Thermodynamics of Molecular Association. VIII. Carbon Tetrabromide/Aromatic Interactions

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Abstract: Bimolecular interactions between 11 mononuclear aromatics (B) and carbon tetrabromide (A) in inert solvents (I) are investigated in the temperature range 10–40° through four experimental techniques: (a) polarization measurements, (b) nuclear magnetic resonance spectroscopy, (c) ultraviolet–visible spectrophotometry, and (d) gas–liquid chromatography (glc). From a it is found that the concentration of AB complexes is negligibly small, while b indicates the absence of significant B to A charge transfer (CT). No discrete CT bands are found with c, and previous c studies are questioned. Consistent with other direct and reliable evidence, it is concluded that A–B interactions primarily involve van der Waals forces and, more or less, random collisions. Solution theory is utilized to interpret the glc partition coefficients of B in mixtures of A + I, where I is squalane. It is estimated that A–B interactions are, on the average, about 1.023 times stronger than the geometric mean of A–A and B–B interactions.

The nature of the interaction between tetrahalomethanes and mononuclear aromatics in inert solvents has been the subject of several recent investigations and much controversy. In question are: (a) the contribution of charge-transfer (*vs.* electrostatic) interactions, and (b) whether the interactions are better described by 1:1 complex formation or by statistical collisional (or "contact") pairing.[1] The earliest evidence of CBr_4/aromatic complex formation came from solid–liquid phase diagrams with benzene[2] and *p*-xylene,[3] which suggested 1:1 solid adduct formation. However, this "adduct formation" is undoubtedly favored by geometric packing effects in the solid state[4] (no evidence of adduct formation was found with *m*-xylene[3]) and has little bearing on the question of possible complex formation in an inert liquid medium. Spectroscopic studies have provided inconclusive evidence as to the existence of bimolecular complexes and the extent of charge-transfer interactions and conflicting values of equilibrium constants.[5–9] Tramer[6] observed uv shifts of a CBr_4 absorption edge which increased as the benzene ring became more alkylated, an effect which was ascribed to charge-transfer transitions, and obtained association constants which ranged from 0.01 l. mol⁻¹ for benzene/CBr_4 to 0.05 l. mol⁻¹ for hexamethylbenzene/CBr_4, certainly indicative of little or no complex formation. On the other hand, Person, *et al.*,[8] obtained a uv value of 0.23 l. mol⁻¹ (from enhanced CBr_4 absorption in a different wavelength region than that analyzed by Tramer) and a Raman result of 0.28 l. mol⁻¹ for benzene/CBr_4 at 25°. Moreover, the nuclear quadrupole resonance (nqr) spectrum of the *p*-xylene/CBr_4 system was interpreted by Hooper[10] as being indicative of little, if any, charge-transfer inter-

action in the ground state and by Gilson and O'Konski[11] as being consistent with a small amount. This may be contrasted with the suggestion[9] (based on uv/visible spectra and semiempirical molecular orbital calculations) that CBr_4 interacts with the aromatic ring through electron acceptance by the empty d orbitals on bromine.

In this paper four experimental techniques are employed to investigate and characterize the interaction of CBr_4 with 11 benzene derivatives: (a) polarization studies (*i.e.*, dielectric constant and refractive index measurements), (b) nuclear magnetic resonance (nmr) spectroscopy, (c) ultraviolet–visible (uv/v) spectrophotometry, and (d) gas–liquid chromatography (glc). In agreement with the bulk of direct and reliable evidence, our findings are shown to be consistent with the concept of short-lived contact pairing involving, primarily, electrostatic interactions, the strength of which is evaluated by applying solution theory to the thermodynamic results from glc.

Polarization Measurements

Complex formation is accompanied by enhanced molar polarization in solution, resulting in a measurable dipole moment for the complex. In the terminology of Mulliken's theory[12,13] the dipole moment of the ground state of the complex arises from a combination of charge transfer from the donor (D) to the acceptor (A) (described by the dative bond wave function $\psi(D^+, A^-)$) and induced moments produced in one molecule by the electrostatic field of the other (described by the no bond wave function, $\psi(D,A)$). The latter is also referred to as the electrostatic or van der Waals contribution.[13] Dipole moment measurements can be used to help establish whether or not a complex actually exists in a given system[14] and to provide some of the necessary data for assessing the extent of D to A charge transfer in a system where the existence of a complex has been established.[15]

