

Theoretical Calculation of Heats of Complexation in Carbon Tetrachloride

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Abstract □ The theoretical absolute (gas phase) interaction energies of complexation are combined with a cavity model for the solvent carbon tetrachloride to calculate the theoretical heats of complexation for the complexes of chloranil, fluoranil, and tetrachlorophthalic anhydride in solution. The agreement between theoretical calculations and experimental results is excellent. The absolute interaction energy and the donor-solvent term increase in a parallel manner within each series, thus approximately canceling, and the overall complexation process may be considered as solvent driven. These results suggest that for planar complexing systems in solution, both the solvent term and the absolute interaction energy term will usually be maximized when maximum overlapping of area occurs.

Keyphrases □ Complexation, heats—theoretical calculation, chloranil, fluoranil, and tetrachlorophthalic anhydride complexes, gas phase interaction energies and cavity model □ Interaction energies (of complexation)—theoretical values combined with cavity model for carbon tetrachloride, used to calculate theoretical heats of complexation for chloranil, fluoranil, and tetrachlorophthalic anhydride complexes in solution □ Carbon tetrachloride—interaction with and contribution to chloranil, fluoranil, and tetrachlorophthalic anhydride complexes, theoretical interaction energies combined with cavity model, used to calculate theoretical heats of complexation □ Solvents—carbon tetrachloride, interaction energies of complexation and cavity model, used to calculate the theoretical heats of complexation for chloranil, fluoranil, and tetrachlorophthalic anhydride complexes in solution

In a preceding article (1), the theoretical, absolute interaction energies and structures of the complexes of fluoranil, chloranil, and tetrachlorophthalic anhydride with various methylbenzenes were reported. A comparison of the absolute interaction energies with

Table I—Molecular Surface Areas

Compound	\bar{r} , Å	Surface Area, Å ²
Benzene	3.68	42.57
Hexamethylbenzene	4.90	75.39
Fluoranil	4.04	51.28
Chloranil	4.46	62.46
Tetrachlorophthalic anhydride ^a	—	78.19

^a A rectangular surface with length of 9.22 Å and width of 8.48 Å was used.

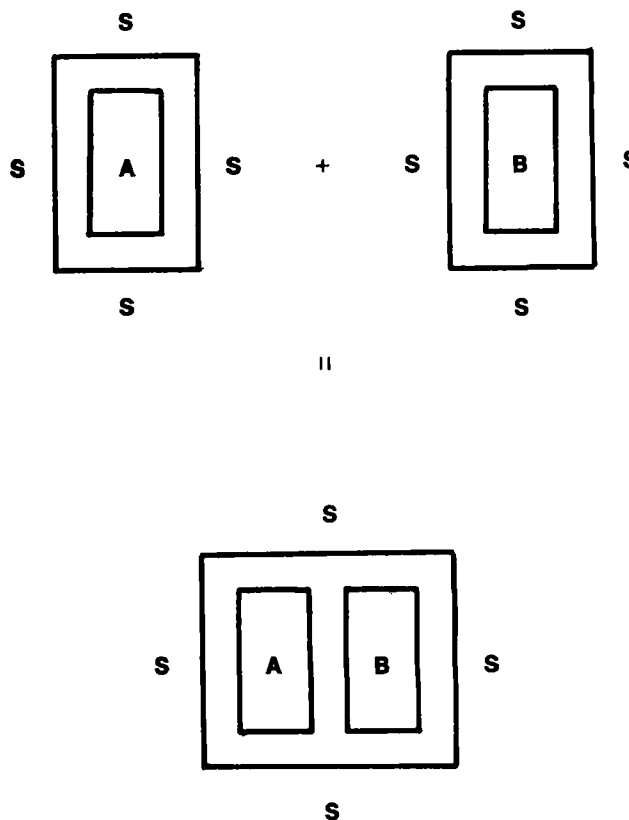
Table II—Solvent Contribution to the Heat of Complexation in Carbon Tetrachloride for the Fluoranil Complexes

