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The HSAB Principle and Extended Solubility Theory

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A semiquantitative approach to the prediction of the hard-soft character of Lewis acid-base species is proposed based on the use of empirical sorting maps, and a map employing Hansen's extended solubility parameters is reported for common basic molecular solvents. This map is compared with previously reported sorting maps for ionic acids and bases and is used to calculate an empirical softness index for the species involved.

Introduction

Since its proposal in 1963, the hard-soft acid-base (HSAB) concept has attained something of the status of a minor chemical principle, as evidenced by its now almost routine inclusion in textbooks [1]. However, in spite of nearly 20 years of scrutiny, the concept still remains essentially qualitative. Only one attempt has ever been made to quantitatively assess the validity of the principle [2, 3], and this was open to criticism [4] because it was based on the model assumptions of a competing approach to the prediction of Lewis acid-base interactions. What has largely stood in the way of attempts to quantitatively assess the validity of the HSAB principle is the lack of a quantitative softness scale. Indeed, it has even been suggested that attempts to establish such scales are ill founded and that both softness and the HSAB concept should be regarded as useful, but intuitive, rules-of-thumb that are inherently incapable of rigorous quantification and theoretical justification [5]. It is our purpose in this note to suggest a compromise approach to the HSAB concept, based on the use of empirical sorting maps, that lies between the dictates of rigorous quantification, on the one hand, and claims of excessive qualitativeness, on the other.

Procedure

A sorting map is a graphical procedure that allows one to display the empirically known dependency of a given property (*e.g.* phase diagram behavior, chemical reactivity of some sort, chemical structure, *etc.*) on parameters for which the exact mathematical dependency is unknown. In its simplest form only two parameters are used and the species in question are plotted in the xy plane as a function of these parameters. This plane is then empirically divided so as to sort the species into regions corresponding to certain values (or ranges of value) for the property of interest (*e.g.*, solubility, insolubility, or compound formation for phase diagrams; ranges of $K_{equil.}$ for reactions; different chemical structures; *etc.*). These divisions cannot be predicted ahead of time because the exact functional dependency is not known; rather they are drawn after the fact so as to optimize the sorting. The value of such plots lies not only in the convenient graphical display of empirically known dependencies, but in the fact that they allow one to interpolate (and so predict) the behavior of species other than those used to make the original plot.

Sorting maps have long been used by geochemists to correlate the behavior of ions towards hydrolysis and other weathering reactions [6] and in the correlation of phase diagram behavior [7–10]. More recently they have become enormously popular among solid-state chemists and physicists for the prediction and correlation of solid-state crystal structures [11, 12]. Some structure-sorting maps have interpolative-prediction success rates as high as 99%.

Sorting maps have also been applied to the HSAB classification of ions, using the charge to radius ratio of the ions as one parameter and some property thought to reflect softness, such as the aqueous reduction potential, ionization potential, electronegativity, or polarizability, as the other [13]*. Here

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*In the plots reported in reference [13] cations and anions of different charges were separately plotted and the regions divided by arbitrarily drawn curved lines. More recent work shows that all of the cations may be combined on a single plot and the regions divided by arbitrarily drawn straight lines like those reported in this note. The same is true for the anions. See W. B. Jensen 'Sorting Maps and the HSAB Principle', to be published.

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we would like to report a successful sorting map for neutral molecular Lewis bases using parameters derived from Hansen's extension [14] of Hildebrand's solubility theory [15]. As the availability of these parameters implies, such species have enormous value as solvents and an approximate knowledge of their softness can play a potentially valuable role in solvent selection for the development of novel syntheses. For example, Ahrland's studies of metal complex formation showed that solvent softness can play a key role in determining such factors as extent of complex formation and ligand preference [16, 17].

In the Hansen system the energy of self-association or vaporization, ΔE_t, of a liquid is assumed to be the additive sum of a dispersion energy interaction, ΔE_d, a dipole interaction, ΔE_p, and a hydrogen bonding interaction, ΔE_h. The square root of the energy per unit volume is then defined as the solubility parameter, δ, for the energy interaction in question

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{1}$$

giving the relation

$$\Delta E_t = V\delta_t^2 = V(\delta_d^2 + \delta_p^2 + \delta_h^2) \tag{2}$$

Use of individual solubility parameters leads to convenient equations for predicting solute solubility, mutual miscibility of liquids, surface tensions, and other solvent phenomena. Hansen and others have also proposed various methods of independently calculating the various solubility parameters contributing to δ_t^2 in eqn. 2 and extensive tabulations of these values are available [18, 19].

