basicity scale. Practical considerations, such as solubility, chemical stability and measurable response of the acceptor, are also important factors in order to obtain a useful scale with wide range and applicability. The closer the effect on the model system is to the investigated solvent-sensitive property, the closer the measured parameters and the solvent index will follow a linear correlation over the series of bases studied.<sup>19</sup> However, such single-term linear expressions can in principle only model the common part of the effects, and variations in other system-specific interactions will cause deviations outside restricted comparisons.<sup>19,20</sup> For example, the hard-soft principles mentioned above show that no single-parameter solvent scale could describe all types of Lewis acid-base interactions for all kinds of acceptors and solvents. However, the deviations could in principle be described by introducing additional non-colinear terms in multiparameter correlations, so-called linear solvation energy relationships, LSERs.<sup>19</sup>

In attempts to model all aspects of solvation effects, statistical methods have been used to construct multiparameter LSER expressions, which have been claimed to give satisfactory correlations for a "major proportion of the properties in chemistry and biology that depend on solute-solvent interactions".<sup>20</sup> This view has been criticized, and for the Lewis acid-base interactions studied here the more modest proposal that the correlations can be seen as "locally valid linearizations of complicated functional relationships",<sup>19,21</sup> seems to be more realistic. In particular, soft-soft interactions including a significant amount of covalency would be difficult to describe by means of averaged parameter values which represent a compromise between general and system-specific effects.

A more direct and less elaborate method is to use a scale with properties as close as possible to those of the system under study. This often requires a certain chemical insight into the cause of the system response, in particular for

soft–soft interactions leading to significant charge-transfer effects. One aim of this paper is to compare different scales of solvent basicity in order to assess their usefulness and range of application, another is to discuss qualitatively the solvation processes on a molecular level in terms of the dominant interaction energies. Special attention will be given to those basicity scales representing soft donor properties of the solvents. One additional complication in these comparisons is, however, that some scales relate the donor properties of the neat solvents, while others deal with isolated solvent molecules in a more or less inert diluting medium. For associated liquids, e.g. water, alcohols and also some sulfides, for which anomalous enthalpy effects have been found,<sup>22</sup> the differences can be large, but even for non-self-associated liquids the conversion from one comparable neat solvent scale to a corresponding diluted “solvent” scale can be hazardous.<sup>23</sup>

*Some proposed scales of Lewis basicity.* The first empirical solvent basicity index to gain widespread use in predicting effects of donor–acceptor reactions in coordination chemistry was the enthalpy-based donor number  $D_N$  scale introduced by Gutmann *et al.*,<sup>24</sup> although the same concept was previously suggested by Lindqvist.<sup>25</sup> The donor number for a solvent is defined as the  $-\Delta H$  value (in kcal mol<sup>-1</sup>) of the formation of the 1:1 adduct between the solvent molecule and the reference acceptor, antimony(V) chloride (SbCl<sub>5</sub>), in a diluting 1,2-dichloroethane medium.

Maria and Gal later used an approach similar to that of Gutmann for their carefully determined  $\Delta H_{BF_3}^\circ$  scale.<sup>26</sup> The  $\Delta H_{BF_3}^\circ$  values are the enthalpies (in kJ mol<sup>-1</sup>) of the adduct formation of gaseous BF<sub>3</sub> and a solvent molecule in a diluting dichloromethane medium. Their selection of boron trifluoride as the reference acceptor and dichloromethane as the diluting medium was made mainly to reduce the number of side-reactions, which cause problems in the determinations of the  $D_N$  values.

Another enthalpy-based scale is the four-parameter expression proposed by Drago *et al.*:

$$-\Delta H = E_A E_B + C_A C_B.$$

Coordinate bond strengths are estimated in the form of Lewis acid–base reaction enthalpies  $\Delta H$  in the gas phase or in a poorly solvating medium.<sup>27–29</sup> The acid A and the base B are both characterized by two empirical parameters  $E$  and  $C$ , and it is assumed that the standard enthalpy of a Lewis acid–base reaction can be partitioned into two terms  $E_A E_B$  and  $C_A C_B$ , which are said to correspond to tendencies of electrostatic and covalent contributions in the interaction, respectively.<sup>30,31</sup> The relative scales of the parameters  $E$  and  $C$  for both the acceptor A and the donor B have been fixed from four arbitrarily chosen reference values, and then statistically optimized from a large set of enthalpy values of adduct formations. Inherent assumptions are that the entropy changes are similar and that 1:1 adducts are formed in all cases.

Solvatochromic effects on solvation have recently been reviewed,<sup>32</sup> and are used in many scales of solvent polarity.<sup>1–4</sup> A basicity scale obtained from the shift of the visible absorption band (Cu  $\lambda_{max}$ ) of the solvated [Cu(tmen)(acac)]<sup>+</sup> complex in the neat solvent, was proposed by Sone and Fukuda.<sup>33,34</sup> A free Cu<sup>2+</sup> ion has the d-electron configuration ( $t_{2g}$ )<sup>6</sup>, ( $e_g$ )<sup>3</sup>, and due to the stabilizing influence of the two chelating ligands, the hole in the  $e_g$  orbitals will be located in the  $d_{x^2-y^2}$  atomic Cu orbital in the unsolvated complex. The shielding of the nucleus will thus be lowest and the strongest bonds formed in the equatorial plane of the ligands. The copper atom therefore has two well defined axial acceptor sites in the direction of the  $d_{z^2}$  orbital. The energy of this orbital will rise at the increasing Pauli repulsion of the orbitals of the axial ligands with increasing donor strength, causing a blue shift in the visible d–d electronic transition. These colour changes can be very illustrative for teaching purposes.<sup>35</sup> The number of solvents studied in the original paper,<sup>34</sup> and in subsequent papers by Soukup *et al.*<sup>35,36</sup> is 17, and has been extended further in this study (see also Ref. 37).

Munakata *et al.* proposed a logarithmic “coordination power” scale,  $CP$ , from spectrophotometric measurements.<sup>38</sup> The relative coordination ability  $CA$ , for 22 oxygen and nitrile donor solvents was obtained from the measured crystal field splitting  $10 Dq$ , of the octahedral [NiA<sub>3</sub>B<sub>3</sub>]<sup>2+</sup> complex in mixtures of two solvents A and B. The coordination power is then obtained with acetonitrile as the reference solvent as:

$$CP = \log (CA_{sol}/CA_{AN}).$$

“Soft” basicity scales, suitable for soft donor solvents or claimed to describe the softness of solvents, have also been proposed. Gritzner observed for a group of ten nitrile and sulfur donor solvents that the Gibbs energies of transfer  $\Delta G_{tr}^\circ$  deviate anomalously for the soft Ag<sup>+</sup> ion in linear correlations with harder cations such as Na<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Tl<sup>+</sup>.<sup>39,40</sup> For a few ions, e.g. Tl<sup>+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>, these deviating values were reported to follow a second linear correlation.<sup>41</sup> The same group of solvents also deviates in a similar correlation between Ag<sup>+</sup> and the small and hard Na<sup>+</sup> ion, (Fig. 3 of Ref. 40), although here the deviating solvents seem to form two subgroups with almost constant  $\Delta G_{tr}^\circ$  values of Na<sup>+</sup>. This deviating group of solvents were labelled soft, and the  $\Delta G_{tr}^\circ$  values of the silver(I) ion from benzonitrile, “the weakest soft donor solvent”, to solvents with still larger  $\Delta G_{tr}^\circ$  values in this group were used to obtain a solvent softness parameter  $SP$ .<sup>41</sup>

Marcus recently constructed the related  $\mu$  scale from the discrepancy between the solvation properties of the soft Ag<sup>+</sup> and the hard Na<sup>+</sup> and K<sup>+</sup> ions in another attempt to characterize specifically the solvent softness. Since the Ag<sup>+</sup> ion is intermediate in size between the Na<sup>+</sup> and K<sup>+</sup> ions, the difference between a mean of the values of the Gibbs energies of transfer of Na<sup>+</sup> and K<sup>+</sup> from water to a given

solvent and the corresponding  $\Delta G_{tr}^{\circ}$  value for  $Ag^+$ , was used to obtain the  $\mu$  parameter.<sup>42</sup>

Donor properties of soft solvents have also been characterized by vibrational spectroscopy. The  $B_{soft}$  scale<sup>43</sup> is obtained from the difference in frequency between the reference solvent tetrachloromethane and the C–I stretching vibration in the ICN molecule dissolved in the neat solvent of interest:

$$B_{soft} = \nu_{CI}(CCl_4) - \nu_{CI}(solv).$$

The donor strength scale  $D_S$ <sup>44</sup> is obtained from the difference in the symmetric stretching frequency of the Hg–Br bond in the  $HgBr_2$  molecule in the gas phase and in the solvated molecules in solution:

$$D_S = \nu_{HgBr_2}(gas) - \nu_{HgBr_2}(solv).$$

For the last two scales soft acceptor molecules are used, in which the intramolecular (C–I or Hg–Br) bond strength decreases at the solvation and a direct relation between the resulting frequency shift and the Lewis basicity of the solvent is assumed. In this work the frequency shifts for both  $HgI_2$  and  $HgBr_2$  molecules in a number of additional solvents have been measured, and  $D_S$  values for 80 solvents are given later in Table 3. Comparisons are made of solvent induced changes on different properties of the  $HgX_2$  molecules with  $X = Cl, Br$  or  $I$ , and correlations with other solvent indices are examined.

The mercury(II) atom in  $HgBr_2$  is a typical soft electron-pair acceptor forming strong bonds with some covalent character to soft donor atoms. Pseudotetrahedral solvated molecular complexes with the composition  $HgBr_2L_2$  seem to be formed in all solvents with monodentate electron-pair donors  $L$ . The  $HgBr_2$  entity is very stable, which allows even very strongly coordinating solvents such as sulfides, amines and phosphines to be studied. The measurements are normally performed in the neat solvent, which means that account is taken of the effect on the donor ability of the coordinated solvent molecules by their interactions with bulk solvent. Steric effects are not expected to have much influence, since there is little crowding of the four ligands in a pseudotetrahedral  $HgBr_2L_2$  configuration.

Taft *et al.* have in an extensive series of papers introduced multiparameter expressions for describing the solvent polarity in LSERs with the main solvatochromic parameters  $\pi^*$ ,  $\alpha$  and  $\beta$ .<sup>1,20,45–48</sup> The solvatochromic parameters are statistically averaged values obtained from a large number of measured data, but have been ascribed to specific solute and solvent properties.<sup>20,48</sup> Of special interest for this discussion is the  $\beta$  parameter of hydrogen-bond-acceptor basicities, which is claimed to be a measure of the ability of a solvent to accept a proton or transfer some electron density in a hydrogen-bond or weak Lewis acid–base interaction. It is determined as a statistically optimized average of non-homogeneous effects for several Lewis acceptors measured with different techniques, which

give both time-averaged or ensemble-averaged values,<sup>20,45</sup> some from measurements in the neat solvents and others with isolated solvent molecules in a diluting medium.<sup>23</sup>

In order to account for the “family dependence” found in the LSER for some groups of oxygen and nitrogen donor solvents with similar types of hydrogen-bond-acceptor or Lewis basicity sites, a coordinate covalency constant  $\xi$ , different for each group, was introduced.<sup>20,46–48</sup>

Abraham and coworkers have recently introduced several other hydrogen-bond-acceptor (proton acceptor) basicity scales.<sup>23,49</sup> They have stressed that even hydrogen-bond-acceptor basicity is influenced by several factors, not only the family dependence mentioned above but also that different hydrogen-bond donors (Lewis acceptors), e.g. O–H and N–H, rank Lewis bases differently. The reference acceptors have been selected by means of a principal component analysis method,<sup>50</sup> and the effects of self-association in the solvents are considered.<sup>23</sup> Their most extensive basicity scale  $\beta_2^H$  is based on a set of selected reference acids, and a diluting tetrachloromethane medium is used. Two related solvatochromic basicity scales, denoted  $\beta_1$ (general) and  $\beta_1$ (special), have also been described.<sup>23</sup> They are based on the shifts in the absorption maxima of aniline-type indicators upon hydrogen-bonding in the neat solvents. The  $\beta_1$ (general) scale is obtained from a regression analysis of 11 aniline-type indicators, and  $\beta_1$ (special) is based on the difference between two selected standard compounds, 4-nitroaniline (which forms hydrogen bonds) and 4-nitro-*N,N*-dimethylaniline.

For the special purpose to simulate the hydrogen bonding effects on functional groups in biological systems they have also constructed the  $\log K_{\beta}$  and  $\beta_{sm}$  parameters for a single reference acceptor, 4-nitrophenol, with dilute solutions of the Lewis base in 1,1,1-trichloroethane. The donor-acceptor effects are measured by UV (or in some cases IR) spectroscopy. They find that the diluting medium imposes significant ranking changes on the Lewis bases because of an increase the charge-transfer energy term at the expense of the electrostatic term in the hydrogen bond.<sup>49</sup> Their choice of a polar but non-hydrogen-bonding solvent for the diluting medium was made as a compromise in order to obtain a scale with biological relevance for drug design.

Other hydrogen-bond related scales have been obtained from, e.g., the shifts of the stretching frequencies measured by infrared spectroscopy,  $\Delta\nu_{OD}$  of methanol,<sup>51</sup> or  $\Delta\nu_{PhOH}$  of phenol,<sup>52</sup> in the solvents. The proton NMR shift of chloroform due to weak hydrogen-bonds with the solvent was used by Hahn *et al.* as a measure of the basicity of 27 nitrogen and oxygen donor solvents.<sup>53</sup> The shift  $\Delta\delta$ , from pure chloroform to infinite dilution in the solvent (with a correction for the bulk magnetic susceptibility), was used in a linear correlation for an extension of the donor number scale  $D_N$  to some hydrogen-bonding solvents for which direct measurements of  $\Delta H(SbCl_5)$  could not be made. In the present work (Table 1) the number of solvents studied in the  $\Delta\delta$  scale has been extended to 45.

**Table 1.** The measured proton NMR shift,  $\delta_{\text{obs}}$  (ppm), of chloroform in solution, the volume magnetic susceptibility  $\chi$ ,<sup>55,56</sup> and the difference between the shift for pure  $\text{CHCl}_3$  (7.21 ppm) and the corrected values in the solvents  $\Delta\delta$ ,<sup>53</sup> given for a number of solvents. Tetrachloromethane with  $\chi = -0.672$  is used as reference.

