solvent-separated pairs by $MgSO_4$ and $MnSO_4$ in water has been measured[21] as 7.3 and 7.4 ml mol^{-1}, respectively.

Conclusions

Our researches on the volume changes which accompany the selective binding of ions by polyelectrolyte gels have led us to the following tentative conclusions.

(1) The binding of singly charged counterions by lightly cross-linked polystyrenesulfonate gels is non-localized (i.e., no site binding) except possibly for Ag^+ ion. Alkaline earth, rare earth, and thorium ions appear to be site bound; solvent-separated ion pairs may be formed.

(2) With moderately and heavily cross-linked gels site binding of all cations except H^+ and Li^+ appears to occur. With singly charged cations the magnitude of ΔV is such that solvent-separated ion pairs are implied. Ba^{2+}, La^{3+}, and Th^{4+} ions, however, appear to form contact ion pairs. The release of water of coordination and changes in water structure are indicated by the positive entropy changes observed.

(3) The selective uptake of the larger tetraalkyl-ammonium cations by lightly cross-linked polystyrene-sulfonate gels appears to involve "structure-enforced"

bonding.[22] The ΔV values are negative and the selective uptake of large R_4N^+ ions is determined by the relatively large entropy increase in the reaction. The volume decrease and entropy increase can be explained by assuming that the "ice like" structure of the external water is destroyed when large, quaternary ammonium ions enter the gel.

(4) The selective binding of the heavier halide ions, especially I^- ion, appears to be a consequence of "charge-transfer complex formation" with the aromatic groups of the exchanger.

(5) The Katchalsky theory of ion-exchange selectivity in lightly cross-linked gels appears to be valid for the alkali-metal cations where field binding dominates. Multiply charged cations show significant site binding, however.

(6) The Rice–Harris theory of ion-exchange selectivity which is based on the assumption of extensive ion-pair formation appears to be supported by the ΔV measurements. Solvent-separated and contact ion pairs evidently occur.

(21) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).

(22) R. M. Diamond and D. C. Whitney, "Ion Exchange," Vol. I, J. A. Marinsky, Ed., Marcel Dekker, New York, N. Y., 1966, p 227.

Thermodynamics of Molecular Association by Gas–Liquid Chromatography. VII. Hydrogen Bonding of Aliphatic Alcohols to Di-n-octyl Ether, Di-n-octyl Thioether, and Di-n-octylmethylamine

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Abstract: Equilibrium constants, enthalpies, and entropies of hydrogen bonding between six aliphatic alcohols and the electron donors of the title have been determined by gas–liquid chromatography in the range 30 to 60°. The equilibrium constants follow the general trend expected on the basis of alkyl group inductive and steric effects. The enthalpies are correlated within experimental error by the equation $|\Delta H_{ij}| = Q_i{}^aQ_j{}^b$, where the Q's represent parameters for acid i and base j, respectively. The ratios of the base parameter values for the amine, ether, and thioether are respectively 2.02:1.48:1.00, in good agreement with previously determined nmr ratios for haloform hydrogen bonding (2.01:1.49:1.00). The enthalpies are also analyzed in terms of Drago's double-scale equation for ΔH of adduct formation. Finally, all systems follow a common linear plot of ΔH vs. ΔS.

This paper represents a further contribution to the systematic study of molecular association in binary nonelectrolytic solutions by gas–liquid chromatography (glc)[1-5] and auxiliary techniques.[6] In 1968 we proposed a quantitative glc method for obtaining thermo-

dynamic parameters (K, ΔH, and ΔS) of 1:1 organic complex formation and applied it to study the hydrogen bonding of eight aliphatic alcohols to di-n-octyl ether and di-n-octyl ketone.[1] Recently, this method was used to investigate the association of various halo-alkanes with di-n-octyl ether and di-n-octyl thioether[2] and with di-n-octylmethylamine and tri-n-hexylamine;[4] n-octadecane was the "reference" liquid phase (chosen to have approximately the same molecular size, shape, and polarizability as the electron donor liquid phase[1,2,4,5]). In conjunction with these association studies, alternative procedures have been developed[7] for obtaining the required bulk (liquid/vapor) partition

(1) Paper I: D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968).

