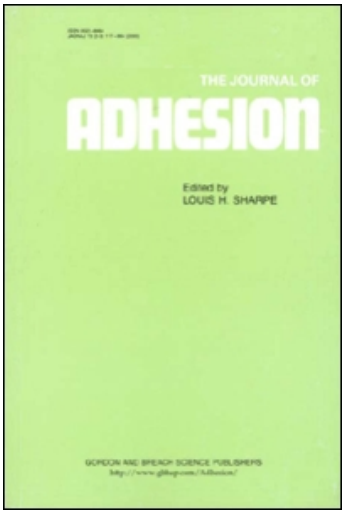

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Acid-Base Interactions between Cellulose/Lignocellulose and Organic Molecules

Anders Larsson[ab]; William E. Johns[c]
[a] Institute for Surface Chemistry, Stockholm, Sweden [b] Pharmacia AB, Uppsala, Sweden [c] College of Engineering, Washington State University, Pullman, WA, U.S.A.

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Acid-Base Interactions between Cellulose/Lignocellulose and Organic Molecules

ANDERS LARSSON†

Institute for Surface Chemistry, Stockholm, Sweden

and

WILLIAM E. JOHNS

College of Engineering, Washington State University, Pullman, WA 99164-2920, U.S.A.

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Literature data on interactions between liquids and cellulose/lignocellulose have been correlated with various parameters describing the liquids. The PLS multivariate data analysis method was employed for the correlation.

The analysis shows that the Lewis basicity is the most important liquid description parameter, followed by the Lewis acidity and the molar volume. Factors such as dielectric constant and solubility parameters show weaker correlations.

A simple relationship has been observed for the strength of paper soaked in various liquids. By correlating with the square root of the sum of the donor number (basicity) and the acceptor number (acidity), 85% of the variance in the tensile energy absorption of blotter paper can be accounted for.

KEY WORDS Lewis acid; Lewis base; donor; acceptor; adhesion; paper.

INTRODUCTION

Recently, a theory based on Lewis acid-base interactions between adhering surfaces has had a certain success in the field of polymer-mineral adhesion.[1] Since this theory is particularly useful for

† Present address: Pharmacia AB, S-751 82, Uppsala, Sweden.

explaining interactions between highly polar materials, it is to be expected that it will be relevant also for cellulose and lignocellulose. In fact, the acid-base concept can be regarded as a more general and quantitative extension of the traditional hydrogen bonding theory which has been extensively used in connection with polysaccharides.

Acid-base parameters

A Lewis base is a molecule that can donate a share in a pair of electrons to a Lewis acid which can accept this share. In this reaction (termed a neutralization reaction) a bond is formed between the two molecules. Depending on the strength of the acid and the base, the bond strength can vary from a covalent bond to a weak intermolecular attraction.

For liquids the acidity and basicity can be numerically expressed using experimentally determined acid and base parameters. Several such parameter systems are available,[2] based on spectroscopic or calorimetric measurements of interactions between the liquids and well-defined reference acids and bases. Most systems involve two parameters, *i.e.* the acidity and basicity of each liquid. Other, more elaborate systems describe the acidity in two parameters and the basicity in another two. With such a system it should be possible to characterize a liquid very accurately. Unfortunately, very few liquids have been fully characterized with all four parameters. Thus, to take account of the amphotericity of liquids, we have limited this analysis to a two-parameter system.

We have employed the system of Gutmann and Mayer,[3] where acidity is expressed as the acceptor number (AN) and basicity as the donor number (DN). AN-values are based upon a shift in the ^{31}P NMR spectrum of triethylphosphine oxide (reference base) dissolved in various liquids. DN values, on the other hand, are calculated from calorimetric measurements of the enthalpy of mixing of antimony pentachloride (reference acid) with the liquids.

In addition we have also employed the $D_{II,I}$ basicity parameter of Selbin and Ortolano,[4] which is based on a shift in the UV spectrum of vanadyl bisacetonate (reference acid) dissolved in the liquid.

The parameter values for 23 different liquids are given in the first three columns of Table I (see table refs).