Given the correlation between softness and polarizability, the dispersion term, δ_d, is the obvious choice for the parameter paralleling the various softness terms used in the ion sorting maps. Likewise, the dipole term, δ_p, is an obvious choice for the parameter paralleling the Z/r parameter of the ion plots. On the other hand, the question of what to do with δ_h is not so obvious as it certainly reflects a combination of effects, including both induced dipole and charge-transfer interactions. Assuming, however, that it does in some way reflect possible hydrogen bonding interactions, then it seems best to combine it with δ_p to give a composite 'specific association' parameter $\delta_{sa} = (\delta_p^2 + \delta_h^2)^{1/2}$. This is consistent with the usual classification of proton donor-acceptor interactions as hard and with recent work which shows that the sum $\Delta E_p + \Delta E_h$ correlates with results obtained using Gutmann's donor and acceptor number parameters [20]. These have long been known to give an adequate description of the donor-acceptor behavior of relatively hard Lewis acids and bases [21].

Results and Discussion

The resulting sorting map is shown in Fig. 1 and the liquids used are listed in Table I by functional class, the order within each class roughly corresponding to the order of appearance from left to right on the plot. As can be seen, the plot nicely sorts the species into regions corresponding to hard, borderline, and soft, giving excellent agreement with Pearson's more qualitative classification of these species. Alkanes, aromatics and sulfides are soft. Oxygen donor species, such as water, alcohols, ethers, ketones, esters, and nitro compounds, are hard, whereas nitrogen donor species vary in their location depending on the hydridization of the donor atom and the polarizability of the attached hydrocarbon group. Thus nitriles (sp) are hard, whereas pyridines (sp^2) and anilines (sp^3) are borderline. This is in keeping with the rule that hardness generally increases as the s-character of the donor orbital increases [22].

In actual fact, however, it is the polarizability of the attached hydrocarbon group which appears to play a key role, as the sp^3 hybridized aliphatic amines, in contrast to the anilines, lie in the hard region. Likewise, attachment of a highly polarizable phenyl group to a nitrile, as in benzonitrile, brings the species close to the borderline region, and in the case of the ethers (*e.g.* anisole), ketones (acetophenone) and nitro compounds (nitrobenzene), is even able to drag oxygen donors into the borderline region itself. This is in part because the δ_d parameter reflects the polarizability of the entire molecule rather than that of the donor atom alone. It is the latter, rather than the former, quantity that should play a key role in determining the softness of the base. Similarly, one would expect the dipole moment of the bond attaching the donor atom to the base, rather than the dipole of the entire molecule, reflected in δ_p, to be of primary interest in determining basicity. Given these limitations, as well as the ambiguous nature of δ_h, it is surprising just how well these parameters work.

It should also be noted that the plot shows that polarizability by itself is not sufficient to establish a softness scale in keeping with Pearson's qualitative classification (*i.e.*, certain alcohols have δ_d values similar to the sulfides). Rather it is the ratio between δ_{sa} and δ_d which appears to be the crucial factor. Using water as an arbitrary zero and the sorting line intercept of 6.5, it is possible to establish a softness value based on this ratio.

$$S = 20.1 - \delta_{sa}/(\delta_d - 6.5) \tag{3}$$

The resulting S values are listed in the table along with the individual δ_{sa} and δ_d values of each species. Again, this result agrees with those obtained from the earlier ion sorting maps which showed that the ratio of Z/r to the so-called softness parameter,