(2) Paper II: J. P. Sheridan, D. E. Martire, and Y. B. Tewari, *J. Amer. Chem. Soc.*, **94**, 3294 (1972).

(3) Paper III: J. P. Sheridan, M. A. Capeless, and D. E. Martire, *J. Amer. Chem. Soc.*, **94**, 3298 (1972).

(4) Paper IV: J. P. Sheridan, D. E. Martire, and F. P. Banda, *J. Amer. Chem. Soc.*, **95**, 4788 (1973).

(5) Paper V: H.-L. Liao and D. E. Martire, *Anal. Chem.*, **45**, 2087 (1973).

(6) Paper VI: J. P. Sheridan, D. E. Martire, and S. E. O'Donnell, *J. Amer. Chem. Soc.*, submitted for publication.

(7) H.-L. Liao and D. E. Martire, *Anal. Chem.*, **44**, 498 (1972).

coefficients or specific retention volumes (V_g^0) when a multiple sorption mechanism (i.e., concurrent solution and adsorption) exists in the glc column. With *n*-octadecane as the liquid phase at 40.0°, *n*-propyl alcohol and *sec*-butyl alcohol were found to adsorb on the solid support and at the gas–liquid interface.[7] This resulted in asymmetric peaks and in peak maximum V_g^0 values which varied with sample size and liquid phase weight fraction and necessitated an extrapolation procedure to extract the infinite dilution bulk V_g^0 value.[7] In our previous study with alcohol solutes[1] no account was taken of solute adsorption at the gas–liquid interface, suggesting that these earlier measurements might contain small systematic error.[7]

Accordingly, the present glc study was undertaken to critically examine our earlier alcohol measurements[1] and to perform a systematic comparison of the hydrogen bonding of a series of alcohols to an ether base (di-*n*-octyl ether), a thioether base (di-*n*-octyl thioether), and a tertiary amine base (di-*n*-octylmethylamine). The need for systematic studies of this type was documented in 1960[8] and still exists at present.[9] The many advantages of the glc method for hydrogen bonding studies have been described before.[1,2] For the present systems, in particular, there is no danger of complications due to alcohol self-association or termolecular acceptor–donor complexes.[1,5] It follows then that the thermodynamic association parameters obtained will be representative of 1:1 (acceptor:donor) complexes only.

Thermodynamic Association Parameters from Glc[1]

Consider the equilibrium for complex formation (AD) between an electron acceptor (A) and an electron donor (D)

$$A + D \rightleftharpoons AD$$

$$K = a_{AD}/a_A a_D \qquad (1)$$
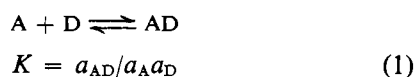
where K is the thermodynamic (as opposed to stoichiometric) association constant and a_i is the activity of species i with the convention that $a_i \rightarrow c_i$ as $c_i \rightarrow 0$ (i.e., $\gamma_i \rightarrow 1$ as $c_i \rightarrow 0$, where γ_i is the activity coefficient). If the acceptor is always present under infinite dilution conditions (as the solute species would be in glc experiments), then $a_{AD} = c_{AD}$ and $a_A = c_A$. Thus

$$K' = K a_D = K \gamma_D c_D = c_{AD}/c_A \qquad (2)$$

where K' is a constant and c_D is the concentration of the pure electron donor (the liquid phase in the glc experiment).

