Thermodynamics of Molecular Association by Gas–Liquid Chromatography. II. Haloalkane Acceptors with Di-*n*-octyl Ether and Di-*n*-octyl Thioether as Electron Donors

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Abstract: Equilibrium constants, enthalpies, and entropies of complex formation between eleven haloalkane acceptors and the electron donors di-*n*-octyl ether and di-*n*-octyl thioether have been determined by gas–liquid chromatography in the temperature range 30–60°. The results are discussed in terms of the possible contributing stabilizing forces for complex formation: hydrogen bonding, n → σ^* charge transfer, and electrostatic interactions.

The common methods for studying the thermodynamics of molecular association in solution are ir, uv–visible, and nmr spectroscopy. However, the efficacy of these techniques is reduced by various experimental difficulties. Self-association of the donor and/or the acceptor and the poor choice of "inert" diluting solvents are but two of the error causing factors. Much of the data for hydrogen-bond equilibrium constants and enthalpies, for the same donor–acceptor systems obtained by different methods and investigators, often differ far in excess of the stated experimental error.[1]

Recently in this laboratory a gas–liquid chromatographic (glc) method was developed for the thermodynamic study of hydrogen-bond formation.[2] The many advantages of this approach over the commonly used spectroscopic ones have been described.[2] Offsetting these, no obvious disadvantages which are not common to other methods can be discerned, except the requirement of a nonvolatile electron donor.

In this initial study,[3] we investigated eight alcohols (methanol, ethanol, the propanols, and the butanols) in di-*n*-octyl ether and di-*n*-octyl ketone. The results obtained for the equilibrium constants, enthalpies, and entropies (K, ΔH, and ΔS) of hydrogen-bond formation were of high precision and within the ranges normally found for OH–O bonds.[4,5] It was concluded that glc should be very useful for the systematic study of variations in K, ΔH, and ΔS with progressive structural changes in a series of electron donors or electron acceptors. Such studies are now being conducted in this laboratory.

Numerous studies have been made,[6–16] both by ir and nmr spectroscopy, which have established that haloforms complex with various n-electron donors through hydrogen bonding. However, only a few of these have been quantitative (*i.e.*, carried to the point of determining the thermodynamic parameters of complex formation), and most of them on chloroform only. Evidence has also existed (heat of mixing measurements,[17,18] solid–liquid equilibrium curves,[19–21] dipole moment measurements,[22,23] and X-ray crystallographic studies[24,25]) of n → σ^* charge-transfer complexes stabilized by interactions between acceptor halogen atoms on haloalkanes and n-electron donors. The conclusion reached from these studies was that the trend of acceptor strength was I > Br > Cl, while the trend of donor strength was N > S > O. Although some observations of charge-transfer bands have been made, little quantitative thermodynamic information is available on these complexes from uv–visible spectroscopic studies.[26] A possible reason for this is the experimental difficulty encountered with weak-to-moderate strength complexes. The limitations and errors inherent in the Benesi–Hildebrand[27] procedure for the spectrophotometric determination of charge-transfer

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association constants are well known.[28-31] Of the modified procedures that have been proposed, one of the most useful forms is the Scott modification.[32] Other modifications, such as those attributed to Ketelaar[33] or Rose and Drago,[34] are not basically different. Using the Scott equation one often finds that, with precise experimental data, a fairly accurate determination of the product $K\epsilon$ can be made (ϵ = the molar extinction coefficient of the complex). Nevertheless, this method is subject to the same difficulties as the Benesi–Hildebrand approach when applied to the case of weak complexes, *viz.*, that there may be much more serious error involved in the separate determination of K and ϵ.[31] Papers are still being written[35,36] in attempts to reduce the combined effects of approximations and experimental error in evaluation of K from Benesi–Hildebrand type plots. In addition, the usual "inert" solvent effects are there to complicate the interpretation of the spectroscopic results.[37-40]

Accordingly, we are now utilizing the glc method to study the association of various haloalkanes to n-electron donors. Studies on di-*n*-octyl ether and di-*n*-octyl thioether are reported in this paper. However, it should be emphasized that, while glc measurements can yield accurate thermodynamic association parameters, no purely thermodynamic measurement can, by itself, serve to establish the definite existence and the nature of a complex. Thermodynamic evidence alone is circumstantial; spectroscopic and/or other methods (*e.g.*, dipole moment measurements) must be employed to confirm the actual presence of and establish the nature of an associated species.