Solvent	$\delta_{\text{obs}}$	$-\chi$	$-\Delta\delta$
1,2-Dichloroethane	7.58	0.744	0.26
Methylphenyl ether (anisole)	7.45	0.672	0.28 <sup>a</sup>
Furan	7.75	0.598	0.74 <sup>a</sup>
Benzonitrile	8.12	0.638	1.02 <sup>a</sup>
Methyl acetate	7.00	0.537	0.11
Diethyl ether	7.45	0.531	0.58
$\gamma$ -Butyrolactone	7.72	0.594	0.72
Methanol	7.52	0.530	0.65
1-Butanol	7.67	0.618	0.49
Ethanol	7.67	0.575	0.71
1,2-Ethanediol (glycol)	8.00	0.699	0.78
Formamide	8.60	0.551	1.69 <sup>a</sup>
<i>N</i> -Methylformamide	8.92	0.580	1.94
Trimethyl phosphate	8.23	0.735	0.93 <sup>a</sup>
1-Butanethiol	7.46	0.654	0.33
Aniline	7.81	0.691	0.60 <sup>a</sup>
Pyridine	9.07	0.611	2.03
Di- <i>n</i> -butyl sulfide	7.55	0.650	0.43
Tetrahydrothiophene	7.87	0.726	0.59
Di- <i>n</i> -butylamine	8.12	0.767	0.75
Piperidine	8.62	0.650	1.50
Tri- <i>n</i> -butyl phosphite	7.78	0.611	0.74
Tri- <i>n</i> -butyl phosphine	8.43	0.610	1.39

<sup>a</sup>Uncertain values, solvent proton shift in the same range as the chloroform shift.

## Experimental

**Chemicals.** All reagents used in this study were of analytical or spectrophotometric grade when available. Tri-*n*-butylphosphite of 96 % purity was obtained from Aldrich. The  $[\text{Cu}(\text{tmen})(\text{acac})]\text{ClO}_4$  and  $\text{BPh}_4$  salts were prepared as described previously.<sup>33,36,54</sup> The products were recrystallized twice from ethanol. Solutions of suitable concentrations for the spectrophotometric measurements were prepared in the neat solvents.

**Spectrophotometry.** The Cu  $\lambda_{\text{max}}$  absorption spectra were recorded at room temperature in the range 400–900 nm with a Perkin-Elmer 330 spectrophotometer. The estimated error in the reported  $\lambda_{\text{max}}$  values is 2 nm. No corrections for overlapping bands or decomposition reactions,<sup>36</sup> have been made in the values reported here.

**Proton NMR.** The measurements and data treatment for the  $\Delta\delta$  scale were performed in the same way as described by Hahn *et al.*<sup>53</sup> A 60 MHz JEOL NMR spectrometer was used at 25 °C. The error in the chemical shifts of the  $\text{CHCl}_3$  proton is estimated to be less than 0.02 ppm, except in the indicated cases where the solvent proton shift interferes.

**Laser Raman spectra.** Raman spectra were measured in the same way as described previously.<sup>44</sup> The estimated error in the reported band positions is  $\pm 1 \text{ cm}^{-1}$ . The concentration of the mercury(II) halide solutions was about  $0.1 \text{ mol dm}^{-3}$  at sufficient solubility, otherwise solutions saturated at 25 °C (15 °C for ethylamine) were used.

## Results

The proton NMR shifts of chloroform in a number of solvents and the corresponding  $\Delta\delta$  values determined in this study are given in Table 1. The volume magnetic susceptibilities of the solvents were taken from the literature.<sup>55,56</sup>

The frequencies corresponding to the strongly Raman-active symmetric  $\text{XHgX}$  stretching vibration of the  $\text{HgBr}_2$  and  $\text{HgI}_2$  complexes in some solvents are given in Table 2 as a complement to the data previously reported in Ref. 44. In a few cases a weak asymmetric stretching mode could be discerned in the Raman spectra. Remeasurements of di-

**Table 2.** Vibration frequencies in  $\text{cm}^{-1}$  measured by Raman spectroscopy of the symmetric  $\nu_s$  and asymmetric  $\nu_{\text{as}}$  stretching  $\text{XHgX}$  modes of the mercury(II) bromide and iodide molecules in some solvents.

Solvent	$\text{HgBr}_2$		$\text{HgI}_2$	
	$\nu_s$	$\nu_{\text{as}}$	$\nu_s$	$\nu_{\text{as}}$
Gas <sup>a</sup>	221.8	293	158.4	237
Chloroform	217		156.5	
Carbon disulfide	215		156	
1-Nitropropane	213.5		156	
Thiophene	211		154.5	
Di- <i>n</i> -butyl ether	211		153.5	
Acetic acid anhydride	210.5		154	
Ethyl acetate	208		153	
4-Methyl-2-pentanone (isobutyl methyl ketone)	208		152.5	
2-Methyl-2-propanol ( <i>t</i> -butanol)	206.5	~266		
1-Octanol	205.5			
2-Propanol	204	~260		
Methanol	204	~259		
1-Propanol	203.5	~258		
1-Butanol	203.5			
Di- <i>n</i> -butyl disulfide	200		149.5	
<i>N,N</i> -Diethylformamide	197.5		147	
Dimethyl sulfoxide	194.5	240.5		
Tri- <i>n</i> -dodecyl trithiophosphite			145.5	
Diethylamine	174	~196	136.5	~165
Tri- <i>n</i> -butyl phosphite			132	
Ethylamine <sup>b</sup>	167		131	
Ammonia <sup>c</sup>			122	

<sup>a</sup>Refs. 57 and 58. <sup>b</sup>15 °C. <sup>c</sup>Ref. 59 (see text).

methyl sulfoxide and tri-*n*-butyl phosphite of higher purity than before are also reported in Table 2.

The measured wavelength,  $\text{Cu } \lambda_{\text{max}}$ , of the maximum absorption in the visible region of the complex ion  $[\text{Cu}(\text{tmen})(\text{acac})]^+$  in the neat solvents are given later in Table 3. Most values have been given previously in Ref. 37. For comparison Table 3 also includes previously reported values of a number of other basicity scales. The properties of these scales will be discussed below, and their linear or logarithmic correlations with the  $D_s$  scale are given later in Table 4.

## Discussion

*Intermolecular interactions by theoretical methods.* The solvation energy is the change in the standard molar Gibbs energy of transfer of an ion or molecule from the gas phase to a solvent, and corresponds to the energy difference between all the solute-solvent interactions which are created and all the solvent-solvent forces affected by the solvation. The distortion of polyatomic molecules from their free space conformation by the interactions with the solvent molecules can influence the overlap of the molecular orbitals and the amount of charge transfer at the solvation process. The electrostatic interactions are also modified by the surrounding medium as compared to the gas phase, and induced charge separations in molecular systems with anisotropic polarizability will be different in different directions. It is a formidable task to describe the intermolecular potential for polarizable polyatomic acceptors and donors in the liquid state in sufficient detail to allow simulations of the solution properties.<sup>62,63</sup> It seems clear that for some time to come empirical observations must be used to provide chemically useful correlations of solvent effects on solutes, especially for donor-acceptor interactions with a non-negligible charge-transfer contribution. Nevertheless, a deeper understanding, allowing us to make more reliable predictions of the effects, can hardly be obtained until the systems can be modelled theoretically in an adequate way. It is therefore gratifying that significant progress in the detailed theoretical analyses of interaction energies has been made lately, and a brief outline of the principles is given below.

The intermolecular interactions of importance are of electromagnetic origin, and we can conveniently divide the interaction energy for different types of interaction in the following way:<sup>64-66</sup>

$$\Delta E = \Delta E_{\text{ES}} + \Delta E_{\text{EXC}} + \Delta E_{\text{POL}} + \Delta E_{\text{DISP}} + \Delta E_{\text{CT}} + \Delta E_{\text{MIX}}$$

The electrostatic energy term,  $\Delta E_{\text{ES}}$ , represents the energy of all the classical Coulombic interactions from the charge separations within and between the donor D and the acceptor A with undistorted electron distributions. The electrostatic forces between ions, dipoles and multipoles give rise to long-range interactions. For ionic systems this term is the dominating one, but it is also important in systems

containing polar molecules. Charge-dipole interaction energies are generally one order of magnitude greater than interactions between polar molecules without a net charge.<sup>2</sup>

The exchange energy,  $\Delta E_{\text{EXC}}$ , is a short-range repulsive contribution arising due to the Pauli exclusion principle when the electronic shells of the donor and acceptor atoms overlap. This leads to a decrease in the electron charge density in the overlap region, and the incompletely shielded nuclei will then be mutually repelled.<sup>62</sup> The repulsion increases rapidly when the interatomic distance is reduced and is often described with a  $1/r^{12}$  term.

The polarization energy,  $\Delta E_{\text{POL}}$ , is caused by the electric field from the permanent moments, which induces small changes in the electron distribution of a neighbouring molecule. The resulting charge delocalization or mixing of the occupied and virtual orbitals within the molecule can also be related to the static polarizability. The induced energy is always attractive but small, unless one of the interacting species is charged.<sup>67</sup>

The London effect gives rise to an attractive dispersion energy,  $\Delta E_{\text{DISP}}$ , which is present for all types of molecules. It is a result of the correlation between the instantaneous dipole moments associated with the movements of the electrons in a pair of interacting molecules. For non-charged species the dispersion effect is a major contribution to the long-range forces with a distance dependence which is typically proportional to  $1/r^6$ .<sup>62</sup>

In the intermediate region of separation other types of attractive interactions can occur, which are of great importance for chemical systems. The charge-transfer interaction energy,  $\Delta E_{\text{CT}}$ , is the energy of the charge transferred in the related donor-acceptor and hydrogen-bond interactions. The first type of interaction is of major importance when a molecule with low ionization potential interacts with another which has a high electron affinity. This gives rise to a transfer of some charge of an electron pair from the donor to the unoccupied virtual orbitals of the acceptor molecule, often characterized by a new so-called charge-transfer absorption band in the visible wavelength region of the electronic spectrum. For weak donor-acceptor (DA) complexes with a small amount of charge transfer in the ground state, the charge-transfer electronic excitation is therefore accompanied by a transfer of almost a whole electron, giving a charge separation in the excited complex corresponding to a  $\text{D}^+\text{A}^-$  state. For strong donor-acceptor interactions, however, when a covalent bond is formed, the promotion energy becomes larger and the charge-transfer band may then occur in the UV region.<sup>68</sup>

Neutral hydrogen bonds are formed when a hydrogen atom, covalently bonded to an electronegative atom A, forms a bridge to another electronegative atom B. The electrons of B, particularly if B has a lone pair, can then interact strongly with the partially exposed H atom in the polar A-H bond, in which the H atom acts as the acceptor. For such systems the hydrogen-bond energy, which contains an electrostatic and a charge-transfer part, is often

less than for a strong donor–acceptor interaction. The self-association which occurs in most solvents capable of forming strong hydrogen bonds has, however, profound effects on the solubilities of solutes. In amphiprotic liquids such as water, the degree of self-association can be high, and a large number of hydrogen bonds often have to be broken or rearranged to form a cavity for the solute.

The  $\Delta E_{\text{MIX}}$  energy contribution has no descriptive meaning in classical terms and is a result of the inadequacy of the models used to account for the total interactions energy. It represents the coupling between the terms described above and increases as the interaction gets stronger. Schemes for further decoupling of the  $\Delta E_{\text{MIX}}$  term have been proposed.<sup>65,69–71</sup>

A division of the intermolecular interaction energy into a sum of components related to classical models is useful for several reasons. It helps us to understand the strength of the interaction in relation to the properties of the separate molecules. The main energy contributions can be identified for different types of interactions and related to molecular properties such as the dipole and quadrupole moments, and the polarizability. This model-based separation of the energy terms is, however, somewhat interrelated and serves mostly to give a reasonable classical interpretation to quantum-chemical effects.<sup>65,66,71</sup>

Quantum-chemical calculations of varying degrees of approximation have been used for such partitioning of the intermolecular interaction energy,<sup>71</sup> but almost invariably in the gas phase without attempting to account for environmental solvent effects. For weakly interacting molecular systems with a small amount of charge transfer, perturbation methods allow the interaction energy to be evaluated directly as a sum of energy terms for the different types of interactions, including the dispersion energy. However, for stronger interactions higher-order terms have to be included, and strong interactions between polarizable molecules become increasingly difficult to handle with this approach.<sup>67,71</sup> Variational “supermolecule” methods, where the system of interacting species A and B is treated as a unit, are often used in order to obtain the interaction energy as a small difference by subtracting the total energies of the subsystems A and B:  $\Delta E = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$ .

With the use of SCF methods, electron correlation and basis-set superposition errors (BSSE) will be present,<sup>71</sup> which are difficult to distinguish from the physical effects. The size of the systems which presently can be handled with the extreme accuracy required and with sufficiently large basis sets to reduce the BSSE effects is still too small to describe interactions in condensed phases. However, for isolated donor–acceptor complexes with light atoms, interesting attempts have been made to separate the different components of the interaction energy,<sup>66,71</sup> although the results obtained so far serve mainly as a qualitative identification of the main contributions. Moreover, these calculations correspond to gas-phase solvation, and therefore only represent a part of the interactions in solutions.<sup>65</sup>

*From soft to hard basicity scales.* The properties of the acceptor determine the character of the basicity scale. Soft donor scales are typically based on soft and polarizable acceptors. As described by Pearson,<sup>17</sup> the absolute hardness,  $\eta = (I - A)/2$ , defined as one half of the difference between the ionization potential  $I$  and the electron affinity  $A$ , should be small for both the acid and the base in order to maximize the covalent bonding for neutral molecules. Soft–soft interactions give an additional energy gain which is not present for electrostatic interactions and is excluded or averaged out in the fitting process for the hard acceptors generally used for multiparameter scales. Large deviations from these scales therefore often occur for soft–soft interactions. In order to describe effects on soft solutes with increasing softness of the solvent molecules, a scale based on a soft acceptor should be used.