Martire and Riedl[1] have derived the following expression for obtaining K' from glc measurement of solute specific retention volumes (V_g^0)

$$K' + 1 = \frac{(V_g^0)_D (\bar{V}_g^0)_R}{(V_g^0)_R (\bar{V}_g^0)_D} \qquad (3)$$

where the terms without bars refer to the electron acceptor solute, the terms with bars to an alkane solute, the subscript D to the electron donor liquid phase, and the subscript R to a "reference" alkane liquid phase. The reference, which is chosen to have approximately

the same molecular size, shape, and polarizability as the electron donor, is supposed to take account of the nonspecific interactions between the donor and acceptor. Equation 3 is applicable to donors which do not self-associate, preferably those with a single well-defined donor site (e.g., a di-*n*-alkyl ether). Finally, the activity coefficient of the pure electron donor can be estimated from the following derived expression[1]

$$\gamma_D = (\bar{V}_g^0)_D M_D / (\bar{V}_g^0)_R M_R \qquad (4)$$

Thus, from knowledge of the donor molecular weight (M_D), the reference molecular weight (M_R), and the donor liquid density and from the measurement of four specific retention volumes, one can determine the equilibrium constant for donor–acceptor complex formation through eq 2–4. By determining K at several temperatures, one can also obtain the thermodynamic parameters ΔH and ΔS, the enthalpy and entropy, respectively. The validity of the assumptions employed in this approach was demonstrated in a recent publication.[5] Note that the specific retention volumes referred to in the above equations are infinite dilution bulk (liquid/vapor) quantities.[5]

Experimental Section

Liquid Phases. The source, purification procedure, purity determination, and densities for the electron donors, di-*n*-octyl ether (DOE), di-*n*-octyl thioether (DOTE), and di-*n*-octylmethylamine (DOMA), and the reference, *n*-octadecane (OD), are given elsewhere.[2,4]

Solutes. The electron acceptors (hydrogen donors), methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, *sec*-butyl alcohol, and *tert*-butyl alcohol, were J. T. Baker analyzed grade. Subsequent glc studies indicated that no major impurities were present and that minor impurities were sufficiently removed from the solute peak so as to offer no complications.[7]

Apparatus. The glc apparatus used in this study has been described before.[1,10] A Perkin–Elmer hot-wire thermal conductivity detector (P-E part no. 008-0686) and Sargent SR-G 1-mV recorder were employed. All external tubing connections were wrapped with heating tape to prevent solute condensation.

Preparation of Columns. The solid support material used was Johns-Manville Chromosorb W, 60–80 mesh, acid washed and DMCS treated. The supports were coated with the liquid phases in the usual manner and packed into 0.25-in. o.d. copper tubing. Column lengths of 4.0, 3.0, 3.3, and 2.5 ft, respectively, were used for OD, DOE, DOTE, and DOMA. For each liquid phase four columns, each containing a different weight fraction of liquid phase, were made. The exact liquid weight fractions (weight of liquid phase/weight of packing), determined by a previously described ashing procedure,[1] were: for OD (0.0717, 0.0999, 0.1498, and 0.2448), for DOE (0.0758, 0.1051, 0.1495, and 0.2379), for DOTE (0.0791, 0.1030, 0.1548, and 0.2504), and for DOMA (0.0848, 0.0990, 0.1483, and 0.2475).

Procedure. The determination of association constants requires infinite dilution bulk V_g^0's for the alcohol solutes in the electron donor and reference liquid phases (see eq 2–4). The procedure used for obtaining these values was the "modified Martire-Riedl method" described previously.[7] Briefly, the detector block temperature (210° here), detector current, and recorder setting are held constant for a given column. At least seven elution peaks, corresponding to sample sizes ranging from about 0.3 to 5.0 μl, of constant initial retention time are recorded with each column. The infinite dilution peak maximum retention time is obtained by plotting the observed peak maximum retention time against sample size (proportional to the peak area, measured with a planimeter) and extrapolating to zero sample size. The extrapolated retention time is converted to an infinite dilution specific retention volume in the usual manner.[10] This procedure corrects for adsorption of the solute on the solid support[1] (observed with all of the alcohols) but

(8) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(9) G. C. Pimentel and A. L. McClellan, *Annu. Rev. Phys. Chem.*, 22, 347 (1971), and references therein.