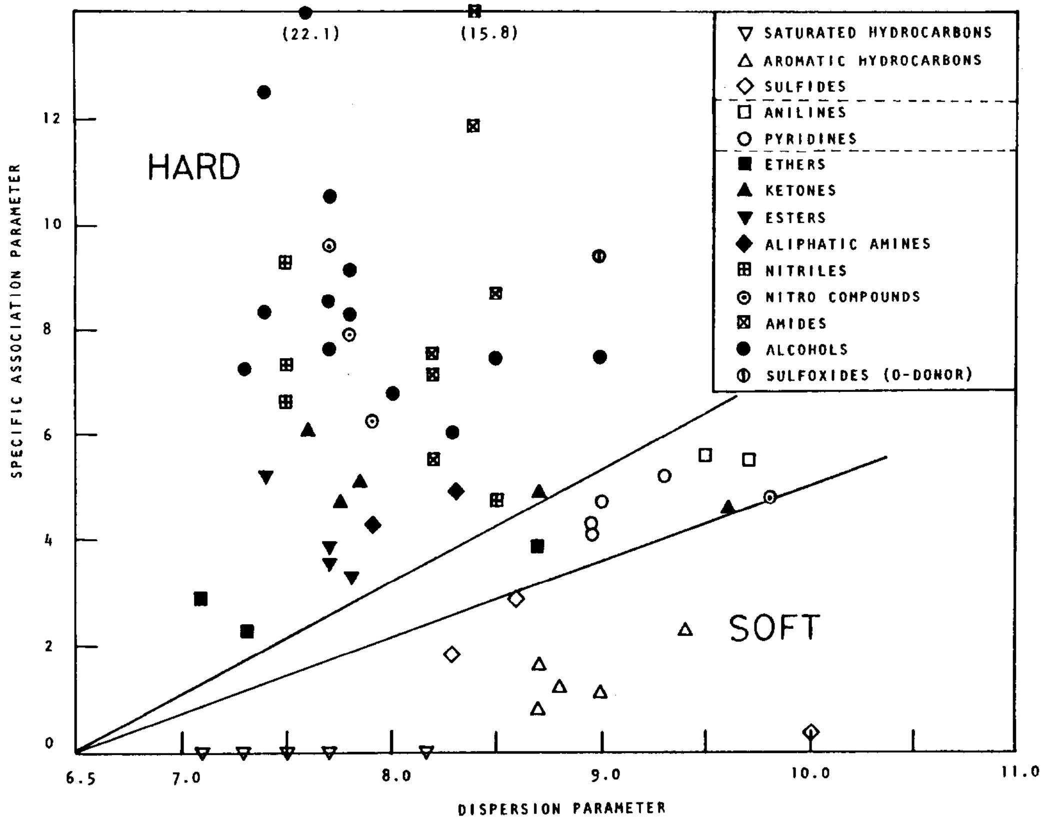

Fig. 1. A hard-borderline-soft sorting map for neutral molecular Lewis bases based on the use of Hansen's extended solubility parameters.

TABLE I. Molecular Lewis Bases and Solubility Parameters[a].

Liquid	δ_d	δ_p	δ_h	δ_{sa}	S
Saturated Hydrocarbons					
pentane	7.1	0	0	0	20.1
hexane	7.3	0	0	0	20.1
heptane	7.5	0	0	0	20.1
decane	7.7	0	0	0	20.1
cyclohexane	8.2	0	0	0	20.1
Aromatic Hydrocarbons					
ethylbenzene	8.7	0.3	0.7	0.8	19.8
1,2-dimethylbenzene (*o*-xylene)	8.7	0.5	1.5	1.6	19.4
methylbenzene (toluene)	8.8	0.7	1.0	1.2	19.6
benzene[b]	9.0	0.5	1.0	1.1	19.7
naphthalene[b]	9.4	0.3	2.3	2.3	19.3
Sulfides					
diethyl sulfide	8.3	1.5	1.0	1.8	19.0
dimethyl sulfide[c]	8.6	1.8	1.2	2.9	18.7
carbon disulfide	10.0	0	0.3	0.3	19.1
Anilines					
aniline	9.5	2.5	5.0	5.6	18.2
2-methylaniline (*o*-toluidine)[c]	9.7	2.0	5.1	5.5	18.4
Pyridines					
2,4,6-trimethylpyridine[c]	8.9	3.4	2.2	4.1	18.4
2,6-dimethylpyridine[c]	8.9	3.6	2.4	4.3	18.3

(continued overleaf)