The hard character of many electron-pair donor scales for solvents based on their hydrogen-bond or proton acceptor abilities is consistent with theoretical analyses of the interaction energies in hydrogen-bonded interactions.<sup>65</sup> It is generally found that the repulsive term  $\Delta E_{\text{EXC}}$  is approximately cancelled by the attractive terms  $\Delta E_{\text{POL}} + \Delta E_{\text{CT}}$ . Consequently the total interaction energy  $\Delta E$  becomes similar in value to  $\Delta E_{\text{ES}}$ , the electrostatic energy term,<sup>64–66</sup> and the effects of covalency are suppressed in the hydrogen-bond scales. However, the relative energy contributions change not only for different kinds of hydrogen-bond acceptors or Lewis bases (e.g. O, N or S donors), which sometimes have been described as family-dependent relations connected by covalency parameters,<sup>20,46–48</sup> but also with the type of Lewis acceptor or hydrogen-bond donor used (e.g. O–H, N–H or C–H).<sup>49</sup>

Even though there is no strict borderline, we find it practical for this study to divide the basicity scales into two main groups, based on borderline-to-soft Lewis acceptors in the first and the hard type of hydrogen-bond donors in the second, and to focus the discussion on the first group. The fundamental assumptions and the properties of the  $D_{\text{S}}$  scale, which covers the whole range from borderline to soft donor properties, are discussed below, and this scale is then used as a basis for correlations with other scales in order to find similarities or differences for an assessment of their ranges of application.

*Solvation and bonding of the  $\text{HgX}_2$  molecules as the basis of the  $D_{\text{S}}$  scale.* As late as 1982 evidence was gathered in favour of the view that the  $\text{HgX}_2$  molecules retain their linearity in solution in a review on the Lewis acidity of mercury(II) compounds.<sup>72</sup> This view still seems to persist in a recent <sup>199</sup>Hg NMR study of the interaction of Lewis bases with mercury(II) chloride and acetate.<sup>73</sup> However, it is now well established that with an excess of strong n-donor solvent molecules,  $L$ , pseudotetrahedral solvated molecular complexes  $\text{HgX}_2L_2$  are formed, in solids as well as in solution.<sup>44</sup> The transition from linearity to even less than tetrahedral XHgX angles is accompanied by a correspond-

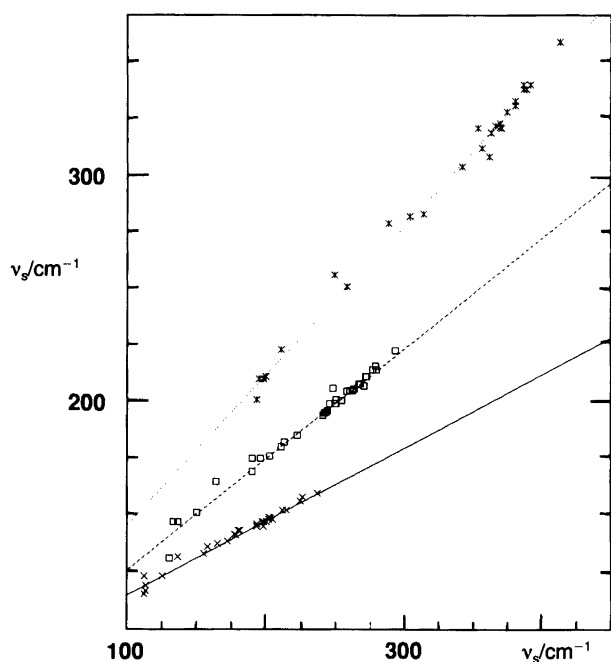


Fig. 1. The symmetric X-Hg-X stretching vibration frequency  $\nu_s$  in  $\text{cm}^{-1}$  (from Raman spectra) plotted against the asymmetric frequency  $\nu_{as}$  (mostly from IR data), for the  $\text{HgX}_2$  complexes in different solvents (the lines are: dotted,  $\text{HgCl}_2$ , dashed,  $\text{HgBr}_2$ , and solid,  $\text{HgI}_2$ ). The values are obtained from Table 1, Ref. 44 and Table 2, this work.

ing increase in the Hg-X distances, which have been determined for some solvents (Table 3 of Ref. 44). The linear correlations found between the frequencies of the symmetric  $\nu_s$  and asymmetric  $\nu_{as}$  stretching vibrations of the  $\text{XHgX}$  entities in solution (Table 4 and Fig. 4), show that the transition is gradual and depends on the strength of the interaction. The difference  $\Delta\nu = \nu_{as} - \nu_s$  for an  $\text{HgX}_2$  molecule is primarily caused by the coupling between  $\nu_s$  and  $\nu_{as}$  modes, which is at its maximum for a linear  $\text{XHgX}$  molecule and ideally should be zero at an angle of  $90^\circ$ .<sup>74</sup> The continuous and gradual transition of a well defined molecular entity led to the idea that some measure of the decrease in the Hg-X bond strength could be used as an indicator of the strength of the interaction with the solvent.<sup>44</sup>

Vibrational spectroscopy is a sensitive and convenient technique, and the similarity of the correlations found for  $\text{HgI}_2$ ,  $\text{HgBr}_2$  and  $\text{HgCl}_2$  (Fig. 1 and Table 4) show that a gradual decrease in the coupling of the stretching vibrations takes place, and is consistent with a continuously decreasing angle X-Hg-X at an increasing interaction strength (Fig. 1 of Ref. 44). The largest response is found for  $\text{HgCl}_2$  although its lower stability and higher tendency of the halide atoms to participate in hydrogen bonding with the solvent led us to use the shift in the  $\nu_s$  symmetric stretching frequency of the  $\text{HgBr}_2$  molecule as a better index. The high degree of linearity in Fig. 1 also shows that the  $\nu_{as}$  frequency would be an even better indicator of the  $D_s$  scale because of its more sensitive solvent response. However,

there are often severe practical difficulties in measuring far-IR spectra in highly absorbing polar solvents,<sup>44</sup> which is the reason why Raman measurements of the  $\nu_s$  frequency of  $\text{HgBr}_2$  was preferred. There is also a closely linear correlation between the  $\nu_s$  values of  $\text{HgBr}_2$  and  $\text{HgI}_2$  (Fig. 2 and Table 4), and when practical problems arise,  $\text{HgI}_2$  can often be used as an alternative probe. The average factor between  $\Delta\nu = \nu_{\text{gas}} - \nu_{\text{solvent}}$  values for  $\text{HgBr}_2$  and  $\text{HgI}_2$  is 1.935.

The solvent effect on the  $\text{HgX}_2$  molecules ( $X = \text{I}, \text{Br}$  or  $\text{Cl}$ ) as measured by  $^{199}\text{Hg}$  NMR in 14 solvents<sup>75</sup> is plotted against the  $D_s$  values in Fig. 3. The chemical shift is found to increase with increasing donor strength, and it also increases from  $\text{HgI}_2$  to  $\text{HgBr}_2$  and  $\text{HgCl}_2$ , corresponding to a deshielding of the mercury nucleus. These trends can be approximately related to changes in the paramagnetic shielding term if the diamagnetic term is neglected:<sup>76</sup>

$$\sigma_p = -(\mu_0 e^2 \hbar^2 / 6\pi m^2 \Delta U) \langle 1/r^3 \rangle_p P_u$$

$\Delta U$  is the average excitation energy,  $\langle 1/r^3 \rangle_p$  the average inverse cube distance of the valence  $p$  electron from the nucleus (proportional to the field gradient), and  $P_u$  represents the  $p$ -electron population.<sup>76</sup> The gradually reduced shielding (increase in chemical shift, Fig. 3) found at increasing donor strength of the solvent molecules  $L$  in  $\text{HgX}_2L_2$  complexes for the same  $X$ , has been connected to an expected increase in  $P_u$  at a coordination change.<sup>77</sup> For linearly bonded mercury the maximum value of  $P_u$  is 1, which can reach  $3/2$  for four-coordination.<sup>75</sup> However, when the ligand  $X$  in the  $\text{HgX}_2L_2$  complexes is changed from  $\text{Cl}$  to  $\text{Br}$  and  $\text{I}$  with the same  $L$ , the coordination strength of the halide atoms increases and the charge on the mercury atom is reduced in the same order,<sup>77</sup> and consequently an increase in  $P_u$  and a decreasing shielding would be expected. Instead a large increase in the shielding is observed (Fig. 3). This apparent contradiction is probably coupled to changes in the other variable terms,  $\Delta U$  and

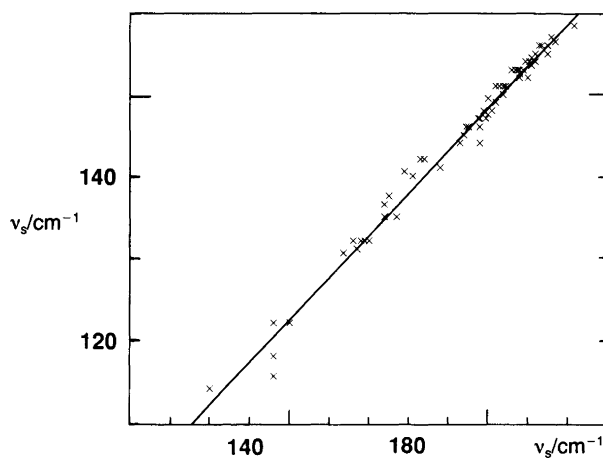


Fig. 2. The symmetric stretching frequencies  $\nu_s$  of  $\text{HgI}_2$  versus  $\nu_s$  of  $\text{HgBr}_2$  (Raman data, Table 1, Ref. 44, and Table 2, this work) in a number of solvents. The slope of the correlation is 1.935.



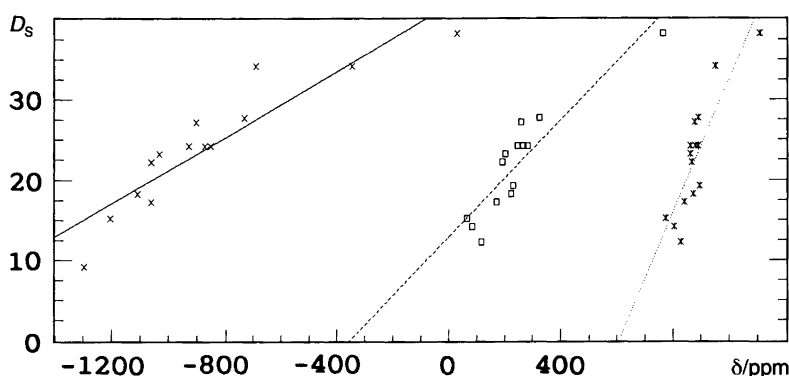


Fig. 3. Relationship between the  $D_s$  parameter for different solvents (numbering as in Table 3) and the NMR chemical shifts  $\delta(^{199}\text{Hg})$  in ppm of the  $\text{HgX}_2$  (solid line,  $\text{HgI}_2$ , dashed line,  $\text{HgBr}_2$ , and dotted line,  $\text{HgCl}_2$ ) complexes in solution.<sup>76</sup>

$\langle 1/r^3 \rangle$ , in the expression for  $\sigma_p$  above. Because of the smaller size of the halide ligand a larger contraction of the p orbitals occurs for Cl than for Br and I, and therefore the field gradient and the  $\langle 1/r^3 \rangle$  term will be reduced in the order  $\text{Cl} > \text{Br} > \text{I}$ , as also have been found in theoretical calculations for the isoelectronic  $\text{AuX}_2^-$  complexes.<sup>77</sup> The contraction effect also implies that the  $\text{HgCl}_2$  molecule would be the least susceptible to deformation at the solvation, which seems consistent with the greater slope for the  $\text{HgCl}_2$  line in Fig. 2, and with the angle-dependent correlations in Ref. 44.

Smaller but significant contributions of similar type as from the p-orbitals would also be expected from the  $d_{z^2}$  electron field gradients.<sup>76</sup> They are, however, almost constant for the linear  $\text{CuX}_2^-$  and  $\text{AuX}_2^-$  complexes,<sup>77</sup> and will probably not be of importance for the trends discussed here.<sup>76</sup> Even though the relations are rather complex, the gradual change in coordination discussed above in a  $\text{HgX}_2L_2$  complex upon increasing donor strength of the solvent  $L$ , would be consistent with the trends found in the  $^{199}\text{Hg}$  chemical shifts.

The  $\text{Hg}^{2+}$  ion is a soft acceptor in itself, but the softness of the mercury atom is substantially enhanced in the  $\text{HgBr}_2$  molecule because of the partial neutralization of its cationic charge by the soft bromide ligands.<sup>13,17</sup> Several estimates, which vary considerably, of the residual charge on the Hg atom have been given (Table 25, Ref. 77). Another recent value from a theoretical calculation is +0.78 in a linear  $\text{HgCl}_2$  molecule.<sup>78</sup>

For the  $d^{10}$  ion  $\text{Hg}^{2+}$  two different bonding schemes have been proposed to explain its preference to form two strong linear bonds in the  $\text{HgX}_2$  molecules.<sup>77</sup> The low  $d^{10} \rightarrow d^9s$  promotion energy led Orgel to suggest a  $d_{z^2} - s$  mixing, which would reduce electron charge in the  $z$ -direction and favour two strong bonds.<sup>79</sup> A bonding scheme with localized mercury  $sp$  hybrid orbitals is also possible, and this description is consistent with the low vibration bond-bond interaction constants in the  $\text{HgX}_2$  species.<sup>77</sup> A recent theoretical calculation on the  $\text{HgCl}_2$  molecule shows the bonding to be mainly of  $s-p$  character, although with a non-negligible  $d$ -contribution.<sup>78</sup>

In aqueous solution hexacoordinated  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$  complexes are formed with an anomalously large spread in the

mean  $\text{Hg}-\text{O}$  distance.<sup>80</sup> Theoretical SCF calculations have been performed on an isolated complex ion  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ , but do not show any energy minima corresponding to a static distortion reducing the highest possible symmetry  $T_h$  to  $D_{2h}$ .<sup>81</sup> However, a weakened ground state was found, consistent with a weak second-order (or pseudo-) Jahn-Teller effect.<sup>82</sup>

The main part of the bonding energy in the  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$  complex is of electrostatic character, and even though the effective charge on the Hg atom in an  $\text{HgX}_2$  molecule is reduced, it is not obvious why the  $\text{HgX}_2$  molecule only accepts two n-donor ligands  $L$  to form pseudo-tetrahedral  $\text{HgX}_2L_2$  complexes in a solution with a large excess of donor molecules  $L$ , instead of forming pseudo-octahedral species. A possible reason could be the following: on the coordination of a soft neutral n-donor ligand to an  $\text{HgX}_2$  molecule, a net charge-transfer takes place to the mercury atom and further reduces its positive charge. The charge delocalisation reduces the  $I - A$  difference and increases the softness.<sup>17</sup> This would lead to a decrease in the energy difference between the valence  $s$ - and  $p$ -orbitals and promote the participation of all  $p$ -orbitals in the bonds ( $sp^3$  hybridization) and thus the addition of another n-donor solvent molecule. This could explain why three-coordination does not seem to occur in an excess of uncharged n-donor ligands. Moreover, most light n-donor atoms lack  $d$ -orbital  $\pi$ -acceptor abilities and cannot provide the additional  $\pi$  back-bonding stabilization, which is usual in octahedral symmetries.<sup>83</sup> The reduced charge on the mercury atom in the solvated  $\text{HgX}_2$  complexes would then be insufficient to support six-coordination as in  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$ . The well-defined  $\text{HgBr}_2L_2$  complexes formed in solution and the gradual weakening of the  $\text{Hg}-\text{Br}$  bond strength as measured by vibrational spectroscopy when the n-donor interaction increases, seem to be the main reasons for the wide range and good sensitivity obtained for soft donor solvents with this acceptor.