(10) Y. B. Tewari, D. E. Martire, and J. P. Sheridan, *J. Phys. Chem.*, 74, 2345 (1970).

not for any gas–liquid interfacial adsorption that may exist.[7] Accordingly, the infinite dilution V_g^0 values obtained on the four columns for a given liquid phase are then plotted against the reciprocal weight fraction of the liquid phase (f^{-1}), consistent with the derived equation[7]

$$(V_g^0) = (V_g^0)^{\text{bulk}} + \frac{K_I A_I' 273.2}{fT} \qquad (5)$$

where $(V_g^0)^{\text{bulk}}$ is the desired infinite dilution bulk specific retention volume, T is the experimental temperature in Kelvin, and K_I and A_I' are respectively the partition coefficient and surface area per gram of packing relevant to gas–liquid interfacial adsorption. (The second term on the right-hand side of eq 5 may be regarded as $(V_g^0)^{\text{interfacial}}$.) If V_g^0 is found to be independent of f^{-1}, yielding a straight line of zero slope and intercept $(V_g^0)^{\text{bulk}}$, this would be a clear indication of the absence of liquid surface effects for the system in question. On the other hand, if V_g^0 is observed to increase with increasing f^{-1}, then liquid surface effects exist and $(V_g^0)^{\text{bulk}}$ is determined by extrapolation to $f^{-1} = 0$. The final procedural step of note is the use of four alkane solutes (n-hexane, 3-methylpentane, 2,3-dimethylbutane, and 2,4-dimethylpentane) as standards for calibrating the present V_g^0 values with those previously determined[2,4] on OD, DOE, DOTE, and DOMA and for correcting for some minor day-to-day liquid phase bleeding from the column.

Results

Infinite dilution V_g^0 values were obtained at 30.0, 40.0, 50.0, and 60.0° for the alcohol solutes on four columns of different liquid weight fraction (f) for each of the liquid phases (OD, DOE, DOTE, and DOMA). With DOE and DOMA, V_g^0 was found to be independent of f^{-1} (see eq 5) for all alcohols at all temperatures. Hence, the infinite dilution bulk V_g^0's listed in Table I

Table I. Infinite Dilution Bulk Specific Retention Volumes with Di-n-octyl Ether and Di-n-octylmethylamine[a]

Solute	30°	40°	50°	60°
Di-n-octyl Ether				
Methanol	53.4	33.7	22.2	15.2
Ethanol	117.1	72.7	47.1	31.8
n-Propyl alcohol	395.5	237.3	149.2	98.2
Isopropyl alcohol	180.6	112.9	73.7	50.1
n-Butyl alcohol	1304	742	444.6	279.9
Isobutyl alcohol	882	512	312.0	199.5
sec-Butyl alcohol	585	349.4	219.0	143.5
tert-Butyl alcohol	235.4	147.2	96.0	65.3
Di-n-octylmethylamine				
Methanol	101.7	62.3	39.4	25.6
Ethanol	200.1	121.0	75.4	48.3
n-Propyl alcohol	698	400.9	238.4	146.3
Isopropyl alcohol	262.2	159.3	99.8	64.3
n-Butyl alcohol	2330	1262	710	413.1
Isobutyl alcohol	1643	900	511	300.6
sec-Butyl alcohol	858	495.6	296.3	182.7
tert-Butyl alcohol	292.7	181.1	115.4	75.6

[a] No evidence of adsorption at the gas–liquid interface was found for any of these systems.

were determined by averaging the values for the four column loadings used. The results for methanol and ethanol are included in Table I for future reference but should be regarded as tentative, given the short retention times (for DOE) and scatter (for DOE and DOMA) observed. Excluding these two alcohols, the average standard deviation is about 1.2% with the DOE systems and 0.4% with DOMA. Comparison with our earlier DOE V_g^0 measurements for the C_3 and C_4 alcohols at 30, 40, and 50°[1] indicates an average discrepancy of less than 2%, with the largest discrepancy (for the n-butyl alcohol–DOE system at 40°) being less

than 4%. Further, our new V_g^0 value for isopropyl alcohol–DOE at 50° gives an infinite dilution activity coefficient of 5.46,[1] which is in excellent agreement with the values of 5.5 ± 0.1 and 5.5 ± 0.3 determined from elution and frontal chromatography, respectively.[11]

With OD and DOTE, V_g^0 was found to increase with increasing f^{-1} for most of the alcohols at the lower temperatures. The results are summarized in Table II.