TABLE I
Compilation of literature data

Liquid	$D_{II,I}$	DN	AN	MW	ε	δ_0	δ_d	δ_p	δ_h	TEA	lg (Accessibility)	lg (swelling + 0.5)	Reference for $D_{II,I}$,	DN, AN, swelling
H_2O	5.49	18.0	54.8	18.0	78.5	23.5	7.0	15.3	16.7	0.90	1.13	2.00	4, 14, 16	6, 17
FA	5.15	24	39.8	39.7	109	17.8	8.4	12.8	9.3	1.43	1.13	2.09	4, 15, 16	17
DMF	3.94	26.6	16.0	77.0	30	12.1	8.52	6.7	5.5	2.11	1.14	—	4, 14, 16	—
MeOH	4.42	19	41.3	40.5	32.6	14.3	7.42	6.0	10.9	3.5	1.09	1.98	4, 15, 16	17
HAc	3.69	25	52.9	57.2	6.15	10.4	8.10	3.9	6.6	—	0.901	1.88	4, 2, 16	17
Py	4.39	33.1	14.2	80.6	12.3	10.6	9.25	4.3	2.9	2.9	0.877	2.07	4, 14, 16	6
EtOH	4.26	20	37.1	58.4	24.3	12.9	7.73	4.3	9.5	6.7	0.711	1.92	4, 15, 16	17
NM	2.26	2.7	20.5	53.7	38.6	12.3	8.03	9.2	2.5	9.4	0.320	—	4, 14, 16	—
Ac	2.89	17.0	12.5	73.5	20.7	9.77	7.58	5.1	3.4	9.5	0.450	1.80	5, 14, 16	17
Dox	4.02	14.8	10.8	85.2	2.21	9.74	8.55	0.9	3.6	14.2	0.438	1.80	4, 14, 16	6
$CHCl_3$	1.94	7	23.1	80.5	4.81	9.21	8.85	1.5	2.8	15.9	0.093	0.57	4, 2, 16	17
Et_2O	3.10	19.2	3.9	104	4.34	7.62	7.05	1.4	2.5	—	—	0.54	5, 14, 16	17
NB	1.95	4.4	14.8	102	34.8	10.6	9.73	6.0	2.0	16.5	0.104	1.15	4, 14, 16	17
Bz	1.58	0.1	8.2	89.1	2.28	9.15	9.03	0.5	1.0	20.5	−0.071	−0.30	4, 14, 16	17
CCl_4	1.07	3	8.6	96.5	2.24	8.65	7.85	0	0	20.3	−0.051	0.34	4, 2, 16	17
Hep	—	0	0	147	2	7.2	7.2	0	0	19.2	—	−0.30	—, 2, 16	—
Oct	—	0	0	164	1.95	—	—	0	0	20.1	—	−0.30	—, 2, 16	—
BuOH	4.1	—	—	91.8	17.8	11.3	7.81	2.8	7.7	13.7	−0.027	1.15	4, —, —	17
Tol	1.55	—	—	106	2.4	8.91	8.67	0.7	1.0	18.0	0.068	0.32	4, —, —	17
AcN	2.60	14.1	18.9	52.9	37.5	11.8	7.90	8.8	3.0	—	0.149	—	4, 14, 16	—
MeAc	2.84	16.5	—	79.7	6.7	9.49	7.56	—	—	—	0.176	1.91	5, 14, —	17
THF	3.14	20.0	8.0	74.0	7.6	9.52	9.25	2.8	3.9	—	0.185	—	4, 14, 16	—
EtAc	2.90	17.1	—	98.5	6.0	9.10	7.44	2.6	4.5	13.7	0.342	1.74	5, 14, —	17

Abbreviations: FA—Formamide, Py—Pyridine, NM—Nitromethane, Ac—Acetone, Dox—Dioxane, NB—Nitro-benzene, Bz—Benzene, Hep-*n*—Heptane, Oct—Isooctante, Tol—Toluene, AcN—Acetonitrile DN—Donor number, AN—Acceptor number, MV—Molar volume, ε—Dielectric constant, δ_0—Solubility parameter, δ_d—Dispersive component of δ_0, δ_p—Polar component, δ_h—hydrogen bonding component.