A major factor for the additional stabilization of a soft-soft interaction is often  $\pi$  back-bonding with participation of the valence  $d$ -orbitals on the metal atom.<sup>14-16</sup> However, for metal ions such as  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  with a filled  $d^{10}$  outer shell,  $\pi$ -bonding can only be expected to be of importance if the ligands have empty  $d$ - or  $p$ -orbitals of suitable sym-

entry and energy to receive the d-electrons.<sup>83</sup> If the donor atom also has filled d- or p-orbitals a repulsion between the occupied  $\pi$ -orbitals on the donor and acceptor will occur instead, although this effect can be reduced for polarizable atoms by a mixing of the filled d or p with empty p or d orbitals, respectively, on the same atom.<sup>16,17</sup>

*New solvents to the  $D_s$  scale.* In this work some common solvents have been added to the  $D_s$  scale<sup>44</sup> (Table 2). Re-measurements of dimethyl sulfoxide, tri-n-butyl phosphite and tri-n-butyl phosphine are also reported. The number of alcohols has been extended, and for the short-chain primary alcohols up to 1-butanol and 2-propanol there is as expected hardly any difference in the  $\nu_s$  frequency. However, for 1-octanol and 2-methyl-2-propanol slight deviations are found indicating a weaker solvation, probably due to the steric effect of the bulky alkyl chains.

Only a few significantly deviating points occur in  $D_s$  values derived from  $\text{HgCl}_2$  and  $\text{HgI}_2$ , e.g. for  $\text{HgCl}_2$  in water, which probably is an effect of hydrogen-bond interactions with the chloride atoms. However, the  $\nu_s$  value of the dimethyl ethyl phosphine complex of  $\text{HgBr}_2$  measured in  $\text{CDCl}_3$  solution (Table 1, Ref. 44) seem to be anomalously low, and a corrected  $D_s$  value  $\approx 86$ , based on the  $\text{HgI}_2$  value, is given in Table 3.

*Donor properties of alkylamines.* The  $D_s$  value for ammonia is based on a Raman study of  $\text{HgI}_2$  in liquid ammonia at ambient temperature under pressure.<sup>59</sup> A strong polarized band was found at  $122\text{ cm}^{-1}$  and assigned to the  $\text{Hg-I}$  stretch in a  $(\text{NH}_3)_3\text{HgI}^+$  species, but for the following reasons an assignment to  $\nu_s(\text{HgI}_2)$  seems more likely. The frequency is lower and the intensity is stronger than expected from a comparison with  $\text{HgI}^+$  species in other solvents.<sup>77,84</sup> The polarization ratio of  $\approx 0.1$  is similar to the value normally obtained for a bent  $\text{HgI}_2$  species, and the non-observed  $\nu_{as}$  frequency, which will become Raman active, will be hidden by the overlapping  $\nu_s$  band (cf. Table 1, Ref. 44).

An interesting comparison is provided by the solvent series ammonia, ethylamine, diethylamine and triethylamine, with the use of  $\text{HgI}_2$  as acceptor. The symmetric stretching  $\nu_s$  frequency of  $\text{HgI}_2$  was found to increase with the wavenumbers 122, 131, 146.5 and  $148\text{ cm}^{-1}$ , respectively (Table 2), reflecting a reduction of the coordinating ability of the nitrogen atom at increasing alkyl substitution. A decrease in the  $^{199}\text{Hg}$  NMR chemical shifts  $\Delta\delta$  is also found for mercury(II) chloride and acetate in dimethyl sulfoxide solutions with excess of amine,<sup>73</sup> for  $\text{HgCl}_2$  and butylamine ( $\Delta\delta = 492\text{ ppm}$ ), diethylamine (363) and triethylamine (282).<sup>73</sup> In agreement with Peringer's  $^{199}\text{Hg}$  NMR measurements, cf. Fig. 3 and the discussion above, these results are also consistent with a decreasing Lewis base strength at increasing alkylation of the amines.

Interestingly, the reverse basicity order is found in the gas phase.<sup>85</sup> Steric hindrance to solvation has been suggested as an explanation,<sup>73,86</sup> but no significant differences

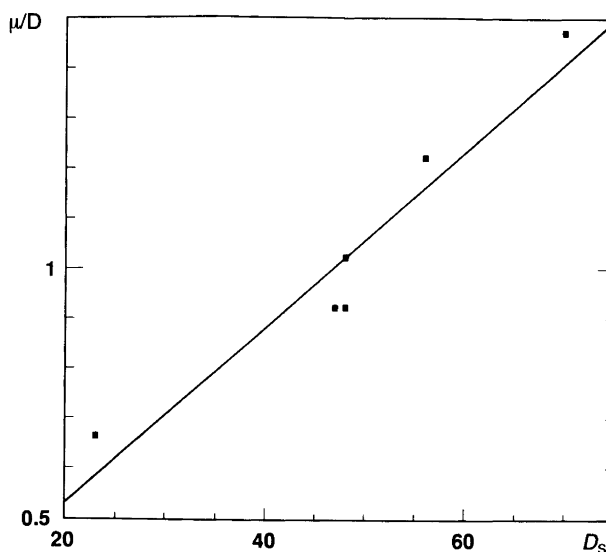


Fig. 4. Gas-phase dipole moments  $\mu$  (in D)<sup>85</sup> of the alkylamines versus  $D_s$ . The values are: triethylamine (0.66, 23), di-n-butylamine (0.92, 47), diethylamine (0.92, 48), piperidine (1.02, 48), ethylamine (1.22, 56) and ammonia (1.47, 70).

are found in the  $D_s$  values in comparisons between piperidine and diethylamine or di-n-butylamine (Table 3).

A remarkably good correlation is obtained in a plot of the  $D_s$  values against the gas-phase dipole moments of the alkylamines (Fig. 4 and Table 4). However, the  $D_s$  value of triethylamine seems to be slightly lower than expected from the trend of the other amines. For this bulky ligand steric effects may contribute to the weak coordination, although the value does not deviate as much as in several of the other scales (Table 3). The total dipole moment is a complex quantity, with contributions from the equilibrium charge distribution of the bond moments and of the polarization of the nitrogen sp-orbitals, bonding and non-bonding.<sup>86</sup> Upon complex formation with an acceptor atom, equilibrium geometry, intramolecular bond strength and polarization effects may change, and the overall molecular moment is therefore in general not a good indicator of the coordination properties.<sup>44</sup> In the alkylamines, however, there is a limited charge migration from nitrogen (at least when  $\text{BF}_3$  is used as the acceptor),<sup>87</sup> and the electrostatic energy term is then expected to be dominant in the donor-acceptor complexes. The basicities of the amine molecules in solution will be enhanced because of the polarization by the hydrogen bonds formed to other amine molecules in the bulk, in the same way as for water.<sup>68</sup> This effect, which would increase with the number of hydrogen bonds formed, is consistent with the decrease in coordinating ability upon increasing alkylation (Fig. 4). The discrepancy between the relative proton affinities in the gas phase,<sup>85</sup> and the Lewis basicity in solution of the alkylamines, again emphasizes the importance of "solvent effects" in chemical reactions, and the differences between basicities of Lewis bases in the neat associated solvents and in dilute solutions. It is also of interest to note that an alkylation of  $\text{H}_2\text{S}$  and

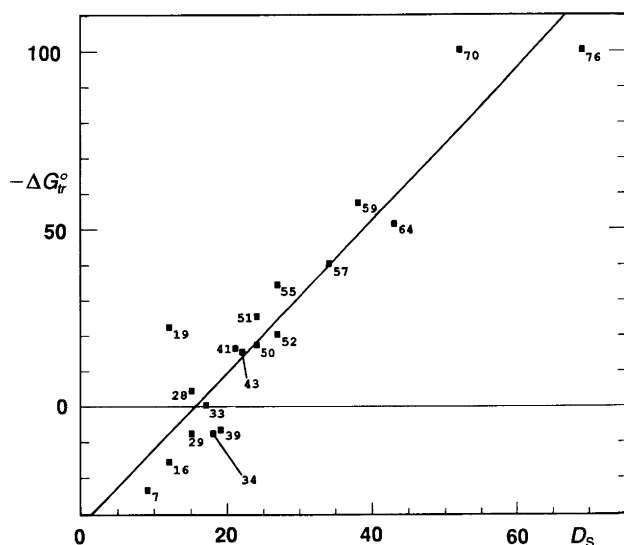


Fig. 5. Gibbs energies of transfer,  $\Delta G_{tr}^0(\text{aq} \rightarrow \text{solvent})$ , of the silver(I) ion in the TATB assumption (values from Table 1, Ref. 40) plotted against corresponding  $D_s$  parameters for 20 solvents with numbers as in Table 3.

$\text{PH}_3$  increases both the gas-phase dipole moment and the coordinating ability, contrary to the effect on  $\text{NH}_3$ .<sup>44,55,86</sup>

*Comparisons with other soft basicity scales.* It seems probable that the softness of the silver(I) ion and of mercury(II) in  $\text{HgBr}_2$  and  $\text{HgI}_2$  is due mainly to polarization of the occupied metal d-orbitals. This would mean that the softness effects measured with these acceptors and soft n-donors, to a large extent would correspond to charge transfer and polarization interaction energies. The  $\pi$  back-bonding from the metal, which would be of a more specific nature for each probe, is not expected to give any major contributions, at least not for light donor atoms with poor  $\pi$ -acceptor ability. The similarity of their bonding properties are consistent with the good correlation found in a plot of Gibbs energy of transfer,  $\Delta G_{tr}^0(\text{aq} \rightarrow \text{solvent})$ ,<sup>40</sup> for the soft  $\text{Ag}^+$  ion against the  $D_s$  values for 20 solvents with large variations in their solvation abilities (Fig. 5 and Table 4).

For hard donors the electrostatic part of the interactions is important in the  $D_s$  scale. This is shown by the limited correlations for mostly oxygen and nitrogen electron-pair donors with the fairly hard or borderline  $D_N$  and  $\Delta H_{\text{BF}_3}^0$  scales (Figs. 6e and 6f), and with the hydrogen-bond basicity scales in Fig. 7.

The  $D_s$  scale is reported to give good linear correlations with Gibbs energies of transfer for a number of solvents with e.g. the  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions as acceptors,<sup>39</sup> and also for  $\text{Ag}^+$ ,  $\text{Tl}^+$ <sup>41</sup> and  $\text{Hg}^{2+}$ .<sup>40</sup> For the moderately hard or borderline acceptors  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , soft sulfur donor solvents were found to deviate considerably, but not for the soft  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  ions.<sup>40,41</sup> This shows that the  $D_s$  scale is able to give a fair account also for the soft-soft interactions for which hard and borderline acceptors deviate.

What is the reason why so different solvent basicity scales still have so many features in common? A thermodynamic model analysis based on integral equations shows that the main contributions to the solvation energy are the exothermic solute-solvent interaction energy, the endothermic solvent-solvent reorganization (cavity) term, and an opposing entropy term.<sup>88</sup> It was shown that in a system dominated by electrostatics a simple relation is obtained between the free energy of solvation and the average solute-solvent energy. Even though the cavity energy would be different in different solvents,<sup>89</sup> the residual term in  $\Delta G_{tr}^0$  would be counteracted by the opposing entropy difference. This would then be consistent with the often good correlations found between enthalpy-based basicity scales without pronounced cavity effects (e.g.  $D_N$  and  $\Delta H_{\text{BF}_3}^0$ ) or solvent indices related to free energies for which the cavity and entropy terms cancel, and the solvatochromic scales discussed below. This is also supported by the fairly good correlation found in the recent comparison by Abraham *et al.*<sup>23</sup> of the hydrogen-bond basicity of non-self-associated solvent molecules in bulk or in a diluting tetrachloromethane medium. Solvents with strong self-association do, however, deviate as expected.

The Gibbs energy of transfer of a single ion from one solvent to another can alternatively be viewed as a composite of electrostatic, general non-electrostatic and specific chemical contributions.<sup>2</sup> However, the solvation of small cations is strongly coupled to the absolute electronegativity  $\chi^\circ$  of the Lewis acid and base, and the difference ( $\chi_A - \chi_B$ ) determines the direction of the net electron transfer.<sup>16</sup> For hard Lewis acids like  $\text{Na}^+$ , it is safe to assume that  $\sigma$ -bonding<sup>16</sup> will occur in the form of electrostatic bonding (mainly ion-dipole). For soft cations such as  $\text{Ag}^+$ , polarization and  $\pi$ -bonding effects (see above) can stabilize the bonding with soft bases. These effects have been utilized in the two recent attempts discussed below, which aim to characterize empirically the property "softness of solvents".