Table II. Infinite Dilution Bulk Specific Retention Volumes with n-Octadecane and Di-n-octyl Thioether[d]

Solute	30°	40°	50°	60°
n-Octadecane				
n-Propyl alcohol	80.9[a]	59.4[a]	44.5[c]	33.8*
Isopropyl alcohol	45.9[b]	34.0[c]	25.7*	19.7*
n-Butyl alcohol	276.1[a]	192.1[b]	136.8[c]	99.4*
Isobutyl alcohol	186.6[b]	132.9[b]	96.7[c]	71.7*
sec-Butyl alcohol	166.8[b]	118.0[c]	85.3*	62.8*
tert-Butyl alcohol	78.1*	56.7*	42.0*	31.6*
Di-n-octyl Thioether				
Methanol	28.3[b]	20.2[c]	14.6*	10.8*
Ethanol	69.3[b]	47.9[c]	34.2*	25.3*
n-Propyl alcohol	235.0[b]	158.7[c]	110.0*	77.8*
Isopropyl alcohol	117.9[c]	80.8*	57.3*	42.0*
n-Butyl alcohol	805[b]	509[c]	331.4*	221.2*
Isobutyl alcohol	552[c]	349.3*	230.4*	158.5*
sec-Butyl alcohol	405.3[c]	266.7*	180.2*	124.7*
tert-Butyl alcohol	175.2*	118.2*	82.6*	59.9*

[a] 10–15% interfacial contribution to total V_g^0. [b] 5–10% interfacial contribution to total V_g^0. [c] 2–5% interfacial contribution to total V_g^0, where the per cent interfacial contribution is $100[(V_g^0) - (V_g^0)^{\text{bulk}}]/(V_g^0)$. [d] An asterisk denotes no observable adsorption at the gas–liquid interface.

The values marked with asterisks represent average V_g^0 values for the four columns of the liquid phase; these systems and temperatures did not exhibit liquid surface effects. The average standard deviation is about 1.3% for the asterisked OD systems and about 0.8% for the asterisked DOTE systems (again, excluding methanol and ethanol). Infinite dilution bulk V_g^0 values for the other systems and temperatures were determined from the intercepts of linear V_g^0 against f^{-1} plots (see eq 5). The extent of solute adsorption at the gas–liquid interface is indicated (see superscripts and footnotes) for each system in Table II. The largest per cent interfacial contribution to V_g^0 was observed for n-propyl alcohol at 30°, for which $(V_g^0)^{\text{interfacial}}$ constitutes about 13% of the total V_g^0 with OD (at $f = 0.0717$) and about 8% of the total with DOTE (at $f = 0.0791$). For all systems the percentage decreases rapidly with increasing temperature (as expected[12]), becoming negligible at 60° (50° for DOTE). These findings confirm the suggestion[7] that the V_g^0 values for the alcohol–n-heptadecane systems in ref 1 are up to 10% too large as a result of failure to account for liquid surface effects. Hence, the thermodynamic association parameters reported there[1] should be regarded as semiquantitative, although the general trends and magnitudes are correct (see later).

Listed in Table III are the values for $[(\bar{V}_g^0)_R/(\bar{V}_g^0)_D]$, c_D, and γ_D from ref 2 and 4. With these values and the results from Tables I and II, the association constants

(11) J. F. Parcher and C. L. Hussey, *Anal. Chem.*, **45**, 188 (1973).

(12) D. E. Martire, "Progress in Gas Chromatography," J. H. Purnell, Ed., Interscience, New York, N. Y., 1968, p 93, and references therein.