Particularly difficult to identify and categorize are charge-transfer complexes. The mere appearance of a charge-transfer band is neither conclusive proof of the existence of a complex nor proof that charge-transfer interaction is the main stabilizing force in the formation of the complex, if it does indeed exist. So-called "contact pairing"[29,31,41-43] (*i.e.*, statistical collision pairing) can give rise to such a band. Furthermore, when the complex is weak and the interaction energy is small (less than a few kilocalories), "classical" intermolecular forces, rather than charge transfer can often account for the bulk of the stabilization energy.[44,45] Hence, in the absence of other information, purely thermodynamic results on association must be interpreted with care.

Thermodynamic Association Parameters from Glc[2]

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

$$\mathrm{A} + \mathrm{D} \rightleftharpoons \mathrm{AD}$$

$$K = a_{\mathrm{AD}}/a_{\mathrm{A}}a_{\mathrm{D}} \qquad (1)$$

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 $a_{\mathrm{AD}} = c_{\mathrm{AD}}$ and $a_{\mathrm{A}} = c_{\mathrm{A}}$. Thus

$$K' = Ka_{\mathrm{D}} = K\gamma_{\mathrm{D}}c_{\mathrm{D}} = c_{\mathrm{AD}}/c_{\mathrm{A}} \qquad (2)$$

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

$$K' + 1 = \frac{(V_g^0)_{\mathrm{D}}(\bar{V}_g^0)_{\mathrm{R}}}{(V_g^0)_{\mathrm{R}}(\bar{V}_g^0)_{\mathrm{D}}} \qquad (3)$$

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[2]

$$\gamma_{\mathrm{D}} = \frac{(\bar{V}_g^0)_{\mathrm{D}}}{(\bar{V}_g^0)_{\mathrm{R}}}\frac{M_{\mathrm{D}}}{M_{\mathrm{R}}} \qquad (4)$$

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.

Experimental Section

Liquid Phases. The electron donors, di-*n*-octyl ether and di-*n*-octyl thioether, and the reference, *n*-octadecane, were obtained from Humphrey Chemicals. Only the thioether needed further purification; this was done by vacuum distillation on a Nester-Faust spinning-band column. High-temperature glc then indicated that all liquids had a minimum purity of 99%. The densities of the donors at the experimental temperatures are required for determination of K. These were available for the ether[46] and were determined by pycnometry for the thioether. The data are given in Table I.

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Table I. Densities (g/ml) of the Pure Electron Donors

	30.0°	40.0°	50.0°	60.0°
Di-*n*-octyl ether	0.800	0.793	0.786	0.779
Di-*n*-octyl thioether	0.837	0.830	0.823	0.816

Preparation of Columns. The solid support material used was Johns-Manville Chromosorb W, 60–80 mesh, acid-washed and DMCS treated. Two different coatings were made with each liquid phase, one containing about 8% by weight liquid phase and the other about 12% (except for the runs with CBr_4 where the liquid phase coatings used were 8 and 5%). The exact liquid weight percentages were determined by a combustion or ashing method.[2] The coated supports were packed into 0.25-in. o.d. copper tubing. Lengths of about 5 ft were used as columns for the moderate retention time solutes, and lengths of about 2.5 ft for the long retention time ones. In the case of CBr_4 special conditions had to be employed in view of the extremely long retention times obtained even with the use of the 2.5-ft column of 5% coated support. To reduce retention times and sharpen the peaks 2.5 ft stainless steel columns of $^1/_{16}$-in. o.d. containing 8 and 5% coated supports were prepared.