The linearities of the correlations found between a few borderline cations and the softness parameter  $SP$  scale,<sup>41</sup> should reflect a charge-transfer effect at the solvation of these ions, similar in type although smaller than that for  $\text{Ag}^+$ . From the slope of these lines one might conclude that those effects would be largest for the softer  $\text{Cu}^+$  and  $\text{Tl}^+$  ions, but less pronounced for the somewhat harder  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions. It is not surprising, however, that the reported correlation<sup>41</sup> of the  $SP$  parameter with  $\Delta G_{tr}^0$  values is equally as good as that with redox potentials (approximated with half-wave potentials  $E_{1/2}$ ), because the  $\Delta G_{tr}^0$  values were derived directly from the measured  $E_{1/2}$  values.<sup>40</sup>

The  $SP$  scale is one of many examples where the effects of different solvents on a particular acceptor ( $\text{Ag}^+$ ) have been used to construct a single parameter scale, in this case restricted to a small group of selected solvents and with a reference state chosen on entirely empirical grounds. There seems to be little reason to limit the number of soft solvents only to those which deviate anomalously for  $\text{Ag}^+$  in com-



Table 3. (contd)

No.	Solvent	$D_s$	$SP$	$B_{\text{soft}}$	$\mu$	$\Delta\nu_{\text{PHOH}}$	$D_N$	$-\Delta H_{\text{BF}_3}^{\circ}$	$\text{Cu } \lambda_{\text{max}}$	$CP$	$-\Delta\delta$	$\beta$	$\beta_{\text{gen}}^{\text{a}}$	$\beta_{\text{spec}}^{\text{b}}$	$\beta_2^{\text{H}}$	$\log K_{\beta}$
62	2,2'-Thiodiethanol	39	66													
63	Di-n-butyl sulfide	41				252			NS		0.43			0.31	0.29	
64	Tetrahydrothiophene, THT	43	73		0.80				606 <sup>c</sup>		0.59			0.25	0.26	
65	Tetrahydrosephenophene	45														
66	Cyclohexylisocyanide	45							NS							
67	Di-n-butylamine	47				691			NS		1.56	0.70				
68	Diethylamine, Et <sub>2</sub> NH	48				637	50									
69	Piperidine, C <sub>5</sub> H <sub>10</sub> NH	48		91		706	40									
70	<i>N,N</i> -Dimethylthioformamide	52	107		1.35											
71	Hexamethylthiophosphoric triamide	53	89		0.67											
72	1-Hexylamine	54														
73	1-Methyl-2-thiopyrrolidinone	56	115		1.35											
74	Tri-n-butyl phosphite	56							NS		0.74					
75	Ethylamine, EtNH <sub>2</sub>	56				667	40									
76	Ammonia, NH <sub>3</sub>	69			0.86	473	59									
77	Triethyl arsine, Et <sub>3</sub> As	72														
78	Tri-n-butyl phosphine	76										1.39				
79	Triethyl phosphine, Et <sub>3</sub> P	76														
80	Dimethyl ethyl phosphine	~86														

NS: The [Cu(tmen)(acac)]ClO<sub>4</sub> or [Cu(tmen)(acac)]BPh<sub>4</sub> compounds are not soluble.

<sup>a</sup>Ref. 44. <sup>b</sup>Refs. 40 and 41. <sup>c</sup>From Ref. 43 with additional values from Refs. 52 and 61. <sup>d</sup>Ref. 42. <sup>e</sup>From the compilation in Ref. 60 (values in parentheses are for neat solvents). <sup>f</sup>Ref. 26. <sup>g</sup>Refs. 35–37. <sup>h</sup>Ref. 38. <sup>i</sup>Ref. 53. <sup>j</sup>Ref. 48. <sup>k</sup>Ref. 23. <sup>l</sup>Ref. 49. <sup>m</sup>Calorimetrically determined. <sup>n</sup>Reference values. <sup>o</sup>Values probably affected by decomposition or reduction reactions of the acceptor complex (Ref. 36). <sup>p</sup>Uncertain values solvent proton shift in the same range as the CHCl<sub>3</sub> shift.

comparisons with some borderline ions, e.g. Zn<sup>2+</sup>, Cd<sup>2+</sup> and Tl<sup>+</sup>.<sup>39,41</sup> The “softness” measured by the  $SP$  parameters will then include the special features of the Ag<sup>+</sup> solvation. Thermodynamic measurements of the transfer energies from water to acetonitrile for the Cu<sup>+</sup> and Ag<sup>+</sup> ions show anomalously low values of  $\Delta H_{\text{tr}}^{\circ}$ , indicating much stronger bonding in acetonitrile,<sup>90</sup> while for Zn<sup>2+</sup>, Cd<sup>2+</sup> and the soft Hg<sup>2+</sup> ion much more positive  $\Delta H_{\text{tr}}^{\circ}$  values are found.<sup>91</sup> However, in acetonitrile the entropy terms are rather similar for these ions,<sup>90,91</sup> probably because of a rather strong self-association of the solvent. Consequently, large differences occur in the corresponding  $\Delta G_{\text{tr}}^{\circ}$  values as a result of the special affinity of Cu<sup>+</sup> and Ag<sup>+</sup> for acetonitrile and very likely also for other nitriles. If this “softness” measured by differences in the  $\Delta G_{\text{tr}}^{\circ}$  values is a property connected to the solvent only, then the soft Hg<sup>2+</sup> ion should have been more strongly solvated in acetonitrile than e.g. Cu<sup>+</sup>. This is the case in pyridine, which is a softer solvent than the nitriles, and it is curious that pyridine is not considered in the  $SP$  scale. With available data for  $\Delta G_{\text{tr}}^{\circ}$  from acetonitrile to pyridine for Ag<sup>+</sup> (−35 kJ mol<sup>−1</sup>),<sup>40</sup> Tl<sup>+</sup> (−11)<sup>40</sup> and Cd<sup>2+</sup> (−63),<sup>91</sup> recalculated to benzonitrile and plotted in Fig. 1 of Ref. 41 and Fig. 1 of Ref. 39, respectively, pyridine would belong to the “soft” group for Tl<sup>+</sup>, but to the “hard” for Cd<sup>2+</sup>.

Despite the special features of the nitriles a fairly high linear correlation,  $r = 0.975$ , is found between the  $SP$  values and the  $D_s$  scale (Fig. 6a). However, this is an ill-conditioned case with only nine values forming two clusters of points,<sup>92</sup> and a linear correlation would for the sulfur

donor solvents be a consequence of the more general correlation found between the  $D_s$  scale and the  $\Delta G_{\text{tr}}^{\circ}$  values for Ag<sup>+</sup> (Fig. 5). Note, however, that acetonitrile (No. 19) deviates in this correlation, which is to be expected from the arguments above.

To conclude, in the  $SP$  scale a few sulfur donor solvents have rightly been identified as soft, but the nitriles have been included in this “soft” group because of their special affinity for the Ag<sup>+</sup> ion, which hardly can be considered as a general indicator of softness.

The  $B_{\text{soft}}$  scale is another “soft” scale derived from the shift  $\Delta\nu_{\text{Cl}}$ , in the asymmetric stretching C–I vibration frequency in a D···ICN donor–acceptor interaction in CCl<sub>4</sub> solution.<sup>43</sup> The iodine atom is capable of  $\pi$  back-bonding, and the shift  $\Delta\nu_{\text{Cl}}$  was found to correlate with the enthalpy of the complex formation with I<sub>2</sub> in the same solvents.<sup>43</sup> The linearity between the  $B_{\text{soft}}$  and  $D_s$  scales is satisfactory, especially if the outlying value for triethylamine is excluded (Fig. 6b and Table 4).

The related  $\mu$  scale of solvent softness,<sup>42</sup> is instead based on the difference in the effects of a particular solvent on acceptors with very different properties (Ag<sup>+</sup> versus Na<sup>+</sup> and K<sup>+</sup>).

The principal uncertainties in this empirical attempt to enhance the covalent part of the solute–solvent interaction, seem to be the following: (i) For polar solvents interacting with a charged species, the dominant energy contributions are electrostatic, the ion–dipole and ion–quadrupole terms. They depend non-linearly on the distance especially at short range (Fig. 3.10, Ref. 65), and a mean value will not

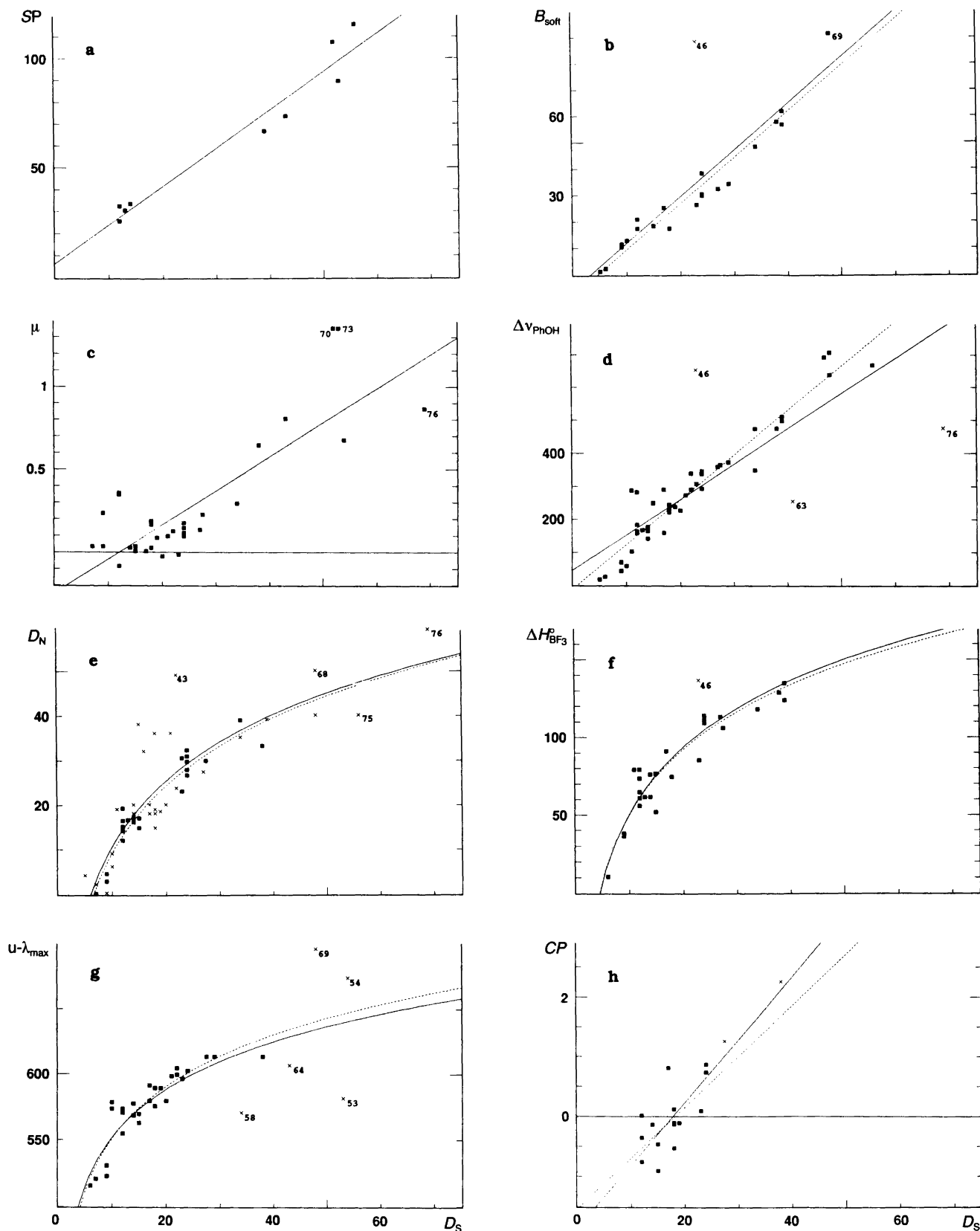


Fig. 6. Scatter plots of the corresponding parameter values for soft and borderline basicity scales (= y) versus  $D_S$  (= x) with data from Table 3. The curves are the linear regression lines of y on x, or logarithmic curves  $y = a + b \ln x$ , solid lines for all data points, dotted for the reduced (crosses excluded) data sets in Table 4. The numbers in the figures refer to the solvents in Table 3: (a) SP, (b)  $B_{\text{soft}}$ , (c)  $\mu$ , (d)  $\Delta v_{\text{PhOH}}$ , (e)  $D_N$ , (f)  $\Delta H_{\text{BF}_3}^B$ , (g)  $u-\lambda_{\text{max}}$ , (h) CP.