Interactions with cellulose/lignocellulose

The usual way to determine the acid-base properties of a solid surface is to measure its interactions with a series of liquids with known acidity and basicity. Methods such as contact angle and adsorption enthalpy measurements have been used to determine the interaction energy.[1]

For a porous, swelling polymeric material such as lignocellulose these methods are cumbersome and of limited accuracy. However, in the literature there is a considerable amount of data for interactions with cellulose and lignocellulose determined with other methods. These include† volumetric swelling measurements of softwoods[6,17], chemical accessibility measurements of cellulose swollen in various liquids[7] and measurements of the tensile energy absorption (TEA) of paper sheets soaked in liquids.[8] The authors of these investigations have, as a rule, obtained rather loose correlations with traditional solvent properties, *e.g.* dielectric constant, cohesive energy density, molar volume and qualitative hydrogen bonding properties.

DATA ANALYSIS

In Table I we have compiled published data for 23 different liquids. The data include acid-base parameters as described above, molar volume (MV)[9] and dielectric constant (ε)[9] together with the Hildebrand solubility parameter (δ_0) (the square root of the cohesive energy density) and its dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) components according to Hansen.[10] The interactions between the liquids and cellulose/lignocellulose have been characterized with the three methods described above. The swelling and the accessibility values have been transformed to the logarithms to distribute the data more evenly over the interval and to give a better linear correlation with the liquid parameters.

In an initial correlation investigation, the three interaction variables (TEA, swelling and accessibility) were chosen as dependent variables. These were individually correlated with each liquid characterization variable using standard linear regression analysis.

† A more detailed description is given in Appendix 1.

TABLE II
Correlation coefficients (r) from linear regression analysis

Independent variable	Correlation TEA	Coefficients for dependent variables lg (Accessibility)	lg (Swelling + 0.5)
$D_{II,I}$	−0.86	0.80	0.76
DN	−0.86	0.76	0.85
AN	−0.75	0.69	0.71
MV	0.78	−0.72	−0.77
ε	−0.71	0.60	0.49
δ_0	−0.75	0.68	0.55
δ_d	0.20	−0.24	−0.10
δ_p	−0.81	0.65	0.67
δ_h	−0.79	0.69	0.69

Symbols: DN—Donor number, AN—Acceptor number, MV—Molar volume, ε—Dielectric constant, δ_0—Solubility parameter, δ_d—Dispersive component of δ_0, δ_p—Polar component of δ_0, δ_h—Hydrogen bonding component of δ_0, TEA—tensile energy absorption.

The correlation coefficients were calculated and are compiled in Table II. Evidently, all independent variables except the dispersive component of the solubility parameter show some degree of correlation. The best correlation is, however, invariably obtained with either the donor number or the $D_{II,I}$ parameter. The second best is either the other of these two variables or, in the case of volumetric swelling, the MV. The correlation with the other variables is, over all, considerably lower.

For a more sophisticated data treatment we have resorted to an extended form of principal component analysis, named *P*artial *L*east *S*quares Modelling with Latent Variables (PLS)[11,12]. This method is very useful for studying the dependence of a data matrix Y on another matrix X, especially when the number of variables is large and when the X variables are intercorrelated. It is based upon the approximation of the multivariable X and Y matrices by two simplified matrices, termed T and U respectively. The T and U matrices are projections of the X and Y matrices with few and orthogonal columns. The projection is performed using principal component analysis and cross validation for checking the number of relevant dimensions in the T and U matrices. The T and U matrices are then modified to develop a model such that T predicts U on a linear regression basis, while they still approximate the X and Y

TABLE III
Partial least squares modelling with latent variables (PLS) analysis

Independent variables used in the PLS model	Percentage of the variance in the dependent variables accounted for ($100 \cdot r^2$) by the PLS model		
	TEA	lg (Accessibility)	lg (Swelling + 0.5)
$D_{II,I}$, DN, AN, MV, ε, δ_0, δ_d, δ_p, δ_h	87.2	74.4	79.8
MV, ε, δ_0, δ_d, δ_p, δ_h	64.6	54.2	40.1
$D_{II,I}$, DN, AN, MV	84.5	73.7	75.4
$D_{II,I}$, DN, AN	82.9	75.1	75.9
$D_{II,I}$, DN, MV	85.6	71.7	79.6
$D_{II,I}$, DN	78.5	68.0	76.8