Solutes. The electron acceptors selected for this study were dichloromethane, bromoform, bromochloromethane, carbon tetrachloride, dibromomethane, bromotrichloromethane, chloroform, carbon tetrabromide, dichlorobromomethane, 1,1,1-trichloroethane, dibromochloromethane. All were commercially available, with the exception of dichlorobromomethane and dibromochloromethane which were gifts from the Dow Chemical Co. Specific retention volumes on some alkane solutes are required for evaluation of *K*. Thus, the following solutes were also studied: *n*-hexane, 3-methylpentane, 2,3-dimethylbutane, 3-methylhexane, and 2,4-dimethylpentane. Since solute purity is not an important consideration here, all were used without further purification.

Apparatus and Procedure. The glc apparatus used in this work is described elsewhere.[2,47] In the present study the detector block temperature was held at about 250° and the injection port at about 220°. The column bath temperature was controlled and measured to within ±0.05°. The general procedure used for obtaining meaningful and accurate specific retention volumes is also described elsewhere.[47] Use of two different liquid loadings (8 and 12%) enabled us to screen our systems for possible interfacial effects. No evidence was found for solute adsorption at either the gas–liquid or liquid–solid interface. For the large majority of our systems the actual V_g^0 measurements were carried out on the 8% columns, although some systems were studied on both the 8% and the 12% ones. In the case of CBr_4, stainless steel $^1/_{16}$-in. o.d. columns were used to obtain most of the data. The CBr_4, being a solid at room temperature, was dissolved in bromobenzene in order to inject it onto the columns. The volumes of liquid phase on the columns were so small that overloading effects were almost inevitable. However, this problem was overcome by injecting several samples of decreasing sample size and extrapolating the peak maximum retention times to zero sample size. The specific retention volumes obtained using the two different loadings agreed to within ±1%. Values were obtained at 40, 50, 60, and 70° for all solvents and plots of log V_g^0 *vs.* $1/T$ yielded good straight lines from which extrapolated values of V_g^0 at 30° were obtained.

Table II. Specific Retention Volumes (cc/g) with *n*-Octadecane

	30°	40°	50°	60°
n-Hexane	410.3	280.0	195.6	139.6
3-Methylpentane	332.4	231.0	164.2	119.1
2,3-Dimethylbutane	271.7	191.1	137.3	100.7
2,4-Dimethylpentane	568.3	383.2	264.8	187.1
3-Methylhexane	947.5	622.0	419.1	289.2
Dichloromethane	94.4	70.3	53.3	41.1
Bromochloromethane	242.7	173.7	126.9	94.5
Dibromomethane	615.9	420.5	293.9	210.0
Chloroform	278.3	197.0	142.4	105.1
Dichlorobromomethane	728.8	493.9	342.9	243.4
Dibromochloromethane	1852	1198	795.0	541.3
Bromoform	4716	2925	1869	1228
Carbon tetrachloride	601.9	411.0	287.4	205.3
Bromotrichloromethane	1577	1030	691.0	474.9
Carbon tetrabromide	26800	15310	9063	5538
1,1,1-Trichloroethane	441.4	306.6	217.8	158.0

Table III. Specific Retention Volumes (cc/g) with Di-*n*-octyl Ether

	30°	40°	50°	60°
n-Hexane	412.2	277.7	191.7	135.3
3-Methylpentane	338.2	230.2	160.5	114.4
2,3-Dimethylbutane	275.9	190.1	134.0	96.5
2,4-Dimethylpentane	579.3	382.2	258.7	179.4
3-Methylhexane	958.8	618.9	410.5	279.1
Dichloromethane	181.1	126.3	90.1	65.6
Bromochloromethane	473.6	314.6	214.3	149.4
Dibromomethane	1215	771.3	503.5	337.4
Chloroform	635.2	408.8	270.3	183.2
Dichlorobromomethane	1696	1045	663.6	433.1
Dibromochloromethane	4368	2536	1523	943.0
Bromoform	11050	6250	3661	2216
Carbon tetrachloride	738.7	487.0	329.4	228.1
Bromotrichloromethane	2141	1327	847.4	555.9
Carbon tetrabromide	38260	20580	11500	6659
1,1,1-Trichloroethane	596.7	396.3	269.8	188.1