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To test for possible complexes between CBr_4 and aromatics, dielectric constants and refractive indices were measured and analyzed using the procedure of Guggenheim[16] and Smith,[17] as utilized recently in the study of tetracyanoethylene/aromatic complexes.[15] The CBr_4 used in this and our other experiments was obtained from J. T. Baker Chemical Co., recrystallized twice from n-hexane, and refrigerated in a dark container as a precaution against photodecomposition (see later). Solutions were prepared at $20.00 \pm 0.05°$ (the temperature of the experiment) by accurately weighing appropriate amounts of the aromatic solutes in 10-ml volumetric flasks and, then, adding sufficient 0.588 M solution of CBr_4 in n-decane to reach the 10-ml mark. The concentration of CBr_4 (fixed) was in excess of that of the solute (concentration range of 0.03 to 0.30 M). The dielectric constants of the solutions were measured by a WTW DM01 Dipole Meter, using a cylindrical gold-plated condenser cell, Type DFL2. The refractive indices were determined by the use of a Bausch and Lomb Abbe-3L refractometer. The dipole meter scale readings were calibrated and converted to dielectric constants (ϵ) by the use of neat liquid reference substances, for which ϵ's were known to within 0.1% at $20°$. The temperature control was achieved with a Neslab PBC-2 immersion cooler and Vycor immersion heaters operated through a Fisher relay and a Beckman thermoregulator.

When the appropriate data plots[15-17] were made and analyzed, it was found that, within the limits of experimental error (less than 0.1 D), the dipole moments of benzene, p-xylene, and mesitylene were zero in the 0.588 M CBr_1 solution, while those of chlorobenzene and toluene were 1.55 ± 0.02 and 0.48 ± 0.07 D, respectively. These values are in excellent agreement with those reported in inert solvents[18] and with those we determined in pure n-decane (e.g., 0.47 ± 0.09 D for toluene).

Thus, it is apparent that the dipole moment or the concentration of these CBr_4/aromatic "complexes," or both, are close to zero. It is conceivable, but unlikely, that complexes with zero dipole moment are being formed and, hence, could account for our measurements. However, it is not clear how such complexes could form without some charge transfer or distortion. Most likely, the concentration of complexed species in these mixtures is, effectively, zero. Sharpe and Walker[14] have also found that the dipole moment data for CBr_4 in benzene do not indicate the formation of a polar complex between such components. Therefore, the polarization evidence suggests that CBr_4/aromatic interactions do not produce bimolecular species which exist for a sufficiently long lifetime to be regarded as discrete entities. Most likely, CBr_4/aromatic interactions result in contact pairing,[1] the lifetime of which is of the order of the duration of a molecular collision. Support for this contention can be found in the submillimeter dielectric absorption studies of North and Parker.[19] They found that the collision frequency of the CCl_4/benzene pair (>10 cm^{-1}) was less than a factor of 2

smaller than that of the CCl_4/CCl_4 pair (17 cm^{-1}) and less than a factor of 5 smaller than that of the benzene/benzene pair (50 cm^{-1}). They termed the heteromolecular event a "sticky" collision.

Nuclear Magnetic Resonance (Nmr) Studies

Experimental. All nmr measurements were made using a Varian A-60/nmr spectrometer equipped with a variable temperature probe and controller. The only exceptions to this were several measurements made at high CBr_4 concentrations which were carried out using a Bruker HFX-90 nmr spectrometer in conjunction with a Bruker B-ST 100/700 variable temperature probe. Both spectrometers were used in the ^1H mode.

All spectra obtained on the Varian instrument were calibrated relative to internal TMS (0.5%) using the conventional side-band technique, which allows accurate measurement of the chemical shift independent of external variations in the magnetic field. For this purpose, a General Radio Oscillator 2C-2MC, Type 1310A, was employed as an external oscillator, with the frequencies determined by a Hewlett-Packard Model 522B counter. For the spectra which were recorded on the Bruker instrument, the internal lock system was employed and frequencies read out on a Hewlett-Packard Model 5216A 12.5-MHz electronic counter. For both the experiments run on the Varian and Bruker instruments, triplicate readings were taken for each sample, to a precision of ±0.1 Hz.

The aromatic solutes studied (benzene, p-xylene, and mesitylene) were Phillips 99.0% pure reagents. High purity chromatographic grade squalane (from Applied Science) and J. T. Baker Spectrograde cyclohexane were used as solvents. All chemicals were used without further purification. The choice of squalane as one of the inert solvents for the nmr study was based on its use as the inert medium in the glc experiment (see later). Squalane, due to its high viscosity at the temperatures of these experiments, is not the ideal nmr solvent, since considerable line broadening is introduced, even for the strong singlet absorption of the dissolved solute. Nevertheless, squalane has been successfully used as an nmr solvent by others.[20,21]

For our experiments the aromatic solute concentration was kept constant at 0.02 M, while the concentration of the CBr_4 was varied and kept in large excess (0.2–0.6 M in squalane and cyclohexane). In addition, to cover a larger "saturation fraction" range,[22] we also extended our benzene measurements to approximately 6 M CBr_4 in cyclohexane. (For the squalane solutions, the upper limit of CBr_4 solubility is about 0.7 M at room temperature.) Solutions were made up at room temperature by weighing the required amount of CBr_4 into 10-ml volumetric flasks and then adding 1 ml of aromatic stock solution (exactly 0.2 M in squalane or cyclohexane). The flasks were then filled up to the 10-ml mark with the appropriate solvent and transferred to 5-mm o.d. precision nmr tubes (Wilmad Glass Co.). The small quantity of aromatic liquid required in making up the stock solution was pipetted accurately into a 10-ml flask using a 50-μl Hamilton syringe. All