Fluoranil Complex	Surface Area Loss, Å ²	E_{SS} , kcal/mole	γ/γ_0	E_{SS}' , kcal/mole
Benzene	93.85	-7.27	0.50	-5.94
Toluene	99.32	-7.70	0.51	-6.33
<i>p</i> -Xylene	104.79	-8.12	0.52	-6.72
Mesitylene	110.26	-8.55	0.53	-7.11
Durene	115.73	-8.97	0.54	-7.51
Pentamethylbenzene	121.20	-9.40	0.55	-7.91
Hexamethylbenzene	126.67	-9.82	0.56	-8.32

Table III—Solvent Contribution to the Heat of Complexation in Carbon Tetrachloride for the Chloranil Complexes

Chloranil Complex	Surface Area Loss, Å ²	E_{SS} , kcal/mole	γ/γ_0	E_{SS}' , kcal/mole
Benzene	105.02	-8.14	0.52	-6.73
Toluene	110.50	-8.56	0.53	-7.13
<i>p</i> -Xylene	115.96	-8.99	0.54	-7.52
Mesitylene	121.43	-9.41	0.55	-7.92
Durene	126.90	-9.84	0.56	-8.33
Pentamethylbenzene	132.37	-10.26	0.57	-8.74
Hexamethylbenzene	137.84	-10.68	0.58	-9.15

the experimental values in carbon tetrachloride solution indicated that, while the general trends within each series were correctly predicted, the increase in the absolute interaction energy per methyl group was less than the experimental solution value. Furthermore, the predicted increase in the absolute interaction of chloranil over the fluoranil complexes with the various methylbenzenes is not present in the solution heats of complexation. These factors indicate the importance of the solvent in determining the overall heat of complexation. In this report, a cavity model for the solvent (2, 3) is used to calculate the



Scheme I—Cavity model of complexation

Table IV—Solvent Contribution to the Heat of Complexation in Carbon Tetrachloride for the Tetrachlorophthalic Anhydride Complexes

Tetrachlorophthalic Anhydride Complex	Surface Area Loss, Å ²	E_{SS} , kcal/mole	γ/γ_0	E_{SS}' , kcal/mole
Hexamethylbenzene	153.58	-12.67	0.63	-10.49
Benzene	120.75	-9.97	0.55	-7.87

solvent contribution to the overall heat of complexation. These results, combined with the absolute energies for the donor-acceptor (1), donor-solvent, and acceptor-solvent interactions can then be compared with the experimental solution values.

The goal of this work is to determine which, if any, terms dominate the complexation process in solution and if overall agreement between the theoretical and experimental complexation energies in solution can be achieved.

THEORETICAL

The model considered here is shown schematically in Scheme I for the complexation reaction $A + B = A \cdot B$. The energy of complexation is given by Eq. 1:

$$\Delta E_{\text{comp}} = E_{AB} + E_{SS} - E_{AS} - E_{BS} \quad (\text{Eq. 1})$$

where E_{AB} is the absolute interaction energy of the complex, E_{AS} and E_{BS} are the solute-solvent interaction terms, and E_{SS} is the solvent term. Since the surface area of the $A \cdot B$ complex will usually be less than the surface area of A plus the surface area of B , the solvent term will tend to drive the reaction to the right—the “sol-

vophobic force” (2). The magnitude of this contribution to the heat of complexation is given by the surface energy of the solvent per unit surface area, E^S , times the area lost on complexation, ΔSA (Eq. 2):

$$E_{SS} = E^S \cdot \Delta SA \quad (\text{Eq. 2})$$

The surface energy, E^S , is calculated using the surface tension, γ , Eotvos constant, k_E , and molar volume, V , of the liquid (4):

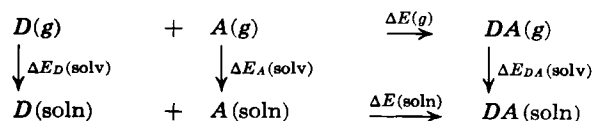
$$E^S = \gamma - T d\gamma/dT \quad (\text{Eq. 3})$$

$$\frac{d\gamma}{dT} = -k_E \cdot V^{-2/3} \quad (\text{Eq. 4})$$

Since the surface energy, E^S , is relatively temperature independent, at points significantly below the critical temperature of the liquid, small changes in the choice of T have no effect on E^S .