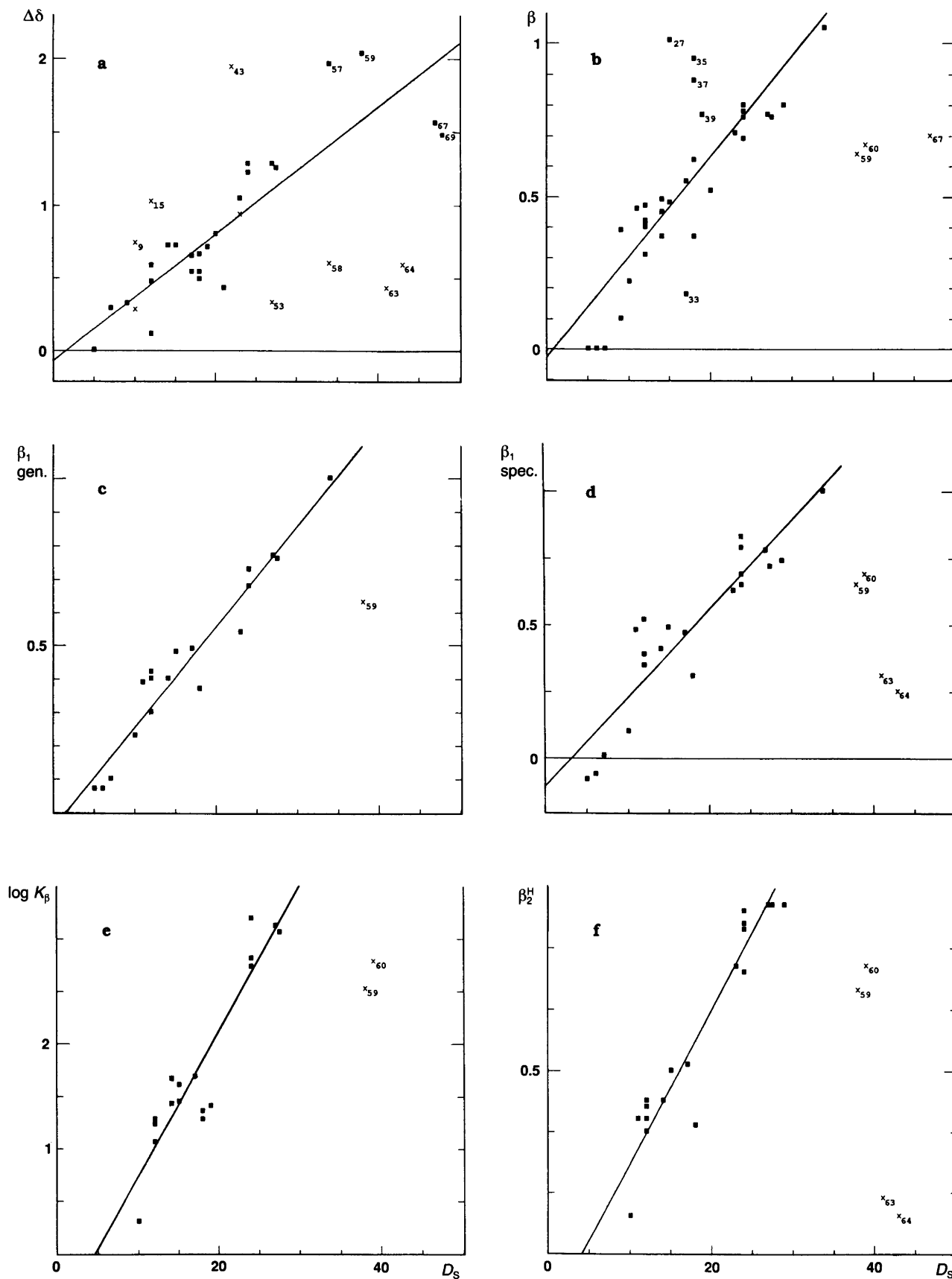


Fig. 7. Scatter plots of some hydrogen-bond basicity scales as in Fig. 6 with data from Table 3. The regression lines are drawn with some poor hydrogen-bonding solvents excluded (crosses, Table 4), (a)  $\Delta\delta$ , (b)  $\beta$ , (c)  $\beta_1$ (general), (d)  $\beta_1$ (special), (e)  $\log K_\beta$ , (f)  $\beta_2^H$ .

in principle account for all of the difference between ions of different sizes. (ii) Another, probably more important factor, is the different dispersion energies, with the largest values expected for the polarizable  $\text{Ag}^+$  ion. (iii) Also, even for the hard donor  $\text{OH}_2$  in water, which is used as the reference state, the bonding differences between  $\text{Ag}^+$  and the hard alkali metal ions  $\text{Na}^+$  and  $\text{K}^+$  are evident. For  $\text{Ag}^+$  neutron diffraction studies on aqueous  $\text{AgClO}_4$  solutions show four loosely coordinated water molecules with a mean  $\text{Ag}-\text{O}$  distance of 2.41 Å,<sup>93</sup> in agreement with X-ray scattering results.<sup>94</sup> For  $\text{Na}^+$  a coordination of about six water molecules at a  $\text{Na}-\text{O}$  distance of about 2.3 Å has been obtained from molecular simulations.<sup>67,95-98</sup> Experimental X-ray data give slightly longer distances close to 2.4 Å, but uncertain coordination numbers between 4 and 6.<sup>99-102</sup> The first hydration sphere around the  $\text{K}^+$  ion is even less well-defined. The simulations gave between 5 and 8 water molecules at 2.7 to 2.9 Å,<sup>95-97</sup> consistent with approximate X-ray diffraction results.<sup>102</sup> The first attempt at a neutron study was reported to give  $\approx 4.2$  water molecules at  $2.6 \pm 0.1$  Å.<sup>100</sup> A discussion on the differences in  $\text{Na}^+$  and  $\text{K}^+$  hydration is given in Ref. 103.

When the  $\Delta G_{\text{tr}}^\circ$  energies of these ions are compared, a change in the coordination number would mean a different cavity energy contribution in a self-associated solvent.<sup>104</sup> The variations in the coordination numbers, structures and distances thus make the basis of the  $\mu$  scale concept uncertain even for the reference state. Changes in the relative coordination numbers may occur in solvents of different donor strength, giving rise to deviations from the general trend. The scatter between the 32 values in common for the  $\mu$  and  $D_s$  scales is considerable (Fig. 6c and Table 4). Nevertheless, in Ref. 42 the  $D_s$  values have been used in an attempt to extend the  $\mu$  scale.

For another extension of the  $\mu$  scale Marcus attempted to eliminate the "basicity" component of the  $B_{\text{soft}}$  scale, and subtracted a weighted frequency shift of phenol  $\Delta v_{\text{PhOH}}$ , from the  $\Delta v_{\text{Cl}}$  values in Ref. 43. A straight line was then drawn through the resulting  $\Delta \Delta v$  and  $\mu$  values for ten solvents in common.<sup>42</sup> Even though this linear correlation relies heavily on one outlying estimated  $\mu$  value and thus is ill-conditioned,<sup>92</sup> the line was used to add further values to the  $\mu$  scale. Moreover, the  $\Delta v_{\text{PhOH}}$  values are based on the hydrogen-bond donor properties of phenol, which is found for N-donor solvents to be of similar type as the enthalpy values for  $\text{I}_2$  complexes of the same donors in  $\text{CCl}_4$ .<sup>105</sup> A linear enthalpy-wavenumber relationship for phenol adducts with a wide range of n-donors has also been reported and justified by theoretical comparisons.<sup>106</sup> That these correlations are of similar type is also consistent with the high degree of linearity found between the  $B_{\text{soft}}$  and  $\Delta v_{\text{PhOH}}$  scales versus  $D_s$  (Figs. 6b and 6d), both with  $r = 0.96$  for the 21 solvents (triethylamine excluded) in common in Table 3. For these mostly weakly coordinating solvents both the  $B_{\text{soft}}$  ( $= \Delta v_{\text{Cl}}$ ) and  $\Delta v_{\text{PhOH}}$  (surprisingly also called  $B_{\text{hard}}$ )<sup>43</sup> basicity indexes thus show similar character as those found for the soft  $\text{I}_2$  and  $\text{HgBr}_2$  acceptors. In a more exten-

sive comparison of 68 solvents between the  $B_{\text{soft}}$  and  $\Delta v_{\text{PhOH}}$  scales, a "family" dependence was reported,<sup>43</sup> although it seems to be mainly a group of eight sulfur donor solvents which shows a significant deviation.

To conclude, the  $\Delta v_{\text{PhOH}}$  scale is something of a paradox, a "soft" hydrogen-bond basicity scale. This classification is

**Table 4.** Correlations between solvent scales and some other solvation indexes. The correlation coefficients  $r_{\text{lin}}$  and  $r_{\text{log}}$  are obtained as described in Ref. 92. The equation for the logarithmic curves is:  $y = a + b \ln x$ .

Scales		Fig. No.	No. of data	$r_{\text{lin}}$	$r_{\text{log}}$
<i>x</i>	<i>y</i>				
$v_s(\text{HgI}_2)$	$v_{\text{as}}(\text{HgI}_2)$	1	29 <sup>a</sup>	0.990	0.988
$v_s(\text{HgBr}_2)$	$v_{\text{as}}(\text{HgBr}_2)$	1	36 <sup>a</sup>	0.992	0.988
		1	21 <sup>b</sup>	0.993	0.982
$v_s(\text{HgCl}_2)$	$v_{\text{as}}(\text{HgCl}_2)$	1	31 <sup>a</sup>	0.996	0.993
$v_s(\text{HgI}_2)$	$v_s(\text{HgBr}_2)$	2	60	0.993	0.991
$D_s$	$\delta(^{119}\text{HgI}_2)$	3	14	0.91	0.97
$D_s$	$\delta(^{119}\text{HgBr}_2)$	3	14	0.91	0.90
$D_s$	$\delta(^{119}\text{HgCl}_2)$	3	15	0.86	0.87
$\mu(\text{amines})$	$D_s$	4	6	0.96	0.98 <sup>c</sup>
$\Delta G_{\text{tr}}^\circ(\text{Ag}^+)$	$D_s$	5	20	0.95	0.92
<i>SP</i>	$D_s$	6a	9	0.975	0.95
$B_{\text{soft}}$	$D_s$	6b	22 <sup>a</sup>	0.85	0.81
		6b	21 <sup>d</sup>	0.97	0.90
$\mu$	$D_s$	6c	32 <sup>a</sup>	0.83	0.72
$\Delta v_{\text{PhOH}}$	$B_{\text{soft}}$	—	22	0.95	0.87
$\Delta v_{\text{PhOH}}$	$D_s$	6d	50 <sup>a</sup>	0.84	0.87
		6d	47 <sup>e</sup>	0.96	0.93
$D_N$	$D_s$	6e	53 <sup>a</sup>	0.83	0.88
		6e	25 <sup>f</sup>	0.91	0.96
$\Delta H_{\text{BF}_3}^g$	$D_N$	—	27 <sup>a</sup>	0.95	0.94
		—	22 <sup>g</sup>	0.95	0.96
$\Delta H_{\text{BF}_3}^g$	$D_s$	6f	29 <sup>a</sup>	0.88	0.93
		6f	28 <sup>d</sup>	0.90	0.94
$\text{Cu } \lambda_{\text{max}}$	$D_s$	6g	33 <sup>a</sup>	0.76	0.82
		6g	28 <sup>g</sup>	0.84	0.91
<i>CP</i>	$D_s$	6h	17 <sup>a</sup>	0.88	0.84
		6h	15 <sup>h</sup>	0.66	0.64
$\Delta \delta$	$D_s$	7a	36 <sup>a</sup>	0.51	0.59
		7a	25 <sup>i</sup>	0.88	0.87
$\beta$	$D_s$	7b	37 <sup>a</sup>	0.66	0.77
		7b	34 <sup>j</sup>	0.80	0.83
$\beta_1(\text{general})$	$D_s$	7c	21 <sup>a</sup>	0.90	0.92
		7c	20 <sup>k</sup>	0.96	0.94
$\beta_1(\text{special})$	$D_s$	7d	27 <sup>a</sup>	0.59	0.74
		7d	23 <sup>l</sup>	0.92	0.94
$\beta_2^H$	$D_s$	7e	24 <sup>a</sup>	0.38	0.52
		7e	20 <sup>l</sup>	0.95	0.95
$\log K_\beta$	$D_s$	7f	20 <sup>a</sup>	0.80	0.85
		7f	18 <sup>m</sup>	0.92	0.90
$\beta_{\text{sm}}$	$D_s$	—	20 <sup>a</sup>	0.84	0.88
		—	18 <sup>m</sup>	0.87	0.87
$\Delta v_{\text{SbCl}_5}$	$D_N$	8	11	0.92	0.92
$b^2 + abS_{01}$	$-C_A C_B / \Delta H$	Table 5	7	0.82	0.78

<sup>a</sup>All data in Table 3. <sup>b</sup> $v_{\text{as}}$  only from IR data in the neat solvents. <sup>c</sup>Exponential correlation  $y = \exp(a + bx)$ . <sup>d</sup>Triethylamine excluded. <sup>e</sup> $\text{Et}_3\text{N}$ ,  $\text{Bu}_2\text{S}$  and  $\text{NH}_3$  excluded. <sup>f</sup>Calorimetrically determined values only (Table 3). <sup>g</sup>All uncertain values excluded (Table 3). <sup>h</sup>Pyridine and DMSO excluded. <sup>i</sup>*N*-methylformamide, all S and P donors and all uncertain values (Table 1) excluded. <sup>j</sup>Py, 4-Mepy and  $\text{Bu}_2\text{N}$  excluded. <sup>k</sup>Py excluded. <sup>l</sup> $\text{Bu}_2\text{S}$ , THT, Py and 4-Mepy excluded. <sup>m</sup>Py and 4-Mepy excluded.



also supported by a principal component analysis on the character of some hydrogen-bond donors.<sup>23</sup> This is certainly a result of the connection of the O–H group to an aromatic ring, which facilitates polarization and enhancement of the bond dipole moment  $\mu_{\text{O-H}}$  at the interaction with the lone pair of the donor, and increases the electrostatic attraction in the hydrogen bond.

In a hydrogen bond the amount of charge transfer is normally rather limited,<sup>65,67</sup> and is likely to remain so even for soft electron-pair donors, while the charge transfer can become substantial within a soft–soft interaction. However, the assumption in the  $\Delta\Delta\nu$  concept that the hydrogen bonds from phenol to electron-pair donor molecules have a typically hard character clearly different from that measured by the  $\Delta\nu_{\text{Cl}}$  frequency of ICN does not seem to be justified, at least not for the solvent range covered in Table 3. The uncertainties in the basic concept of the  $\mu$  scale as discussed above, and in the ways it has been extended, make it doubtful that its empirical parameters extracted as differences between effects of complex processes are reliable enough to be used as a measure of the property of “softness” in a meaningful way.

*Comparisons with borderline to soft donor scales.* In the enthalpy-based donor number  $D_N$  scale, the reference acceptor antimony(V) chloride has been described as moderately hard.<sup>107</sup> The free  $\text{SbCl}_5$  molecule would in octahedral configuration have one free acceptor site of the vacant orbital  $\sigma$ -type, and can thus give specific localised interactions with n-donor solvent molecules. However, its fairly low chemical stability restricts the useful range and applicability, and substitution or redox reactions occur easily with strongly coordinating solvents. The calorimetric enthalpy measurements for the determination of the donor numbers were made with the solvent in an “inert” diluting medium 1,2-dichloroethane, and should therefore correspond to the donor ability of the isolated molecules, only solvated by van der Waals forces.

The reason for the diluting medium is mainly that in associated neat solvents additional enthalpy contributions due to cavity effects will occur.<sup>104</sup> Also, the donor effect of polar solvent molecules can often be enhanced, in particular when strong intermolecular hydrogen-bonding occurs, because of the polarizing effect on the coordinated solvent molecules by the bonds formed to those in the bulk.<sup>60,108</sup> However, the opposite effect has been observed for some organic sulfides, where the isolated molecules have markedly stronger donor properties than in the neat solvent.<sup>109,110</sup> Moreover, with an excess of solvent molecules their interactions with the chlorine atoms of  $\text{SbCl}_5$  can further reduce the stability of the  $\text{SbCl}_5$  complex.