TABLE I *(continued)*

Liquid	δ_d	δ_p	δ_h	δ_{sa}	S
4-methylpyridine[c]	9.0	3.9	2.6	4.7	18.2
pyridine	9.3	4.3	3.0	5.2	18.2
Ethers					
diethyl ether	7.1	1.4	2.5	2.9	15.3
dipropyl ether[c]	7.3	1.1	2.0	2.3	17.2
methylphenyl ether (anisole)	8.7	2.0	3.3	3.9	18.3
Ketones					
propanone (acetone)	7.6	5.1	3.4	6.1	14.6
3-pentanone[b]	7.7	3.7	2.9	4.7	16.2
2-butanone	7.8	4.4	2.5	5.1	15.4
cyclohexanone	8.7	4.1	2.5	4.8	17.9
phenylmethyl ketone (acetophenone)	9.6	4.2	1.8	4.6	18.6
Esters					
ethyl ethanoate	7.4	2.6	4.5	5.2	14.3
propyl ethanoate[c]	7.7	2.1	3.3	3.9	16.9
butyl ethanoate	7.7	1.8	3.1	3.6	17.1
hexyl ethanoate[c]	7.8	1.5	2.9	3.3	17.6
Aliphatic Amines					
butylamine[b]	7.9	2.2	3.7	4.3	17.0
propylamine	8.3	2.4	4.2	4.8	17.4
Nitriles					
acetonitrile	7.5	8.8	3.0	9.3	10.8
propionitrile	7.5	7.0	2.0	7.3	12.8
butryonitrile	7.5	6.1	2.5	6.6	13.5
benzonitrile	8.5	4.4	1.5	4.7	17.8
Nitro Compounds					
nitromethane	7.7	9.2	2.9	9.6	12.1
nitroethane	7.8	7.6	2.3	7.9	14.1
2-nitropropane	7.9	5.9	2.0	6.2	15.7
nitrobenzene	9.8	4.2	2.0	4.7	18.7
Alcohols					
water	7.6	7.8	20.7	22.1	0
methanol	7.4	6.0	10.9	12.5	6.2
2 methyl-1-propanol	7.4	2.8	7.8	8.3	10.9
2 methyl-2-propanol[c]	7.3	2.5	6.8	7.2	11.1
ethanol	7.7	4.3	9.6	10.5	11.4
2-propanol	7.7	3.0	8.0	8.5	13.0
2-butanol	7.7	2.8	7.1	7.6	13.8
1-propanol	7.8	3.3	8.5	9.1	13.1
1-butanol	7.8	2.8	7.7	8.2	13.8
1-hexanol	8.0	2.1	6.3	6.7	15.6
1-octanol	8.3	1.6	5.8	6.0	16.8
cyclohexanol	8.5	2.0	6.6	7.4	16.4
benzyl alcohol	9.0	3.1	6.7	7.4	17.1
Amides					
diethyl acetamide[c]	8.2	4.1	3.7	5.5	16.9
dimethyl acetamide	8.2	5.6	5.0	7.5	15.7
diethyl formamide[c]	8.2	5.6	4.3	7.1	15.9
N-methyl formamide[c]	8.4	10.1	6.1	11.8	13.9
formamide	8.4	12.8	9.3	15.8	11.8
dimethyl formamide	8.5	6.7	5.5	8.6	15.8
Sulfoxides					
dimethyl sulfoxide	9.0	8.0	5.0	9.4	11.8

[a] Data from Ref. [19] unless otherwise noted. All values in $(\text{cal/cc})^{0.5}$. [b] Data recalculated from Ref. [19]. [c] Previously unpublished data by A. Beerbower.

rather than the softness parameter alone, was crucial in reproducing Pearson's classification.

All of the species used in this study are basic or slightly amphoteric. A trial plotting, using the same sorting lines, of the few molecular acids for which Hansen values are available, such as glycols and carboxylic acids, placed them, as predicted, in the hard region. However, the lines also placed chloroform in the soft region. In addition, there have been several attempts to dissect Hansen's δ_h parameter into a contributing proton acceptor or basicity parameter, δ_b, and a contributing proton donor or acidity parameter, δ_a [23, 24]. The use of the δ_b parameter in place of the inherently amphoteric δ_h parameter could lead to a further refinement of the plot.

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