Symbols: DN—Donor number, AN—Acceptor number, MV—Molar volume, ε—Dielectric constant, δ_0—Solubility parameter, δ_d—Dispersive component of δ_0, δ_p—Polar component of δ_0, δ_h—Hydrogen bonding component of δ_0, TEA—Tensile energy absorption.

matrices. To evaluate this model, predicted values of the Y variables are calculated for each object and the residual variance in the Y variables is determined. For the analysis we have used the program package SIMCA, supplied by Sepanova AB, Stockholm, Sweden, using an ABC-806 8-bit microcomputer. The results are shown in Table III and in Figures 1–3.

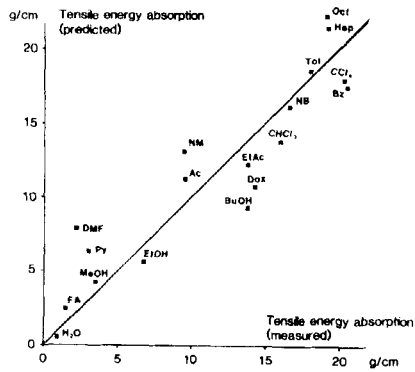

FIGURE 1 Plot of the PLS predictions for the tensile energy absorption against the original data. Abbreviations: see Table I.

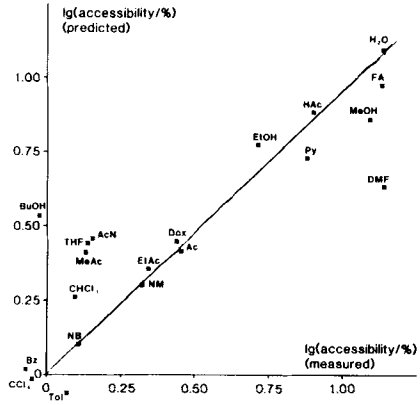

FIGURE 2 Plot of the PLS predictions for the accessibility against the original data. Abbreviations: see Table I.

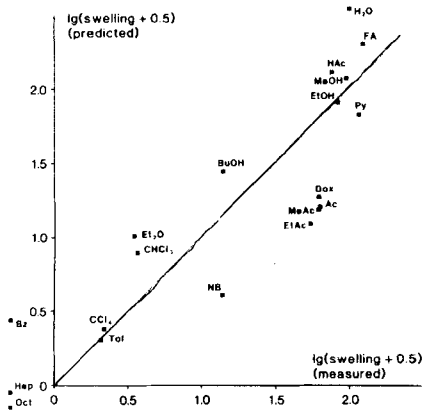

FIGURE 3 Plot of the PLS predictions for the volumetric swelling against the original data. Abbreviations: see Table I.

RESULTS

The analysis shows that the TEA is the variable best described by the independent variables. This is also to be expected since the breaking of fiber–fiber bonds in a soaked paper sheet mainly involves interactions at the fiber–fiber interface. The volumetric swelling and the accessibility measurements both involve the

penetration of molecules into the cellulose/lignocellulose matrix. In this matrix steric factors not completely accounted for in the independent variables may have a considerable influence. Nevertheless, even for these two vaiables, 75–80% of the variance can be accounted for with the PLS model using all variables. As a point of interest, values for the tensile strength of paper taken from Ref. 8 were also evaluted with the PLS method. The results were almost identical to the results for the TEA values.

To provide a more simplified model we have successively removed certain independent variables and calculated the residual variances for the reduced data matrix. As Table III shows, removing the acid-base parameters is disastrous for the model whereas removing the solubility parameters and the dielectric constant only deteriorates the fit to a small extent. Further removal of either the acceptor number or the MV only affects the fit slightly, while the removal of both deteriorates the fit. We can thus conclude that the interactions between cellulose/lignocellulose and the liquids studied can be reasonably well described by the basicity of the liquids and either the acidity or the MV of the liquids. (Incidentally, these two latter variables are highly correlated with each other). This imples that cellulose is mainly acidic, although it also possesses a certain amphotericity.