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Table I. Ring Proton Frequencies ν_B (Hz) at Various CBr$_4$ Concentrations C_A (mol l.$^{-1}$)

Benzene[a,c]		p-Xylene[a,c]		Mesitylene[a,c]		Benzene[a,d]		Benzene[b,e]		Benzene[b,f,g]	
C_A	ν_B	C_A	ν_B	C_A	ν_B	C_A	ν_B	C_A	ν_B	C_A	ν_B
0.000	433.7	0.000	415.8	0.000	399.1	0.000	432.5 ± 0.3	0.000	433.1	0.000	648.5 (432.5)
0.201	433.2	0.201	414.7	0.209	398.5	0.198	432.6 ± 0.6	0.198	433.4	4.054	649.5 (433.2)
0.300	432.8	0.300	415.5	0.298	398.4	0.295	433.1 ± 0.4	0.305	433.3	4.962	649.8 (433.4)
0.402	433.5	0.402	415.9	0.405	398.4	0.396	432.6 ± 0.1	0.397	433.0	Sat soln (<6 M)	648.7 (432.6)
0.500	433.1	0.498	416.2	0.492	398.3	0.492	432.9 ± 0.2	0.501	433.5		
0.600	432.7	0.627	414.9	0.609	399.0	0.591	433.1 ± 0.3	0.602	433.8		
Av[h]	433.2 ± 0.4		415.5 ± 0.4		398.6 ± 0.3		432.8 ± 0.2		433.4 ± 0.3		(432.9 ± 0.4)

[a] Squalane solution. [b] Cyclohexane solution. [c] 10.3 ± 0.3°. [d] 30.1 ± 1.7°. [e] 29.3 ± 1.5°. [f] 29.4 ± 0.5°. [g] Measured on a Bruker 90-MHz unit. [h] Average and standard deviation of vertical column.

solution concentrations were corrected for thermal expansion. The lower limit of solute concentration employed was governed by the magnitude of the instrumental noise and the diffusiveness of the absorption frequency. For these reasons, only symmetrical aromatics (with single ring proton absorptions) were chosen for this study.

To check if there was any appreciable shift of the TMS standard frequency with solution composition, several experiments were run with a coaxial cell employing TMS externally as well as internally. The results showed that the TMS frequency was independent of CBr$_4$ concentration. Finally, temperature determination of the sample probe was achieved through the methanol calibration method of Van Geet.[23]

Results. The following ring proton chemical shifts (in ppm) were observed in dilute squalane solution: 7.23, 6.93, and 6.65 for benzene, p-xylene, and mesitylene, respectively. The excellent agreement with the reported values for neat aromatic liquid[24] (7.23, 6.90, and 6.69, respectively) indicates that there is little solvent effect. In Table I are listed the observed frequencies of the three solutes at 10.3 ± 0.3° at different concentrations of CBr$_4$ in squalane and cyclohexane. The standard deviations (based on triplicate measurement) listed for the benzene–CBr$_4$–squalane system at 30° reflect, in part, the thermal probe instability and are in the general range reported by others using the side-band technique.[21,25,26] Examination of Table I reveals that, within experimental error, there is little (if any) variation in the proton frequency with CBr$_4$ concentration, and, for benzene, there is little (if any) variation with temperature or inert solvent. Note that the value listed at the bottom of each frequency column represents an average over all concentrations (with the corresponding standard deviation).

Of particular note are the benzene values listed in the last two columns (highly concentrated CBr$_4$ solutions), which are in good agreement with those in less concentrated solutions. It is apparent that even at these high concentrations the ring proton is virtually unperturbed by the presence of CBr$_4$. In addition, comparison of the values in parentheses in the last column (Bruker results converted to 60 MHz values) with those ob-

tained with the Varian instrument gives added confidence in these measurements.

There are nmr results reported for similar systems which corroborate our findings. Schug[27] noted that if a CCl$_4$/benzene complex does indeed form, then its chemical shift relative to uncomplexed benzene must be relatively small (i.e., appreciably less than 1 ppm). Foster and Fyfe[25] have found a frequency shift of only 0.04 ppm for the hexamethylbenzene absorption when solutions in CCl$_4$ were successively diluted from 0.6 to 0.01 M.

Thus, given that no significant frequency shifts were observed up to very high CBr$_4$ concentrations, the nmr experiment indicates that there is no significant withdrawal of electronic charge from the aromatic ring system, i.e., that charge-transfer forces play, at best, a minor role in CBr$_4$/aromatic interactions. This finding is consistent with the nqr results cited previously[10,11] and the conclusion reached by Person, et al.[8]

Ultraviolet (Uv) Studies

All of our spectral observations cited below were made with a Cary Model 14 uv–visible spectrophotometer. Precision Scientific Corp. cylindrical cells (1-mm path length) were used and spectra were recorded against a solvent blank in a matched cell placed in the reference beam. All solutions were degassed of O$_2$ by purging them with a stream of N$_2$ gas. Examination of the uv/visible spectra for many CBr$_4$/aromatic solutions (in cyclohexane and n-hexane) revealed no discrete bands which could be assigned to charge-transfer (CT) transitions.