Since surfaces of molecular dimensions are involved, it is necessary to consider a curvature-corrected surface energy. The surface energy, E^S , represents the energy required to move a molecule from a bulk situation to a planar surface, where it has a lower coordination number. Since the coordination number of a molecule is somewhat higher at a curved surface, E^S will be somewhat smaller, corresponding to a more bulk-like surface situation. For this purpose, the method of Wakeshima is employed (5).

Another method for considering the solvent effects is to construct the thermodynamic cycle (6) shown in Scheme II:



Scheme II

The energy of complexation in solution (soln) is then related to that in the vapor phase (g) by the following equation:

$$\Delta E(\text{soln}) = \Delta E(g) + [\Delta E_{DA}(\text{soln}) - \Delta E_A(\text{soln}) - \Delta E_D(\text{soln})] = \Delta E(g) + \Delta[\Delta E(\text{soln})] \quad (\text{Eq. 5})$$

Table V—Acceptor-Solvent Interaction Energies^a

Carbon Tetrachloride with	R^b	El ^b	Pol ^b	Disp ^b	Rep ^b	E_{tot}^b
Fluoranyl	3.9	0.001	-0.507	-7.800	3.891	-4.414
Chloranyl	3.6	-0.004	-0.568	-18.092	9.749	-8.914
Tetrachlorophthalic anhydride	3.8	0.012	-0.530	-12.555	6.232	-6.841

^a In kilocalories per mole. ^b R = interplanar distance in Å, El = electrostatic energy, Pol = polarization energy, Disp = dispersion energy, Rep = repulsive energy, and E_{tot} = total interaction energy.

Table VI—Donor-Solvent Interaction Energies^a

Carbon Tetrachloride with	R^b	El ^b	Pol ^b	Disp ^b	Rep ^b	E_{tot}^b
Benzene	4.0	0.000	-0.001	-7.152	3.095	-4.057
Toluene	4.0	0.001	-0.001	-7.328	3.123	-4.205
<i>p</i> -Xylene	4.0	0.002	-0.001	-7.571	3.152	-4.418
Mesitylene	3.9	0.001	-0.001	-9.326	4.371	-4.956
Durene	4.0	0.002	-0.001	-8.175	3.276	-4.899
Pentamethylbenzene	4.0	0.001	-0.001	-8.509	3.347	-5.162
Hexamethylbenzene	3.9	0.001	-0.002	-10.154	4.588	-5.567

^a In kilocalories per mole. ^b See Footnote b of Table V.

Table VII—Summary of Results^a for the Fluoranyl Complexes in Carbon Tetrachloride

Fluoranyl Complex	E_{AB}	E_{SS}	E_{SS}'	E (donor- CCl ₄)	E_{th}	E_{th}'	E_{exp}^b
Benzene	-4.39	-7.27	-5.94	-4.06	-3.19	-1.86	-2.0
Toluene	-4.61	-7.70	-6.33	-4.21	-3.69	-2.32	-2.3
<i>p</i> -Xylene	-4.80	-8.12	-6.72	-4.42	-4.09	-2.69	-2.7
Mesitylene	-5.24	-8.55	-7.11	-4.96	-4.42	-2.98	-3.0
Durene	-5.32	-8.97	-7.51	-4.90	-4.98	-3.52	-3.9
Pentamethylbenzene	-5.51	-9.40	-7.91	-5.16	-5.34	-3.85	-4.4
Hexamethylbenzene	-5.73	-9.82	-8.32	-5.57	-5.57	-4.07	-5.4

^a In kilocalories per mole. ^b From Ref. 10.