These observations are in general agreement with those of Koppel and Pal'm[18] who have studied the influence of solvents on organic reactivity. These researchers have offered the relationship

$$A = A_0 + yY + pP + eE + bB$$

where

A = the solvent-sensitive characteristic for any given reaction
Y = polarity
P = polarizability
E = electrophilic solvent power (Lewis acidity)
B = nucleophilic solvent power (Lewis basicity)

for studying solvent–solute interactions. Our work identified factors E and B as the most important along with the involvement of the molecular volume.

Next we plotted the predicted values for each dependent variable, using the PLS model with $D_{II,I}$, DN, AN and MV as independent

variables, against the original measured values. The plots are shown in Figures 1, 2 and 3 and indicate that the relationships are fairly linear. In all three figures and especially in Figure 2 it can be noted that the linearity might have been further improved by treating the protic species (water, methanol, ethanol, butanol and acetic acid) separately. This operation would, however, be somewhat dubious due to the limited number of data points.

Having thus identified the importance of the basicity and either the acidity or the molar volume, we explored the possibility that simple relationships between these values and the physical properties of adhering systems may exist. In earlier work Schleicher[13] noted that the squared sum of the donor and acceptor values (based on Gutmann's values) were weakly correlated with the amount of liquid retained in pulp pads subjected to high gravitational loads during centrifugation. Fowkes attempted to relate either basicity *or* acidity to the adhesion between polymers and inorganic surfaces[1]. Our calculations, which show that optimal results may be achieved by accounting for the potential amphotericity of commonly encountered surfaces, are directed at understanding the strength of paper. We aim at building simple mathematical models relating the TEA of paper soaked in various organic liquids[8] with the donor *and* acceptor values for those liquids. Figure 4 shows that the square root of the sum of DN and AN shows a good relationship with the

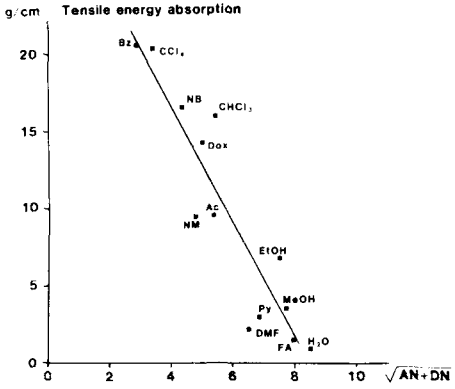

FIGURE 4 Plot of TEA against the square root of the sum of the DN and AN values. Abbreviations: see Table I.

TEA of paper, making it possible to account for approximately 85% of the variance of the strength of paper. No fundamental reason can be offered why this relationship takes the form of the square root of DN + AN.

Paper is often thought of as developing its strength from hydrogen bonds. As mentioned earlier, acid-base interactions can be thought of as a generalization and quantification of the hydrogen bond concept where the bonds possess a wide range of strength values. The values for DN and AN are experimentally determined, empirical values which have their fundamental roots in the bond lengths and bond strengths of shared electron pairs, the grist of quantum mechanics. Thus, it is possible to interpret the abscissa of Figure 4 as an energy spectrum, showing the range of secondary bond strengths present in paper.

Paper provides a surface for adhesives to act upon. The results of our study show that cellulose is amphoteric with primarily acidic qualities. This is reflected in the nature of adhesives used to bond paper substrates; amines and amides (basic), polyalcohols (amphoteric) and phenolics (acid) all being suitable for adhesively bonding to paper. This work also shows that the TEA of paper, a system of fibers bonded to fibers, can also be understood in terms of Lewis acids and bases *via* the square root of DN + AN. This work plus the previously mentioned work of Fowkes suggests that donor and acceptor numbers represents a fundamental way of understanding bonded systems. We presume that similar analyses may apply to all bonded systems.

CONCLUSIONS

The interactions of liquids with cellulose are best described with the acid-base parameters and the molar volume of the liquids in such a way that high basicity, high acidity and low molar volume give strong interactions. From this point of view we conclude that cellulose towards the studied set of liquids is amphoteric but predominantly acidic, since the liquid basicity is the dominating factor. Factors such as dielectric constant and solubility parameters show weaker correlations to the measured dependent variables.

It is possible to account for approximately 85% of the strength

variance of paper when soaked in a variety of organic liquids by correlating the retained strength with the square root of the sum of the donor number and the acceptor number.

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