Marcus has compiled a large number of  $D_N$  values,<sup>60</sup> of which those determined calorimetrically in accord with the original definition are compared in Table 3 and Fig. 6e with the corresponding  $D_S$  values. A logarithmic correlation (Table 4) fits the data better than a linear one, reflecting the more sensitive response of the softer  $\text{HgBr}_2$  acceptor

towards soft solvents. If non-homogeneous  $D_N$  values obtained by correlations with other scales also are included, the scatter increases considerably (Table 4 and Fig. 6e). In particular it is evident that the estimated values of the alcohols in the neat solvents deviate, which is in line with the arguments given above for  $\text{SbCl}_5$  in the neat solvents.

In order to get a more direct comparison of a molecular property with the enthalpy-based values, the symmetric stretching vibration frequency  $\nu_1$  of the  $\text{SbCl}_5$  complex was measured in about 10 solvents.<sup>44</sup> From the wavenumbers measured in the gas phase,<sup>111</sup> 355  $\text{cm}^{-1}$ , in dichloroethane,<sup>44</sup> 353  $\text{cm}^{-1}$ , and in tetrachloromethane 356  $\text{cm}^{-1}$  (this work), no significant changes seem to have occurred in the Sb–Cl bond strength in these “non-coordinating” solvents, and one would expect the trigonal pyramidal shape of  $\text{SbCl}_5$  in gas phase to be retained. In tetrachloromethane solution, however, a dipole moment of  $\mu = 1.14$  D has been reported,<sup>60</sup> indicating a non-symmetrical deformation. The non-coordinating ability of the chlorocarbons has been questioned,<sup>1,45</sup> and recently strong bidentate coordination of  $\text{Ag}^+$  ions by the chlorine atoms of 1,2-dichloroethane and dichloromethane was found to occur in crystal structures.<sup>112,113</sup> For  $\text{SbCl}_5$  in benzene solution<sup>44</sup> the high wavenumber, 365  $\text{cm}^{-1}$ , indicates that the excess benzene molecules in the solvent interact with the Cl atoms and weaken the Sb–Cl bonds. Otherwise the shifts in the  $\nu_1$  frequency and in the  $D_N$  values seem to follow similar trends (Fig. 8 and Table 4).

In strongly coordinating solvents  $L$ , adducts  $\text{SbCl}_5 \cdot L$  with an octahedral Sb coordination are formed. In order to get a good correlation between the measured enthalpy of this reaction and the change in the Gibbs free energy, the entropy contribution should be fairly constant. This has been found to be the case for a limited number of coordinating solvents,<sup>60</sup> but it seems doubtful that the entropy

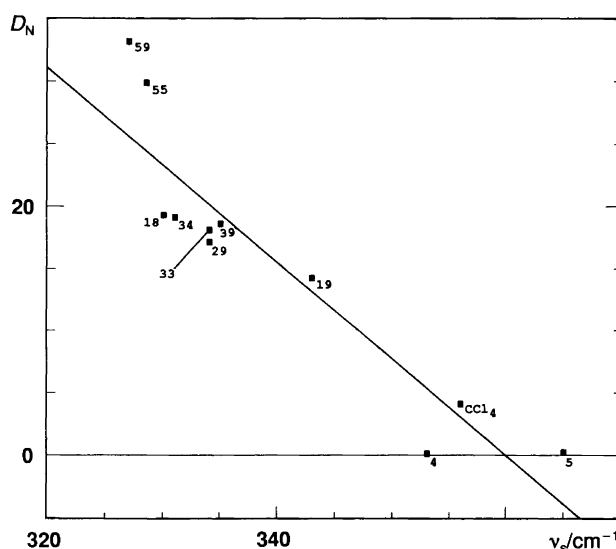


Fig. 8. Relationship between Gutmann's donor number  $D_N$  and the Raman stretching vibration frequency (in  $\text{cm}^{-1}$ ) of the solvated  $\text{SbCl}_5$  molecule.<sup>44</sup> Solvent numbers as in Table 3.

contribution would remain of similar magnitude in weakly coordinating or "non-coordinating" solvents.

The donor number scale has been used successfully in a number of correlations of chemical properties. Its main disadvantage as a Lewis basicity scale is that values for solvents with strong donor properties, such as amines, sulfides and phosphines, cannot be determined directly. Indirectly obtained values often include bulk effects and can give irregularities in the correlations.<sup>60,108</sup> The use of 1,2-dichloroethane as the diluting medium can, in view of its non-negligible coordinating ability,<sup>45,112</sup> be expected to have a significant effect on the measured donor strength on weak donor molecules.

The  $\Delta H_{\text{BF}_3}^\circ$  values follow closely a linear relation with the  $D_{\text{N}}$  scale ( $r = 0.96$ ),<sup>26</sup> although the  $\Delta H_{\text{BF}_3}^\circ$  values in general seem to have a higher precision and to be more reliable.

The simplicity of the  $\text{BF}_3$  molecule has allowed detailed theoretical studies to be performed on some of its adduct compounds.<sup>18,65</sup> The vacant orbital  $\sigma$  on the boron atom contains an appreciable population of electrons from an intramolecular  $\pi$  back-donation from the fluorine atoms, and therefore it does not accept electrons from an external donor atom as readily as an empty orbital would.<sup>18</sup> It is also a weaker Lewis acid than  $\text{BCl}_3$  or  $\text{BBr}_3$ .<sup>17</sup> A qualitative classification of the energy components of the interaction in the gas-phase  $\text{H}_3\text{N}-\text{BF}_3$  complex<sup>65</sup> indicates that the electrostatic term dominates the attractive potential and that the second largest term, the charge transfer, is less than 40% of the electrostatic energy. A moderate amount of charge transfer in the bond is also found in a recent *ab initio* MO calculation of a gas phase  $\text{BF}_3$ -pyridine adduct. The net charge on the  $\text{BF}_3$  molecule from the electron donation of the nitrogen lone pair mainly into the boron 2p ( $\pi$ ) orbital, is not more than  $-0.16e$ .<sup>114</sup> In combination with the non-availability of d-orbitals, this is consistent with the observed moderately hard character of  $\text{BF}_3$ .

Maria and Gal empirically classified the acceptor properties of  $\text{BF}_3$  as halfway between the hard *p*-fluorophenol and the soft  $\text{I}_2$  acceptors.<sup>26</sup> A principal-component analysis showed a more electrostatic character for  $\text{SbCl}_5$  than for  $\text{BF}_3$ .<sup>50</sup> There are, however, strong similarities between the acceptors  $\text{SbCl}_5$  and  $\text{BF}_3$ , and the dominating intermolecular bonding effects probed by the measured enthalpies seem for polar solvents to be the electrostatic dipole-dipole interactions. Non-negligible charge-transfer energies will contribute, but the extent depends strongly on the nature of the donor.

Even though the dichloromethane solvent used for the  $\Delta H_{\text{BF}_3}^\circ$  scale was chosen as being more inert than the 1,2-dichloroethane used for the  $D_{\text{N}}$  scale, it does not seem possible to find such an anomaly as a polar but non-coordinating solvent. The effects measured for weak donor molecules in the  $D_{\text{N}}$  and  $\Delta H_{\text{BF}_3}^\circ$  scales are probably best seen as a relative donor ability versus the "inert" solvent. This is to some extent accounted for in the  $\Delta H_{\text{BF}_3}^\circ$  scale, where the value  $\Delta H^\circ = 10.0 \text{ kJ mol}^{-1}$  has been given for  $\text{BF}_3(\text{g}) \rightarrow \text{BF}_3(\text{CH}_2\text{Cl}_2)$ .

A scatter plot of  $\Delta H_{\text{BF}_3}^\circ$  against  $D_{\text{S}}$  is shown in Fig. 6f. Triethylamine deviates considerably, and the correlation is curved, an effect of the softer character of the  $\text{HgBr}_2$  acceptor in the  $D_{\text{S}}$  scale. As for the  $D_{\text{N}}$  scale a logarithmic correlation curve fits better (Table 4).

In the four-parameter *E & C* method of Drago,<sup>27-29</sup> the scale has been claimed to represent what is normal in a  $\sigma$ -bonded coordination, and the division of the energy into two terms qualitatively justified by a comparison with the approximative wavefunction corresponding to the ground state of a donor-acceptor complex,<sup>18</sup> given as a combination of two resonance structures:

$$\psi_{\text{N}} = a\psi_0(\text{D}, \text{A}) + b\psi_1(\text{D}^+, \text{A}^-)$$

In Mulliken's original treatment the first term is described as corresponding to a no-bond state and the second to a dative structure, which in its turn corresponds to an ionic bond with a covalent contribution. Normalization of the wave functions gives)<sup>18</sup>

$$\int \psi_{\text{N}} \psi_{\text{N}}^* d\tau = a^2 + b^2 + 2abS_{01} = 1$$

where  $S_{01} = \int \psi_0 \psi_1 d\tau$  is the overlap integral between  $\psi_0$  and  $\psi_1$ . The quantities  $F_0 = a^2 + abS_{01}$  and  $F_1 = b^2 + abS_{01}$  have been used by Mulliken as a measure of the fractions of the no-bond and the charge-transfer contributions, with  $F_1$  as an estimate of the charge transferred from the donor D to the acceptor A. The values given for a few DA complexes<sup>18</sup> have been compared in Table 5 with the  $C_{\text{A}}C_{\text{B}}$  fraction of the calculated  $\Delta H$  value. Similar trends are found for the  $-C_{\text{A}}C_{\text{B}}/\Delta H$  and  $F_1$  fractions at least for iodine as acceptor ( $r_{\text{in}} = 0.82$ ), although it is evident that their numerical magnitudes deviate.

There is no clear definition of what is covalent in a donor-acceptor bond, but if the charge-transfer plus the polarization energy could be taken as a measure of the covalent contribution,<sup>115</sup> Morokuma's estimated energy terms of the interaction energy in the adduct  $\text{H}_3\text{N}-\text{BF}_3$  would give a ratio between the covalent and electrostatic contributions:  $(\Delta E_{\text{CT}} + \Delta E_{\text{POL}})/\Delta E_{\text{ES}} = 0.67$ .<sup>65</sup> This can be compared with the  $C_{\text{A}}C_{\text{B}}/E_{\text{A}}E_{\text{B}}$  ratio of 0.42.

Table 5. The fraction  $-C_{\text{A}}C_{\text{B}}/\Delta H$  of the reaction enthalpy from the *E & C* method, see text, compared to the charge transferred from the donor (B) to the acceptor (A) in the complex, as estimated from the fraction  $F_1 = b^2 + abS_{01}$ .<sup>18</sup>

Complex A ← B	$E_{\text{A}}E_{\text{B}}$	$C_{\text{A}}C_{\text{B}}$	$-C_{\text{A}}C_{\text{B}}/\Delta H$	$b^2 + abS_{01}$
$\text{Me}_3\text{N} \cdot \text{I}_2$	0.81	11.5	0.93	0.33–0.41
$\text{Et}_3\text{N} \cdot \text{I}_2$	0.99	11.1	0.92	0.28–0.4
$\text{Py} \cdot \text{I}_2$	1.2	6.4	0.85	0.25–0.29
$\text{C}_6\text{H}_6 \cdot \text{I}_2$	0.71	0.49	0.41	0.02–0.075
$\text{Py} \cdot \text{ICl}$	6.0	5.3	0.47	0.30
$\text{C}_6\text{H}_6 \cdot \text{ICl}$	2.5	0.59	0.19	0.11
<i>p</i> -Xylene · ICl	2.1	3.6	0.41	0.11

For hard and borderline interactions the  $E$  &  $C$  scale is capable of rather precise estimates of enthalpy values, and can be used for various kinds of correlations with reasonable success. Owing to the two-parameter description of the donor properties greater flexibility is achieved than in a single-parameter expression. To some extent the hard-soft principles of Pearson is reflected in the scale, which can be used to predict changes in the order of donor strength of bases relative to Lewis acids of different softnesses.<sup>27,28</sup> A rather poor agreement is obtained, however, in an energy analysis by Morokuma's method on a number of Lewis acid-base interactions,<sup>115</sup> and Drago's  $E$  &  $C$  parameters seem to represent a different blend of intermolecular energies than the theoretical estimates of "covalent and electrostatic" contributions, even in these fairly "hard" interactions. It is therefore not surprising that empirical correlations with  $E$  &  $C$  equation deviate for many strongly interacting systems, since the parameters are mostly obtained for relatively hard donors and thus cannot represent all of the effects in soft-soft interactions.<sup>12</sup>

In an attempt to generalize the use of the  $E$  &  $C$  method to include correlations with any kind of spectral or reactivity parameter  $\chi$ , Drago and Doan<sup>30,31</sup> have introduced an equation of the following type:

$$\Delta\chi = E_A E_B + C_A C_B + SD$$

However, one should keep in mind that "a few term linear relationships can always be found that well approximate to any measured data on the set of investigated reactions".<sup>21</sup> Also, the use of multiple regression to fit a parameter-based model relies on the assumption that the model is capable of completely describing the observed effects.<sup>21</sup> This is the inherent assumption in e.g. the  $E$  &  $C$  method, in the scale proposed by Taft *et al.*, and also in the solvent "acidity and basicity" scales of Swain and coworkers, who were able to correlate more than a thousand data sets of free energy changes with the following relation:<sup>116</sup>

$$P_{ij} = a_i A_j + b_i B_j + c_i$$

Problems arise when attempts are made to interpret the parameters obtained from the optimized fit in terms of certain physical properties and to apply the equation to predict other unknown effects.<sup>21,117,118</sup> It is not obvious to what extent a separation of the specific covalent effects and the general electrostatic interactions has been achieved by the  $E$  &  $C$  approach, and in particular it is doubtful if the covalent effects can be described by a linear expression over a wide range of solvent properties.