Two groups have carried out quantitative uv work on aromatic/CBr$_4$ systems. Tramer[6] analyzed the uv shift to higher wavelength (region of 2900 to 3600 Å) of an absorption edge (attributed to CBr$_4$) as aromatic material was added to CBr$_4$/n-hexane solution at room temperature. The shifts increased as the benzene ring became more alkylated, as did the estimated association constants K (1. mol^{-1}): 0.01 (benzene), 0.02 (toluene), 0.03 (p-xylene), and 0.05 (mesitylene). Person[8] examined absorption enhancement in the region 2300–2900 Å as benzene was added to CBr$_4$/cyclohexane solutions at 25°. In striking disagreement with Tramer, a K value of 0.23 was estimated and was supported by a Raman result of 0.28. Also, from uv measurements[8] at 10 and 40°, the surprising result was obtained that, within experimental error, ΔH of association was zero.

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We question a number of aspects of both studies, particularly the reliability[22,28-30] of such small K values, obtained, in fact, from shifts or enhancements rather that well-defined CT bands.

As a precautionary measure, Person, et al.,[8] added a small amount of allyl alcohol (0.02–0.05 M) to their solutions to remove any Br_2 formed by uv-induced CBr_4 decomposition. However, it is conceivable that the addition of such an active component may have introduced competitive equilibrium processes; e.g., CBr_4/olefinic complexation[31] or hydrogen bonding to benzene. It is possible that residual Br_2 remained in the system (no purification of CBr_4 reported[8]), which would have introduced other error-causing factors, e.g., competitive Br_2/benzene association and spectral interferences. A distinct Br_2/benzene CT band with a maximum at about 2920 Å has been observed and associated with substantial complex formation.[32,33] We have confirmed the above band in benzene/Br_2/cyclohexane mixtures and the fact[34] that Br_2 in cyclohexane absorbs in the region 2000–3000 Å (maximum at about 2500 Å).

Tramer initially purified his CBr_4 but was not concerned about possible Br_2-induced artifacts (from uv decomposition of CBr_4). Of note is the fact that we observed an absorption band starting at about 3300 Å and peaking at 4240 Å for Br_2 dissolved in n-hexane and a higher wavelength band (starting at 3650 Å) for Br_2 in benzene. Furthermore, Tramer made no correction for "donor" absorption.

Another questionable point is the failure to deoxygenate the reagents used. It has been reported that O_2 forms weak CT complexes (or contact pairs) with aromatics[35,36] leading to singlet–triplet transitions in the region 2700–3400 Å. We purposely oxygenated CBr_4/benzene/inert solvent mixtures and observed increased absorption in the region 2500–3500 Å relative to spectra obtained with N_2 purged mixtures. A confirmation of this is provided by Thomson and de Maine[37] who found enhancement in uv spectra of CCl_4/benzene mixtures undergoing absorption of O_2 from the atmosphere. Noteworthy were the erratic K values obtained with solutions containing more than 20% benzene by volume. Also, Koblitz, et al.,[38] have reported on the photochemical oxidation of CBr_4 to bromophosgene and Br_2 at 4360 Å, and Bayliss and Rees[39] observed a CT band for Br_2/O_2 at 3125 Å. The interplay of all these factors presents a host of intriguing possibilities, some of which could have produced spectral perturbations in the wavelength regions studied.[6,8]

We would also like to call attention to the several uv studies on aromatic/CCl_4 systems.[5,29,40-42] First, the

saturation fraction range[22] covered in these studies does not seem to be adequate to establish the existence of 1:1 complexes.[22,28,30] Also, only one group[42] reported the degassing of samples, in spite of the possible complicating effects associated with the presence of O_2.[35-37] Considering these and other error-causing factors,[42] it is perhaps not surprising that such a wide range of K values has been reported, e.g., for CCl_4/hexamethylbenzene at 25°: 0.02 ± 0.01,[5] 0.55 ± 0.16,[29] 0.64 ± 0.12,[41] and 0.04 ± 0.04[42] l. mol⁻¹. In light of the above and previously cited findings,[19,25,27] it appears that little reliance can be placed on these uv results, although those of Hammond[42] seem the most defensible.

Thus, while some uv evidence exists for CT interaction in CBr_4/aromatic systems, the extraction of reliable association constants from the uv measurements is hardly possible, particularly with the absence of discrete CT bands and the presence of various complicating factors. The bulk of direct and reliable evidence indicates that the concentration of complexed species is negligible. Furthermore, as has been noted by many[13,28,43] the mere appearance of a CT band (or spectral shift) reveals nothing about the nature of the heteromolecular interactions. Current evidence (including this study) points to the predominance of electrostatic or van der Waals interactions in CBr_4/aromatic systems.