Table III. Values of $[(V_g^0)_R/(V_g^0)_D]$, c_D (mol/l.), and γ_D for DOE and DOTE[2] and for DOMA[4]

	30°	40°	50°	60°
	Di-*n*-octyl Ether			
$[(V_g^0)_R/(V_g^0)_D]$	0.987	1.005	1.022	1.039
c_D	3.299	3.270	3.241	3.212
γ_D	0.966	0.948	0.932	0.917
	Di-*n*-octyl Thioether			
$[(V_g^0)_R/(V_g^0)_D]$	1.089	1.087	1.085	1.083
c_D	3.238	3.211	3.184	3.157
γ_D	0.932	0.934	0.936	0.938
	Di-*n*-octylmethylamine			
$[(V_g^0)_R/(V_g^0)_D]$	1.004	1.012	1.018	1.024
c_D	3.096	3.072	3.045	3.018
γ_D	1.000	0.993	0.986	0.981

Table IV. Equilibrium Constants K (l. mol^{-1}) with Di-*n*-octyl Ether, Di-*n*-octyl Thioether, and Di-*n*-octylmethylamine

	30°	40°	50°	60°
	Di-*n*-octyl Ether			
n-Propyl alcohol	1.200	0.973	0.803	0.685
Isopropyl alcohol	0.905	0.754	0.639	0.558
n-Butyl alcohol	1.149	0.930	0.769	0.654
Isobutyl alcohol	1.150	0.926	0.761	0.642
sec-Butyl alcohol	0.772	0.637	0.538	0.467
tert-Butyl alcohol	0.620	0.519	0.442	0.389
	Di-*n*-octyl Thioether			
n-Propyl alcohol	0.717	0.635	0.564	0.504
Isopropyl alcohol	0.596	0.528	0.476	0.442
n-Butyl alcohol	0.721	0.627	0.546	0.476
Isobutyl alcohol	0.736	0.619	0.532	0.471
sec-Butyl alcohol	0.545	0.486	0.434	0.389
tert-Butyl alcohol	0.478	0.422	0.380	0.356
	Di-*n*-octylmethylamine			
n-Propyl alcohol	2.475	1.911	1.484	1.159
Isopropyl alcohol	1.529	1.227	0.984	0.791
n-Butyl alcohol	2.414	1.852	1.427	1.100
Isobutyl alcohol	2.532	1.919	1.459	1.112
sec-Butyl alcohol	1.345	1.066	0.845	0.668
tert-Butyl alcohol	0.892	0.732	0.599	0.490

Discussion

We observe (as before[1]) that the association constants in all three bases follow the general trend $1 > 3 > 4 > 2 > 5 > 6$ (see Table V for numbering code), which is exactly what one would predict on the basis of alkyl group inductive and steric effects. We also observe that the enthalpies of hydrogen bonding for these systems can be correlated through the simple expression

$$|\Delta H_{ij}| = Q_i{}^a Q_j{}^b \qquad (6)$$

where $Q_i{}^a$ is the enthalpy parameter for acid i and $Q_j{}^b$ is the enthalpy parameter for base j, both referred to an arbitrarily assigned base value of 1.00 for DOTE. The acid parameters (Table VI) clearly follow the trend $4 > 3 > 1 > 5 > 2 > 6$, which has been observed before by us[1] and others.[13] An interpretation of this trend eludes us at present. Most likely it reflects a complex combination of contributions from covalent bonding, electrostatic attraction, and short-range repulsion terms.[9] The base parameter values (Table VI) for DOMA, DOE, and DOTE are in the following proportions, 2.02:1.48:1.00, in good agreement with previously determined[6] ΔH ratios from nmr for haloform hydrogen bonding (2.01:1.49:1.00). Also, the ΔH values retrieved from eq 6 and the assigned Q values agree with the observed ΔH's to within (on the average) experimental error (about 0.1 kcal/mol). This suggests that a single scale equation is sufficient for correlating the enthalpy of hydrogen bonding to *this class* of bases. It also suggests as a useful "rule of thumb" that an aliphatic tertiary amine is approximately 2.0 times stronger and an aliphatic ether 1.5 times stronger (as measured by ΔH) than an aliphatic thioether as a hydrogen bonding base, all bases being of similar aliphatic chain structure.