The solvatochromic Cu  $\lambda_{\max}$  values, obtained as the position of the d-d transition band, have been compared by Soukup and Sone with Gutmann's donor number scale  $D_N$  for 19 solvents, and a good correlation along a smooth curve was obtained.<sup>36</sup> They found, however, a concentration dependence of many  $\lambda_{\max}$  values. For weak donor solvents a correction for a sloping background should be

made, and for strong donors a partial dissociation of the  $[\text{Cu}(\text{tmen})(\text{acac})]^+$  complex was found to occur owing to solvent attack. According to their results stronger donor solvents than pyridine could hardly be used. In addition, ion-pair formation occurs in weak donor solvents with low dielectric constant for the perchlorate and nitrate salts of the  $[\text{Cu}(\text{tmen})(\text{acac})]^+$  ion,<sup>33</sup> and the tetraphenylborate anion was recommended in such cases.<sup>33</sup>

The limitations of the scale as described in Ref. 36 are also confirmed in this study (Table 3). A number of additional solvents were tested to assess the practical usefulness of this concept, and a preliminary report of the results for most of them was previously given in Ref. 37. For the softest solvents a reduction of the copper(II) atom in the complex to copper(I) can also occur, and a large scatter is found for the values of strong donors (Fig. 6g). If the values for aniline and all four solvents after pyridine in Table 3 are excluded, again a logarithmic correlation gives a better fit with the solvents of the  $D_S$  scale (Table 4).

In the  $CP$  scale variations in the solvent activity in the mixtures and in the mer/fac ratios on the mean  $10Dq$  values have been neglected. For strongly coordinating or chelating solvent molecules in which distorted octahedral or square-planar geometries around  $\text{Ni}^{2+}$  in low-spin complexes would be expected, the scale should not be used. For soft ligands forming octahedral complexes this concept would also be unreliable because both large and small  $10Dq$  values can be found for soft ligands as a result of their different abilities to redistribute the charge, while hard ligands should only give large  $10Dq$  values.<sup>17</sup> Owing to the relatively high charge/radius ratio of the  $\text{Ni}^{2+}$  ion, ion-dipole forces would strongly dominate the interactions with polar solvents, and ion-quadrupole and induced interactions should be important for non-polar media. It would hardly be possible to study solvents with dielectric constants lower than  $\epsilon \approx 10$ , because of ion-pair formation. The strong emphasis on the electrostatic forces could to some extent explain the relatively high sensitivity observed for some oxygen donor solvents and nitriles, although the lower coordinating ability found for some branched alcohols probably is a steric effect.

The  $CP$  scale contains a large number of values for alcohols and nitriles, and for 16 of these solvents  $D_S$  values have been obtained (Fig. 6h). The linear correlation coefficient is not high,  $r = 0.88$  (Table 4), even though there are no  $CP$  values for solvents softer than pyridine. The  $r$  value decreases to 0.66 if pyridine and DMSO are excluded, which shows that for the remaining solvents the correlation is poor. This is a scale of limited applicability in which the charge-transfer effects are of minor importance.

*Comparisons with "hard" hydrogen-bond basicity scales.* The proton NMR shift,  $\Delta\delta$ , of chloroform in dilute solution gives a solvent response due to the hydrogen-bond formation between the chloroform and solvent molecules.<sup>53</sup> The weak bonds of the C-H...O or C-H...N type are expected to have a relatively large charge-transfer part in compari-

son with the main electrostatic energy term.<sup>65</sup> With increasing softness and less electronegative donor atoms the magnitude of the electrostatic term and also the overall hydrogen-bond strength will drop rapidly, and the dispersion forces will become more important. This would explain the poor correlation with other scales based on effects from strong bonds with an appreciable amount of charge transfer for soft solvents. It was also pointed out in the original paper that the shielding effect of the proton in the NMR measurements is composed of several terms, and that for solvents with large polarizable atoms deviations from the correlations with other scales may occur.<sup>53</sup> Very poor correlations are found with the  $D_S$  scale for the 36 solvents in Table 3 (Fig. 7a and Table 4), but an increase to  $r_{\text{lin}} = 0.88$  occurs if all uncertain values and poor hydrogen-bond-acceptor solvents (S- and P-donors) and also the outlying value for *N*-methylformamide are excluded.

The multiparameter scale of Taft *et al.* with the solvatochromic parameters  $\pi^*$ ,  $\alpha$  and  $\beta$ , and the subparameters  $\delta$ ,  $\delta_{\text{H}}$  and  $\xi$ , represents an attempt to find LSERs between many types of solute properties denoted *XYZ* and multiple interacting solvent effects:

$$XYZ = (XYZ)_0 + s(\pi^* + d\delta) + a\alpha + b\beta + e\xi + h\delta_{\text{H}}^2$$

The  $\beta$  scale of solvent hydrogen-bond acceptor (HBA) basicity has been given a central role in a large number of correlations with properties dependent on solvent basicity.<sup>20,104</sup> However, to account for the "family dependence" of correlations between LSER of solvents with similar HBA properties,<sup>46</sup> a coordinate covalency parameter  $\xi$  was introduced, based on plots of  $\beta$  against the IR shift  $\Delta\nu$  (free versus hydrogen-bonded) of the O–H stretching vibration of phenol for several types of polar oxygen donor solvents: nitriles, pyridines and amines.<sup>46</sup> For a restricted range of solvents the principal-component analysis applied by Maria and Gal<sup>50</sup> was also used to discuss the relative electrostatic and covalent character of the  $\beta$  and  $\xi$ , as well as the  $E_{\text{B}}$  and  $C_{\text{B}}$  parameters. It was reported that the  $\beta$  scale was a good descriptor of Gibbs energies of hydrogen bonding.<sup>50</sup> The four-parameter  $b\beta + e\xi$  description of solvent basicities has strong similarities to Drago's *E* & *C* method.<sup>30,46,50</sup> Similar aspects as discussed above on the physical interpretation of the *E* & *C* parameters also apply to this treatment.

In a critical reinvestigation of the  $b\beta + e\xi$  scale, part of its experimental basis has been questioned.<sup>119,120</sup> Moreover, an analysis of the character of the  $\beta$  scale showed that it is related more closely to an N–H rather than an O–H scale of HBA basicity, even though the averaging process of the inhomogeneous data sets used to obtain the  $\beta$  values leads to a lower sensitivity and precision in the correlations.<sup>23,120</sup>

Scatter plots of  $\beta$  against  $\Delta H_{\text{BF}_3}^{\text{B}}$  also revealed a "family dependence" for different types of Lewis bases.<sup>26</sup> This was interpreted as reflecting a more pronounced tendency of  $\text{BF}_3$  for covalent contributions in its Lewis acid–base interactions, i.e. a somewhat softer character of  $\text{BF}_3$  than of the hydrogen-bond donors used to obtain the  $\beta$  parameters.

Even though the  $\xi$  parameter undoubtedly reflects some covalent character, it has as well as  $\beta$  been obtained from hydrogen-bonded indicators,<sup>46</sup> and therefore its sensitivity to covalency and charge transfer in soft–soft interactions is limited. No values for solvents softer than pyridine and hexamethylphosphoric triamide have been reported in the  $\beta$  scale. For the solvents in Table 3 a poor correlation with the  $D_S$  scale is obtained (Table 4), but the  $r$  values increase considerably by excluding the three strongly deviating solvents pyridine, 4-methylpyridine and dibutylamine (Fig. 7b). Also, the alcohols and water show a poor fit, probably because of their strong self-association in the neat liquids.

The traditional basis for the linear free energy relationships (LFERs), of which the LSERs are special cases, is to assume that a number of fundamental properties can be specified and combined linearly in any application to describe an observed effect. Against this view stands the interpretation by Wold *et al.* in which the LFERs are empirical models of similarity, i.e. locally valid linearizations of complicated relationships.<sup>19,21</sup> For the present comparisons the practical consequence of the two philosophies would be whether it is, in principle, useful to try to express system-specific covalent Lewis basicity effects by linear relations.

For small changes in the compared systems or if the fundamental cause of the effect is similar, a linear correlation will be found between the measured properties.<sup>19,21</sup> When deviations occur they can be modelled by the introduction of additional parameters, which then often are connected to some other property. It seems likely that hard non-directional interactions of mainly electrostatic character would conform with LFERs of this type, but in soft–soft interactions the covalent bonding with polarization and  $\pi$  back-donation should, to a larger extent, be directional and too system-specific to be modelled with statistically averaged parameter values. Recent progress in quantifying the hard–soft acid–base principles has been reported,<sup>15,17</sup> but the parameters obtained are yet incomplete and apply primarily to average non-directional properties of molecules in the gas phase. At present it still seems best to describe soft basicities and donor properties by making use of the similarity principle for correlations related to a single clearly defined model process.

In the hydrogen-bond basicity scales introduced by Abraham *et al.*<sup>23,49</sup> the drawback of inhomogeneous data sets has been recognized and the properties of the reference Lewis acids are tested by the principal component method of Maria and Gal.<sup>50</sup> The two related solvatochromic scales  $\beta_1(\text{general})$  and  $\beta_1(\text{special})$  are based on aniline-type indicators in the neat non-self-associating solvents. They show good correlations with the  $D_S$  scale if poor hydrogen-bond-acceptor solvents (pyridines and sulfides) are excluded (Figs. 7c and 7d and Table 4). Their most extensive basicity scale,  $\beta_2^{\text{H}}$ , is based on a set of selected reference acids in a diluting tetrachloromethane medium, and shows similar properties as the  $\beta_1$  scales when compared to the  $D_S$  values (Fig. 7e).

Abraham *et al.* have also introduced proton-acceptor scales for use in drug design,  $\log K_{\beta}$  and  $\beta_{sm}$ , which are based on a single reference acceptor (4-nitrophenol) in a diluting although polar medium (1,1,1-trichloromethane).<sup>49</sup> The correlations with the  $D_S$  scale are somewhat less good when corresponding solvents are compared (Fig. 7f and Table 4). It is, however, noteworthy that the very different types of acceptors employed in the homogeneous  $D_S$  and  $\beta$  scales respond in a similar way towards hard hydrogen-bond-acceptor and electron-pair-donor solvents. The special features of hydrogen bonding are for these indicators only apparent for softer and larger lone-pair donor atoms, for which the electrostatic interaction with the A–H dipole, which is less polarizable than in PhOH, is considerably reduced.

## Conclusions

A number of scales are available for correlations with hard donor solvents or for rank ordering of donor strength of solvents with a strong electrostatic contribution in the donor–acceptor interaction. The  $D_N$ ,  $\Delta H_{BF_3}^{\circ}$  and Cu  $\lambda_{max}$  scales are all based on acceptors with moderately hard or borderline characters, and are useful to correlate properties for solvents with hard to borderline donor atoms. In particular the  $\Delta H_{BF_3}^{\circ}$  scale can be recommended for rankings of borderline donors in non-self-associated solvents because of its homogeneous set of data. The Cu  $\lambda_{max}$  scale has a limited range owing to the instability of the acceptor complex, but is very useful for visible demonstrations of solvent effects. In the CP scale, where the  $Ni^{2+}$  acceptor has a fairly high charge/radius ratio, the electrostatic energy terms will dominate. It is therefore not well suited as a measure of charge-transfer-related donor–acceptor interactions.

The multiparameter  $E$  &  $C$  method and the  $\beta$  and  $\xi$  scales, which are based on parameters fitted to solvent effects averaged for a large number of different donor–acceptor interactions, have similar constructions, with a largely electrostatic part and another term which includes the softer part of the interaction. The softness response is in both concepts limited owing to the hardness of the reference acceptors used, and the sensitivity is reduced because of the averaging procedure of non-homogeneous data used to obtain the solvent parameters.

The hydrogen-bond-acceptor basicity scales derived by Abraham and coworkers have defined areas of applications because of the selection of reference acceptors by a principal-component analysis. The  $\beta_1$  scales, which are based on selected reference acceptors with similar responses, can be recommended for oxygen and hard nitrogen-donor solvents without strong intermolecular hydrogen bonding or self-association in the bulk. The  $\log K_{\beta}$  and  $\beta_{sm}$  scales, which also have been consistently obtained from a single slightly softer acceptor, are intended for a special application, i.e. to simulate hydrogen-bond drug–acceptor interactions in a polar surrounding.

Another hydrogen-bond scale,  $\Delta\delta$ , is related to the very

weak hydrogen-bond properties of chloroform, and has an erratic response towards solvents without strongly electronegative donor atoms. The  $\Delta v_{PhOH}$  scale for neat solvents is, however, of a very different character and shows a sensitive response over a wide range from hard to fairly soft solvents capable of accepting hydrogen bonds.

Soft–soft interactions with polarizable donor and acceptor atoms gain additional energy in a Lewis acid–base reaction. Large deviations can then occur from correlations with hard reference acceptors. In order to correlate effects on soft acceptors caused by soft and strong electron-pair donor solvents, a scale based on a single soft reference acceptor with similar properties should be used for the best result. The  $D_S$  scale is obtained from the solvent effect on a typical soft acceptor, the mercury atom of the  $HgBr_2$  molecule, and has a sensitive response particularly towards soft donor solvents. It covers a very large range of solvents and can be used even for very strongly coordinating neat solvents. With access to a Raman (or far-IR spectrometer) additions of new solvents can easily be made.

Of other “soft” scales for neat solvents the  $B_{soft}$  index is more restricted owing to the lower chemical stability of the ICN acceptor, and has a rather similar response as the  $\Delta v_{PhOH}$  scale.

The  $SP$  scale is a very limited softness indicator, since only those solvents are included which show clear deviations in comparisons of the Gibbs energies of transfer between  $Ag^+$  and harder cations. This scale is related to the special character of the  $Ag^+$  ion as acceptor, which is why the nitriles have been classified as soft solvents.

In the  $\mu$  scale of solvent softness, parameter values are obtained as second-order differences between Gibbs energies of transfer. An additional element of uncertainty is introduced owing to the different variations with the bond distances of the energy terms for the solvation of the  $Ag^+$ ,  $Na^+$  and  $K^+$  ions. Coordination changes and variations in solvation numbers of the reference ions could be other causes of non-uniformity in this scale, and may overshadow the softness effects in the solvent parameters. The correlation with other soft donor scales is poor.

*Acknowledgements.* Support from the Swedish Natural Science Research Council is gratefully acknowledged. We thank Professor G. Gritzner, Johannes Kepler Universität, Linz, Austria, for supplying us with samples of the following solvents: n-butyronitrile, propionitrile,  $\gamma$ -butyrolactone, formamide, *N*-methylformamide, *N,N*-dimethylthioformamide, 1-methyl-2-pyrrolidinone, 1-methyl-2-thiopyrrolidinone, 2,2'-thiodiethanol and hexamethylphosphorothioic triamide.

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Received July 27, 1989.