Gas–Liquid Chromatography (Glc)

Background. In recent years a glc approach has been developed and used to study organic complex formation. Thermodynamic association parameters (K, ΔH, and ΔS) have been measured for systems involving alcohol[44-47] and haloform[48,49] hydrogen bonding and aromatic/aromatic complexes.[50,51] Quite recently[52] it was shown that, rather than yielding the formation constant for 1:1 complexes as a separable term, the glc method always gives the sum $K + \alpha$, where K is the true formation constant and α is a contribution from noncomplexing or "physical" interactions between the acceptor and donor. Others[53-55] have considered the general thermodynamic aspects of this problem. While nonthermodynamic measurements (e.g., spectroscopic ones) yield K values (called "sociation" constants by Guggenheim[53]) separately,[55] thermodynamic ones (such as glc) always reflect a combination of "chemical" and

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Table II. Solute Partition Coefficients with Squalane, $(K_R)_I$

	Solute	10.0°	20.0°	30.0°	40.0°
1.	Benzene	921 ± 1	613 ± 1	419 ± 1	293.8 ± 0.4
2.	Toluene	3,498 ± 6	2,152 ± 4	1,368 ± 2	895 ± 1
3.	Ethylbenzene	10,390 ± 40	6,037 ± 2	3,635 ± 9	2,263 ± 3
4.	o-Xylene	15,810 ± 40	8,990 ± 20	5,310 ± 10	3,244 ± 3
5.	m-Xylene	12,830 ± 30	7,350 ± 20	4,370 ± 10	2,687 ± 3
6.	p-Xylene	12,540 ± 30	7,190 ± 20	4,240 ± 30	2,628 ± 3
7.	n-Propylbenzene	30,520 ± 80	16,620 ± 40	9,430 ± 30	5,550 ± 10
8.	Isopropylbenzene	21,700 ± 50	12,070 ± 30	6,980 ± 20	4,190 ± 20
9.	Mesitylene	46,900 ± 200	24,700 ± 100	13,630 ± 70	7,790 ± 20
10.	Fluorobenzene	923 ± 2	607 ± 1	411 ± 1	285.5 ± 0.3
11.	Chlorobenzene	7,580 ± 20	4,490 ± 10	2,759 ± 6	1,749 ± 2
12.	Cyclohexane	1,283 ± 6	837 ± 4	561 ± 3	386 ± 2
13.	Methylcyclohexane	2,790 ± 10	1,739 ± 9	1,118 ± 5	741 ± 5

"physical" contributions (K and α, respectively, in this case) which cannot be separated without the aid of a detailed molecular model.

The following general glc expression was derived,[52] considering terms up to $C_A{}^2$

$$(K_R)_M = (K_R)_I[1 + (K_1 + \alpha_1)C_A +$$
$$K_1(\alpha_1 + K_2 + \beta_1)C_A{}^2] \quad (1)$$

where C_A is the concentration of additive A (CBr_4 in this case) mixed with inert solvent I (squalane, in this case), $(K_R)_I$ is the partition coefficient of solute B (aromatic, in this case) on a column containing pure I, $(K_R)_M$ is the apparent partition coefficient of B on a column containing A + I at concentration C_A, K_1 is the AB complex formation constant, α_1 is the contribution from random A–B interactions between *uncomplexed* A and B, K_2 is the A_2B complex formation constant, and β_1 results from the nonideal mixing of A and I. Also, the condition $C_A \gg C_B$ applies.

Experimental. High-temperature glc analysis of our CBr_4 and squalane indicated purities in excess of 99% for both. Mixtures of the two developed a reddish brown color when left on a laboratory bench over a period of several weeks (most likely due to photodecomposition of the CBr_4 in solution). However, all columns were made immediately after mixing, and the glc experiment was performed with opaque columns through which a continuous stream of He (the carrier gas) passed. Six different concentrations (C_A) of CBr_4 in squalane (0.000, 0.125, 0.251, 0.371, 0.506, and 0.666 mol l.$^{-1}$) were prepared at 20.0°. The densities of the various solutions (A + I), which are required for the computation of the concentrations at the other experimental temperatures, were determined by pycnometry. The reference liquid was 99.9% pure n-octane (Phillips Petroleum Co.), the density of which is known to four significant figures.[56] The measured solution densities and concentrations at 10, 20, 30, and 40° are tabulated elsewhere.[57] Since solute purity is not an important consideration in this work, the solutes were used without further purification. The 11 aromatic and two alicyclic solutes studied are listed in Table II. The method of column preparation and analysis,[58] the glc apparatus used,[59] and the procedure followed for ob-

taining meaningful and accurate retention volumes[58] are described elsewhere. Net retention volumes (V_N) and specific retention volumes ($V_g°$) were measured for the 78 systems (13 solutes, each at six concentrations) at the four temperatures. The V_N values were converted to partition coefficients (K_R) through the expression[51] $V_N = K_R V$, where V is the total volume of the liquid phase (A + I) in the column.