Drago[14] has proposed a *general* double-scale equation for correlating the enthalpy of adduct formation, *i.e.*

$$-\Delta H = E_A E_B + C_A C_B \qquad (7)$$

Table V. Enthalpies (kcal/mol) and Entropies (eu) of Hydrogen Bond Formation[a]

		DOE		DOTE		DOMA	
		$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
1.	*n*-Propyl alcohol	3.77 (0.09)	12.07 (0.28)	2.36 (0.02)	8.44 (0.06)	5.08 (0.07)	14.93 (0.20)
2.	Isopropyl alcohol	3.25 (0.09)	10.93 (0.28)	2.01 (0.11)	7.68 (0.35)	4.41 (0.08)	13.96 (0.26)
3.	*n*-Butyl alcohol	3.78 (0.08)	12.20 (0.26)	2.78 (0.05)	9.80 (0.15)	5.25 (0.09)	15.57 (0.28)
4.	Isobutyl alcohol	3.91 (0.07)	12.62 (0.22)	3.00 (0.10)	1C.51 (0.33)	5.50 (0.09)	16.29 (0.29)
5.	*sec*-Butyl alcohol	3.37 (0.09)	11.64 (0.30)	2.26 (0.03)	8.65 (0.09)	4.68 (0.10)	14.83 (0.32)
6.	*tert*-Butyl alcohol	3.13 (0.10)	11.30 (0.31)	1.99 (0.15)	8.06 (0.48)	4.01 (0.09)	13.43 (0.28)

[a] Standard deviations in parentheses.

(K) were determined through eq 2–4 and are set out in Table IV. Through the usual formula for propagation of errors, it is estimated that the probable error in the tabulated K values is about 2.0% for the DOE and DOTE systems and about 1.5% for DOMA. Finally, from least-squares linear regression of ln K as a function of reciprocal temperature, ΔH and ΔS were found and are listed in Table V along with the corresponding standard deviations. The thermodynamic parameters for methanol and ethanol hydrogen bonding are not reported due to the poor reproducibility of their V_g^0 values with OD.

where two empirically determined parameters, E_A and C_A, are assigned to each acid and two, E_B and C_B, to each base such that, when substituted in eq 7, they give the observed enthalpy of formation of the acid–base pair. The parameters E_A and E_B are interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interactions and C_A and C_B as the susceptibility to undergo covalent interactions. Taking

(13) D. F. Cadogan and J. H. Purnell, *J. Phys. Chem.*, **73**, 3849 (1969).
(14) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971), and references to previous papers therein.

Table VI. Acid and Base Parameters for Single-Scale (Eq 6) and Double-Scale[14] (Eq 7) Enthalpy Expressions

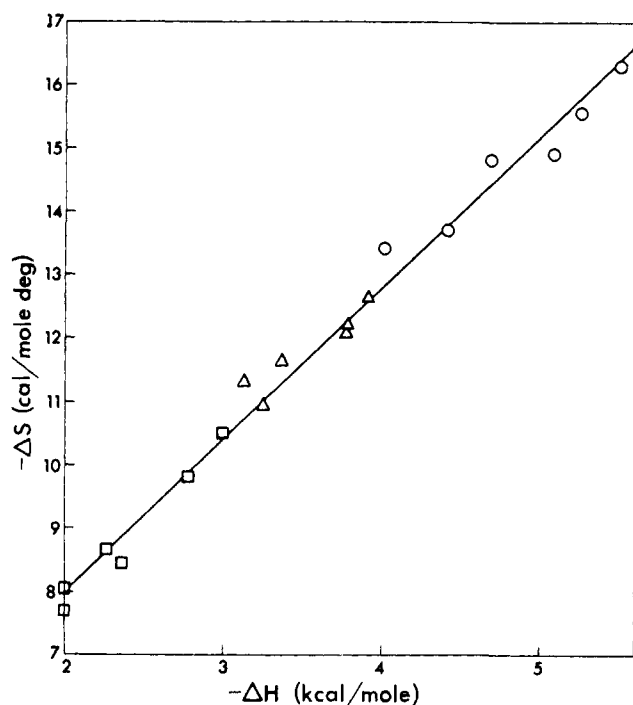| | | Acid parameters | | | | Base parameters | | |
| | | Single scale | Double scale | | | | Single scale | Double scale | |
		Q^a	C_A	E_A			Q^b	C_B	E_B
1.	n-Propyl alcohol	2.49	0.19	2.88					
2.	Isopropyl alcohol	2.15	0.16	2.52		DOE	1.48	3.1	1.1
3.	n-Butyl alcohol	2.63	0.22	2.85					
4.	Isopropyl alcohol	2.76	0.24	2.91		DOTE	1.00	8.3	0.3
5.	sec-Butyl alcohol	2.29	0.19	2.51					
6.	tert-Butyl alcohol	2.03	0.15	2.39		DOMA	2.02	11.2	1.0