Table IV. Specific Retention Volumes (cc/g) with Di-*n*-octyl Thioether

	30°	40°	50°	60°
n-Hexane	376.0	257.3	180.3	129.0
3-Methylpentane	307.0	213.4	151.7	110.1
2,3-Dimethylbutane	249.1	175.8	126.9	93.3
2,4-Dimethylpentane	518.1	350.0	242.3	171.5
3-Methylhexane	873.0	573.6	386.8	267.1
Dichloromethane	180.6	129.6	95.0	71.0
Bromochloromethane	496.7	340.6	239.0	171.4
Dibromomethane	1342	878.6	590.5	406.5
Chloroform	577.9	387.3	266.1	186.9
Dichlorobromomethane	1681	1073	703.6	473.6
Dibromochloromethane	4855	2936	1832	1176
Bromoform	13900	7956	4714	2883
Carbon tetrachloride	782.7	524.2	359.9	252.8
Bromotrichloromethane	2727	1716	1110	738.1
Carbon tetrabromide	93710	47860	25480	14090
1,1,1-Trichloroethane	607.3	410.8	284.4	201.4

Results

Specific retention volumes (V_g^0) were determined for each solute with each of the liquid phases at 30.0, 40.0, 50.0, and 60.0° from the average value of three separately measured retention times. At the higher temperatures small corrections had to be made for liquid-phase loss from the columns. The V_g^0 data for each solute on each solvent were smoothed by a least-squares best linear fit of log V_g^0 against reciprocal temperature. The standard deviation for these plots indicated that, on the average, the precision of the experimental V_g^0 values was within 1%. The smoothed V_g^0 data are set out in Tables II, III, and IV. All subsequent calculations were carried out using these smoothed data. The values for $(\bar{V}_g^0)_R/(\bar{V}_g^0)_D$ at a given temperature were determined by averaging the results for the five alkane solutes studied. The standard deviations for the values in Table V range from

Table V. Average Values of $(\bar{V}_g^0)_R/(\bar{V}_g^0)_D$

	30°	40°	50°	60°
n-Octadecane/di-*n*-octyl ether	0.987	1.005	1.022	1.039
n-Octadecane/di-*n*-octyl thioether	1.089	1.087	1.085	1.083

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±0.001 to ±0.006, with a typical value being ±0.004. The constants K' (strictly, stoichiometric equilibrium constants based on the mole fraction convention, *i.e.*, $K' = X_{AD}/X_A X_D$) were determined through eq 3. The pure electron donor concentrations and estimated (through eq 4) activity coefficients are given in Table VI. From these data and the K' results, the equilibrium constants listed in Tables VII and VIII were computed using eq 2. Taking into account the experimental uncertainty in the measurement of $(V_g^0)_D/(V_g^0)_R$, it is estimated that the probable error in K ranges from ±0.006 to ±0.015, with a typical value being about ±0.01. Finally, from least-squares best linear fit of ln K against reciprocal temperature, the enthalpy and entropy of complex formation were determined for each system. The ΔH and ΔS values are listed in Table IX.

Table VI. Concentrations (c_D) and Estimated Activity Coefficients (γ_D) of Pure Electron Donors

	30°	40°	50°	60°
	Di-*n*-octyl Ether			
c_D (mol/l.)	3.299	3.270	3.241	3.212
γ_D	0.966	0.948	0.932	0.917
	Di-*n*-octyl Thioether			
c_D (mol/l.)	3.238	3.211	3.184	3.157
γ_D	0.932	0.934	0.936	0.938

Table VII. Equilibrium Constants K (l./mol^{-1}) with Di-*n*-octyl Ether

	30°	40°	50°	60°
Dichloromethane	0.280	0.260	0.241	0.223
Bromochloromethane	0.290	0.264	0.241	0.218
Dibromomethane	0.297	0.272	0.249	0.227
Chloroform	0.393	0.350	0.312	0.275
Dichlorobromomethane	0.407	0.363	0.324	0.288
Dibromochloromethane	0.416	0.363	0.318	0.275
Bromoform	0.411	0.370	0.332	0.297
Carbon tetrachloride	0.066	0.062	0.057	0.052
Bromotrichloromethane	0.106	0.095	0.084	0.073
Carbon tetrabromide	0.121	0.106	0.094	0.083
1,1,1-Trichloroethane	0.105	0.096	0.088	0.080