Results. Equation 1 can be rearranged to give

$$Y = [\{(K_R)_M/(K_R)_I\} - 1]/C_A =$$
$$(K_1 + \alpha_1) + K_1(\alpha_1 + K_2 + \beta_1)C_A \quad (2)$$

The results for the 13 solutes were analyzed at all four temperatures through eq 2. Straight lines of effectively zero slope (random scatter of the data points about the horizontal lines) were found for plots of Y vs. C_A, thus indicating that the term in $C_A{}^2$ (eq 1) was negligibly small. This is consistent with our previous conclusion that $K_1 \approx 0$ for these systems. Accordingly, the results obtained from the glc experiment will be referred to as α values (dropping the subscript 1).

The expression

$$(K_R)_M = (K_R)_I[1 + \alpha C_A] \quad (3)$$

was therefore utilized in least-squares analysis of $(K_R)_M$ as a linear function of C_A. Linear correlation coefficients in excess of 0.995 were found for all systems. The values of $(K_R)_I$ (from the intercepts) and the values of α (from the slopes) are listed in Tables II and III, respectively, along with the corresponding standard deviations. The values in Table II are in excellent agreement (average difference of ±0.2%) with the $(K_R)_I$'s actually measured with pure squalane. The expression

$$-R \ln \alpha = (\Delta H/T) - \Delta S \quad (4)$$

was used to determine the concomitant enthalpies and entropies of contact pair interaction from the temperature dependence of α. The ΔH and ΔS values are listed in Table III.

Interpretation of the Glc Results

Examination of Table III reveals that neither α nor ΔH correlates with any obvious single aromatic property (e.g., ionization potential, dipole moment, polarizability, etc.). Undoubtedly, one could devise an empirical scheme involving a linear combination of

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Table III. Values of α (l. mol⁻¹), ΔH (kJ mol⁻¹), and ΔS (J mol⁻¹ deg⁻¹)

Solute	10.0°	20.0°	30.0°	40.0°	$-\Delta H$	$-\Delta S$
1. Benzene	0.415 ± 0.005	0.388 ± 0.005	0.362 ± 0.005	0.336 ± 0.004	5.2 ± 0.2	25.5 ± 1.5
2. Toluene	0.497 ± 0.005	0.461 ± 0.005	0.430 ± 0.005	0.401 ± 0.004	5.3 ± 0.2	24.4 ± 0.5
2. Ethylbenzene	0.559 ± 0.011	0.519 ± 0.008	0.484 ± 0.008	0.450 ± 0.005	5.4 ± 0.3	24.1 ± 1.1
4. o-Xylene	0.649 ± 0.008	0.519 ± 0.009	0.543 ± 0.008	0.495 ± 0.008	6.6 ± 0.2	26.9 ± 0.6
5. m-Xylene	0.513 ± 0.008	0.481 ± 0.008	0.454 ± 0.007	0.425 ± 0.003	4.7 ± 0.2	22.2 ± 0.8
6. p-Xylene	0.565 ± 0.010	0.522 ± 0.008	0.500 ± 0.021	0.448 ± 0.003	5.8 ± 0.4	25.1 ± 2.6
7. n-Propylbenzene	0.557 ± 0.008	0.517 ± 0.008	0.484 ± 0.008	0.456 ± 0.008	4.9 ± 0.3	22.3 ± 1.0
8. Isopropylbenzene	0.545 ± 0.008	0.502 ± 0.008	0.467 ± 0.009	0.433 ± 0.011	5.6 ± 0.3	24.9 ± 1.0
9. Mesitylene	0.536 ± 0.015	0.504 ± 0.015	0.478 ± 0.015	0.446 ± 0.009	4.5 ± 0.3	20.9 ± 1.2
10. Fluorobenzene	0.668 ± 0.007	0.607 ± 0.007	0.566 ± 0.007	0.521 ± 0.004	6.0 ± 0.2	24.6 ± 0.7
11. Chlorobenzene	0.764 ± 0.008	0.695 ± 0.007	0.636 ± 0.009	0.580 ± 0.005	6.7 ± 0.3	26.1 ± 1.1
12. Cyclohexane	0.041 ± 0.002	0.042 ± 0.002	0.041 ± 0.002	0.042 ± 0.002		
13. Methylcyclohexane	0.058 ± 0.002	0.057 ± 0.002	0.057 ± 0.002	0.054 ± 0.002		

various properties to correlate the results. However, a more fundamental interpretation is feasible (see below).

The ΔH values were tabulated mainly to give an indication of the stabilization energies in these systems. It is clear that they are neither very weak ($\ll RT$) nor very strong ($\gg RT$). Their magnitudes (around $2RT$) fall into a "gray area," where it becomes impossible to ascertain, on the basis of the ΔH data alone,[28] whether or not true complexes exist in these systems. In this respect, the terminology "sticky collisions" is as good a description as any.[19] Accordingly, given the previously cited evidence, we will continue to regard the heteromolecular events as random, short-lived collisions that primarily involve van der Waals forces. Consistent with this premise, the solution model described below will be shown to give a physically reasonable interpretation of the α values (and their temperature dependence) in terms of electrostatic interactions.