Figure 1. $-\Delta S$ vs. $-\Delta H$ for hydrogen bond formation. Best straight line, $|\Delta S| = 2.39|\Delta H| + 3.23$: ($\triangle$) DOE, ($\square$) DOTE, ($\bigcirc$) DOMA.

Drago's values for di-n-butyl ether ($C_B = 3.3$, $E_B = 1.1$), diethyl thioether ($C_B = 7.4$, $E_B = 0.3$), and triethylamine ($C_B = 11.1$, $E_B = 1.0$) as our initial trial values for DOE, DOTE, and DOMA, respectively, a set of acid and base parameters was found which minimized the differences between the retrieved (through eq 7) and experimental ΔH values. This set of parameters (listed in Table VI) produced a maximum difference of ± 0.11 kcal/mol and an average difference of ± 0.06 kcal/mol when compared with the observed ΔH's. The contributions $-\Delta H_C$ ($= C_A C_B$) and $-\Delta H_E$ ($= E_A \cdot E_B$) to the total ΔH were also computed. Taken at face value, the results indicate that, with aliphatic al-

cohols, electrostatic forces account for about 83% of the total hydrogen bond energy with DOE (a "hard" base), about 34% with DOTE (a "soft" base), and about 56% with DOMA (a base with both "hard" and "soft" character[14]).

A plot of $|\Delta S|$ against $|\Delta H|$, including all systems, is shown in Figure 1. An excellent linear correlation is found (correlation coefficient of 0.993), leading to the equation

$$|\Delta S| = 2.39|\Delta H| + 3.23 \qquad (8)$$

with a standard deviation of $\sigma = 0.30$ (the uncertainty to be expected in a prediction of ΔS from a known ΔH). Equation 8 may be combined with either eq 6 or 7 for the purpose of predicting K at a given temperature from known acid and base enthalpy parameters.

Averaging $|\Delta H|$ values for DOE, DOTE, and DOMA, one obtains 3.54, 2.40, and 4.82 kcal/mol, respectively. The value for the ether base is in perfect agreement with the average enthalpy of hydrogen bond formation determined from published values for 17 aliphatic alcohol–aliphatic ether systems,[9] while the value for DOMA is in good agreement with a similarly surveyed value[9] of 4.73 for seven aliphatic alcohol–tertiary amine systems. Along the same lines, Pimentel and McClellan[9] found values ranging from 1.31 to 1.85 (depending on the base), with an average of 1.6 ± 0.2, for the ratio ΔH(phenol):ΔH(alcohol) with a common base. A comparison of ΔH's determined for phenol hydrogen bonding to various dibutyl sulfides[15] (seven in all) with our results for the alcohol–DOTE systems yields a ratio of 1.48, which is in the above range.

These findings support earlier observations[2,6,15] that thioethers are stronger hydrogen bonding bases than originally believed. This study also strengthens our conviction[1,2] that glc is a useful supplementary technique, capable of high precision, for molecular association studies.

(15) V. Sára, J. Moravec, V. Horák, and M. Horák, Collect. Czech. Chem. Commun., 34, 2390 (1969).