Table VIII. Equilibrium Constants K (l. mol^{-1}) with Di-*n*-octyl Thioether

	30°	40°	50°	60°
Dichloromethane	0.359	0.335	0.313	0.294
Bromochloromethane	0.407	0.377	0.350	0.326
Dibromomethane	0.455	0.424	0.396	0.370
Chloroform	0.418	0.379	0.345	0.313
Dichlorobromomethane	0.501	0.454	0.411	0.374
Dibromochloromethane	0.615	0.555	0.503	0.457
Bromoform	0.733	0.653	0.583	0.521
Carbon tetrachloride	0.138	0.129	0.120	0.113
Bromotrichloromethane	0.293	0.270	0.249	0.231
Carbon tetrabromide	0.931	0.800	0.688	0.593
1,1,1-Trichloroethane	0.165	0.152	0.140	0.129

Table IX. Enthalpies (kcal/mol) and Entropies (eu) of Complex Formation

	Di-*n*-octyl ether		Di-*n*-octyl thioether	
	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
Dichloromethane	1.52	7.54	1.34	6.45
Bromochloromethane	1.90	8.72	1.49	6.68
Dibromomethane	1.79	8.32	1.38	6.12
Chloroform	2.38	9.69	1.93	8.09
Dichlorobromomethane	2.31	9.40	1.96	7.83
Dibromochloromethane	2.76	10.80	1.99	7.51
Bromoform	2.17	8.92	2.28	8.14
Carbon tetrachloride	1.60	10.66	1.35	8.38
Bromotrichloromethane	2.49	12.65	1.59	7.70
Carbon tetrabromide	2.51	12.47	3.02	10.09
1,1,1-Trichloroethane	1.81	10.44	1.64	9.01

Discussion

The initial purpose of this work was to carry out a systematic study of the hydrogen-bonding propensities of the haloform and dihalomethane systems. However, our results indicate that there are two possible types of charge-transfer interactions present within these systems: (1) hydrogen bonding of the C–H hydrogen of the haloalkane to the n-donor atom of the ether or thioether; (2) charge transfer (n → σ^* type) between the n donor and the halogen atoms. There is direct spectroscopic evidence of hydrogen bonding to both the ether and the thioether with C–H hydrogens. Indirect evidence exists for n → σ^* type complexes involving Cl and Br acceptors with both O and S donors. There is, however, the possibility that the interactions involving the halogen atoms do not arise from charge transfer but rather may be described by electrostatic considerations alone.

Within the haloform series it is difficult to discern any trend in the K values (and the ΔH and ΔS values, for that matter). The probable reason for this is that we are measuring a weighted average of a wide range of "pair-wise" interactions involving not only the hydrogen bonding interactions but also a variety of donor–halogen interactions. Thus the K values (and ΔH and ΔS values) obtained by the glc method will be average parameters for pairwise interactions. If charge-transfer interaction does exist between the n donors and the halogen atoms, the interaction would be expected to be stronger with bromine than with chlorine. Thus, while the hydrogen acidity in the haloform series decreases as Br atoms replace Cl atoms (proceeding down the series $CHCl_3 \rightarrow CHBr_3$), this may be compensated for by an increase in the amount of halogen–n-donor specific interaction yielding a larger K than expected on the basis of simple H bonding. In the case of the haloforms with the ether this is reflected in a slight increase in the K's for both the haloform and dihalomethane series at the lower temperatures. The smaller K values for the dihalomethanes compared to the haloforms is related both to the lower acidity of their C–H hydrogens and the fewer halogen atoms available for halogen–n-donor interaction.