It has been shown[52,60] that α can be related to the infinite dilution activity coefficients of B in M($\gamma_M{}^B$) and B in I($\gamma_I{}^B$) through the equation

$$\gamma_I{}^B v_I/\gamma_M{}^B v_M = 1 + \alpha C_A \qquad (5)$$

where v_I and v_M are the molar volumes of I and the mixture M (A + I), respectively. Equation 5 has already been treated[52,60] for the case $\alpha C_A \ll 1$, a condition which unfortunately does not apply here. Accordingly, to relate α to molecular energetic parameters the following simplifying assumption is made: that α is independent of composition up to the hypothetical (since it is unattainable at these temperatures) state of pure "molten CBr₄." Equation 5 then gives (with M = A)

$$\gamma_I{}^B v_I/\gamma_A{}^B v_A = 1 + \alpha v_A{}^{-1} \qquad (6)$$

where the v's now have units of liters per mole and v_A is the molar volume of the "molten CBr₄" (see below). Assuming random mixing and taking into account the combinatorial term due to the molecular size difference between the solute (B) and the solvent (A or I), the activity coefficient in solvent j can be written in the following general form[58]

$$\ln \gamma_j{}^B = \ln\frac{v_B}{v_j} + \left(1 - \frac{v_B}{v_j}\right) + \chi_j{}^B \qquad (7)$$

where v_B is the solute molar volume and $\chi_j{}^B$ is the so-

called "interaction parameter." Taking the logarithm of both sides of eq 6 and inserting eq 7, one obtains

$$\ln (1 + \alpha v_A{}^{-1}) = v_B(v_A{}^{-1} - v_I{}^{-1}) + \chi_I{}^B - \chi_A{}^B \qquad (8)$$

The parameter of interest, $\chi_A{}^B$, was evaluated as follows. $\gamma_I{}^B$ was determined from the $(K_R)_I$ values in Table II and pure solute properties[61] in the usual manner[50,51,58] and $\chi_I{}^B$ then obtained through eq 7. The densities necessary to compute v_B at the four temperatures were available,[61] while those for component I were measured.[57] (The values of v_I are: 0.5186 (10°), 0.5227 (20°), 0.5269 (30°), and 0.5331 l. mol⁻¹ (40°).) The apparent molar volume of CBr₄ was estimated from the measured solution densities and concentrations[57] by the standard procedure[62] and was taken as being the appropriate v_A. The values are: 0.1053 (10°), 0.1060 (20°), 0.1066 (30°), and 0.1073 l. mol⁻¹ (40°). With these v's and $\chi_I{}^B$'s, the $\chi_A{}^B$'s were determined for the 13 solutes at the four temperatures. As a check on our procedure and assumptions, published high-temperature (93–124°) $V_g°$ data[63] for the system benzene + molten CBr₄ were extrapolated to 40°, and $\gamma_A{}^B$ was calculated[58] at that temperature. The resulting $\gamma_A{}^B$ (0.86) is in good agreement with that calculated in our hypothetical "molten CBr₄" state at 40° (0.83) through eq 7 and 8.

Assuming that $\chi_A{}^B$ is totally energetic in character (i.e., that the "structural" contribution to $\chi_A{}^B$ is negligibly small), one has[52,64,65]

$$\chi_A{}^B = \frac{U_B}{RT}(2\theta) = \frac{U_B}{RT}\left(\frac{2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}}{\epsilon_{BB}}\right) \qquad (9)$$

where U_B is the configurational internal energy of the solute at temperature T and the ϵ's refer to pairwise potential energy well depths per equivalent surface.[64] The ϵ's are absolute quantities and should be regarded as angle-averaged, effective spherical values. They reflect all types of interactions between the given pair, i.e., dispersion, induction, etc. The U_B's, which are negative, can be estimated at the four temperatures of the experiment from available[61] enthalpies of vapor-

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Table IV. Molecular Energetic Parameters[a]

Solute	2θ	δ_B	ξ_B
1. Benzene	0.0149 ± 0.0006	0.0809	1.018
2. Toluene	0.0248 ± 0.0007	0.0696	1.023
3. Ethylbenzene	0.0224 ± 0.0009	0.0599	1.023
4. o-Xylene	0.0297 ± 0.0014	0.0854	1.025
5. m-Xylene	0.0221 ± 0.0008	0.0588	1.023
6. p-Xylene	0.0282 ± 0.0014	0.0552	1.026
7. n-Propylbenzene	0.0162 ± 0.0010	0.0419	1.022
8. Isopropylbenzene	0.0145 ± 0.0012	0.0387	1.021
9. Mesitylene	0.0183 ± 0.0013	0.0503	1.022
10. Fluorobenzene	0.0227 ± 0.0004	0.0570	1.024
11. Chlorobenzene	0.0339 ± 0.0004	0.1477	1.023
12. Cyclohexane	-0.0523 ± 0.0013	0.0000	0.997
13. Methylcyclohexane	-0.0452 ± 0.0022	-0.0264	1.003
		Av[b]	1.023 ± 0.002