The K values for the haloforms and the dihalomethanes with the thioether are all greater than those with the ether. This is most likely due to an enhanced amount of charge transfer with the sulfur atom. Although the sulfur atom is a poorer n donor for hydrogen bonding, it is a significantly better charge-transfer donor than the oxygen atom. It is clear that the haloforms and dihalomethanes follow the trend of a larger K with a greater number of Br atoms. This indicates that, although the acidity of the hydrogen is reduced when a Br replaces a Cl, the increased "charge transfer" more than compensates for the diminished hydrogen bonding. Interestingly, the larger K values appear to be due in greater part to less negative entropy values rather than more negative enthalpy values. This suggests that, in part at least, the increase in K values over the ether is related to the larger sulfur atom being more accessible to the acceptor sites.

When more than one type of complex is possible with a given acceptor, the experimental association parameters are difficult to interpret. In an attempt to sort out the various types, *i.e.*, to resolve the "mixed" association constants into the individual contributions from the various types of complexes, the tetrahalomethanes, CCl_4 and CBr_4, were studied. The results for these systems do provide evidence of complex formation stabilized by some type of halogen-n-donor interaction. The trends are as expected, the smallest K value being obtained for the CCl_4–ether system and the largest for the CBr_4–thioether system. However, the values of K and ΔH obtained for the CBr_4–thioether system preclude any detailed quantitative treatment of the data. Taking them at face value the data indicate that H bonding in the $CHBr_3$–thioether system is negligible and that the bulk of the association constant is largely due to charge transfer. Spectroscopic evidence indicates that this is not the case. Hydrogen bonding should still provide a significant contribution to the overall K measured for the $CHBr_3$–thioether complex. Thus it does not appear to be a valid assumption that a quantitative estimate of the charge-transfer contribution in the haloforms could be obtained from the tetrahalomethane data. Further investigation of the $-CCl_3$ group by studying the solute 1,1,1-trichloroethane yielded interesting results. The K values were fairly small in absolute terms but were larger than those for CCl_4 and the ΔH's were sizable with the haloalkane–ether having a value of $\sim$1.8 kcal mol^{-1}. This ΔH is comparable to that observed for the weak hydrogen-bonded complexes involving the haloforms with thioether and gives an indication of the magnitude of dipolar interactions in mixtures of polar liquids.

The importance of classical electrostatic interactions in the stabilization of weak "collision complexes" has been emphasized in recent publications.[45,48] It is indeed possible that a significant contribution to the stabilization of some of the complexes discussed in this paper is due to dipole–dipole and/or dipole–induced dipole interactions. Bromine is a better charge-transfer acceptor atom than chlorine but it is also a good deal more polarizable. Thus the trend of increasing K values with increasing Br substitution follows the increasing degree of polarizability of the haloform. However, concomitantly with this the C–Cl bond dipoles of the remaining C–Cl bonds are increased due to Br substitution. It is possible that these bond dipoles could interact with the positive end of the ether dipole thus affording another site for interaction. The dipole moment of the thioether is somewhat larger than that of the ether and this could possibly account for some of the increase in K values in the haloalkanes on going from the ether to the thioether. However, that effect alone could hardly explain the large increases in the bromoform and carbon tetrabromide K values. Thus it would appear that while the trends in the K values could be approximately explained by electrostatic considerations, the possibility that all of these types of interactions could contribute in part to the average values of K observed by glc makes it impossible to resolve these values into their most significant contributions. It has been observed[48] that nmr is an experimental method which also averages over many "dipolar" contributions while ir would not show these effects in a direct way. Work is currently underway in this area which may throw further light on the nature of these interactions at the molecular level.

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Thermodynamics of Molecular Association by Gas–Liquid Chromatography. III. Aromatic Compounds with Tetra-*n*-butyl Pyromellitate

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Abstract: Equilibrium constants, enthalpies, and entropies of complex formation between benzene, toluene, the xylenes, and mesitylene and tetra-*n*-butyl pyromellitate have been determined by gas–liquid chromatography in the temperature range 50–80°. Steric effects were found to predominate over electronic factors leading to the trend benzene > toluene > *o*-xylene > *p*-xylene > *m*-xylene > mesitylene for the equilibrium constants.

It is now generally recognized that gas–liquid chromatography (glc) is an effective and advantageous method for studying the thermodynamics of nonelectrolytic solutions. The most recent application is to the accurate and rapid measurement of association constants of organic complexes in nonaqueous solu-