[a] Least-squares fit to eq 14 yielded a value of $(1 + \delta_A) = 1.47 \pm 0.10$ from the intercept. Analysis of the slope and intercept gave $\xi_B = 1.023 \pm 0.005$ for the aromatic solutes. Correlation coefficient 0.991. [b] Average for aromatic solutes only (1–11). Column values computed from eq 14 with $(1 + \delta_A) = 1.47$. Quoted standard deviation is the standard deviation of the mean.

ization (ΔH_B) through the expression

$$U_B = -\Delta H_B + RT \quad (10)$$

The results for 2θ, computed using eq 9 and 10 and the determined $\chi_A{}^B$ values, are summarized in Table IV. These represent values averaged over all four temperatures, since it was found that, as expected, 2θ was virtually independent of temperature (note the small standard deviations). Of interest is the fact that the 2θ values are positive for the aromatic solutes and negative for the alicyclic ones. This indicates that unlike interactions (ϵ_{AB}) are stronger with the former solutes and weaker with the latter solutes than the arithmetic mean of like interactions, which is a physically reasonable result.[64,66] Furthermore, strong A–B interactions are consistent with the negative enthalpies listed in Table III.

A more quantitative assessment of the interactions present in these systems is possible through Kreglewski's[67] successful semiempirical approach. Let us arbitrarily choose cyclohexane as the "reference" solute and denote it by B'. Kreglewski has shown that

$$\frac{\epsilon_{BB}}{\epsilon_{B'B'}} \equiv 1 + \delta_B = \frac{T^c{}_B/(V^*{}_B)^{1/3}}{T^c{}_{B'}/(V^*{}_{B'})^{1/3}} \quad (11)$$

where T^c is the critical temperature and V^* is the molar volume at $T = 0.6T^c$. Values of δ_B, as calculated from available density and critical temperature data[61] through eq 11, are listed in Table IV. Note that $T^c{}_{B'}/(V^*{}_{B'})^{1/3}$ is 114.6 deg cm^{-1} mol$^{-1/3}$ for cyclohexane. Adjusting the 2θ's to the same common reference point (cyclohexane), we obtain

$$2\theta\frac{\epsilon_{BB}}{\epsilon_{B'B'}} = 2\theta(1 + \delta_B) = \frac{2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}}{\epsilon_{B'B'}} \quad (12)$$

where $\epsilon_{AA}/\epsilon_{B'B'}$ ($\equiv 1 + \delta_A$) is not known (no critical data available for CBr$_4$). Utilizing a modified geometric mean combining rule[66] for ϵ_{AB}

$$\epsilon_{AB} = \xi_B(\epsilon_{AA}\epsilon_{BB})^{1/2} \quad (13)$$

where ξ_B is close to unity, and combining eq 12 and 13,

one has

$$(2\theta + 1)(1 + \delta_B) = $$
$$2\xi_B(1 + \delta_A)^{1/2}(1 + \delta_B)^{1/2} - (1 + \delta_A) \quad (14)$$

Considering the aromatic solutes only and assuming that ξ_B is (roughly) constant, least-squares analysis of the data for $(2\theta + 1)(1 + \delta_B)$ as a linear function of $(1 + \delta_B)^{1/2}$ yields values of $1 + \delta_A = 1.47$ (from the intercept) and $\xi_B = 1.023$ (from the slope and intercept). The ξ_B values for the individual solutes that lead to perfect agreement with the experimental 2θ's are listed in Table IV. Note that the aromatic ξ_B's cluster closely around the mean value (standard deviation of only 0.002) and are numerically reasonable[66] for the strong A–B interactions involved. As a further test of our model, the ξ_B's were calculated (via eq 14) for the two alicyclic solutes. The results (Table IV) average 1.000 ± 0.003, indicative of the applicability of the geometric mean expression for the weaker alicyclic/CBr$_4$ interactions.[66]

Conclusion

The proposed solution model, based on random mixing and van der Waals interactions, leads to consistent and realistic molecular energetic parameters for A–B interactions. Aromatic/CBr$_4$ interactions are clearly stronger than the geometric mean of like interactions. Given the highly polarizable π electrons and the polarizable bromine atoms, dispersion interactions are probably quite strong in these systems. Additional contributions might come from interactions between the C–Br bond dipole and the aromatic induced dipole or quadrupole, or, in some cases, permanent dipole (e.g., note the large 2θ value for chlorobenzene). It would be purely speculative to attempt further analysis of the ϵ_{AB} results. They undoubtedly represent statistically averaged values over all relative orientations of A and B, and, as such, some knowledge of the potential energy surface would be required for more detailed interpretations. Finally, it should be noted that the time scale of aromatic–CBr$_4$ interactions clearly needs finer definition. To this end, dielectric absorption studies[19,68] would be most useful.

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