Table VIII—Energy Term Differences between the Fluoranil–Hexamethylbenzene and Fluoranil–Benzene Complexes

Experimental	–3.40
Theoretical	–2.38
Theoretical (curvature corrected)	–2.21
Absolute (ΔE_{AB})	–1.34
Donor–solvent	–1.51
Solvent (ΔE_{SS})	–2.55
Solvent (curvature corrected) ($\Delta E_{SS'}$)	–2.37

within the context of the cavity model:

$$\Delta[\Delta E(\text{soln})] = [E_{DA}(\text{cavity}) + E(DA - \text{cavity}) - (E_A(\text{cavity}) + E(A - \text{cavity})) - [E_D(\text{cavity}) + E(D - \text{cavity})]] \quad (\text{Eq. 6})$$

where $E_X(\text{cavity})$, $X = A, D, DA$, is the energy required to create a cavity for X in the solvent, and $E(X - \text{cavity})$ is the interaction energy between X and the cavity walls (solvent). Rearranging Eq. 6, one has:

$$\Delta[\Delta E(\text{soln})] = [\Delta E(\text{cavity}) - \Delta E(\text{interaction})] \quad (\text{Eq. 7})$$

where:

$$\Delta E(\text{cavity}) = E_{DA}(\text{cavity}) - E_D(\text{cavity}) - E_A(\text{cavity}) \quad (\text{Eq. 8})$$

and:

$$\Delta E(\text{interaction}) = E(DA - \text{cavity}) - E(A - \text{cavity}) - E(D - \text{cavity}) \quad (\text{Eq. 9})$$

By referring to Scheme I, the $\Delta E(\text{cavity})$ term can be calculated by estimating the surface area lost on complexation, and the $\Delta E(\text{in-}$

Table X—Energy Term Differences between the Chloranil–Hexamethylbenzene and Chloranil–Benzene Complexes

Energy Term	ΔE , kcal/mole
Experimental	–2.84
Theoretical	–2.20
Theoretical (curvature corrected)	–2.10
Absolute (ΔE_{AB})	–1.19
Donor–solvent	–1.51
Solvent (ΔE_{SS})	–2.54
Solvent (curvature corrected) ($\Delta E_{SS'}$)	–2.42

The effect of the curvature correction is to lower the absolute value of the solvent contribution to the overall complexation reaction. The increase in the hexamethylbenzene complex strength over the benzene complex remains nearly the same as that without the curvature correction. It should be noted, however, that the curvature correction was applied to the surface free energy term, γ , in Eq. 3, but not the entropy term, $S^s = -d\gamma/dT$, in Eq. 3. This probably leads to an underestimate of the curvature correction to the surface energy since the entropy of surface formation is positive for carbon tetrachloride and would probably be less positive at a curved (more bulk-like) surface. For this reason, as well as the inherent uncertainty in the curvature correction to the surface tension, the curvature-corrected solvent contribution provides only an indication as to the effects of such considerations. Since the curvature correction depends on the radius of the cavity, which is nearly constant in these series, it affects mainly the absolute energy values and has little effect on energy differences.

Solute–Solvent Term—The two solute–solvent terms, E_{AS} and E_{BS} in Eq. 1, were determined by calculating the absolute interaction energies (1) of carbon tetrachloride with the planar faces of

Table IX—Summary of Results^a for the Chloranil Complexes in Carbon Tetrachloride

Chloranil Complex	E_{AB}	E_{SS}	$E_{SS'}$	E (donor– CCl_4)	E_{th}	$E_{th'}$	E_{exp}^b
Benzene	–8.56	–8.14	–6.73	–4.06	–3.73	–2.32	–2.26 (–1.67)
Toluene	–8.80	–8.56	–7.13	–4.21	–4.24	–2.81	
<i>p</i> -Xylene	–9.04	–8.99	–7.52	–4.42	–4.70	–3.23	
Mesitylene	–9.19	–9.41	–7.92	–4.96	–4.73	–3.24	–3.86
Durene	–9.31	–9.84	–8.33	–4.90	–5.34	–3.83	(–4.41)
Pentamethylbenzene	–9.49	–10.26	–8.74	–5.16	–5.68	–4.16	
Hexamethylbenzene	–9.75	–10.68	–9.15	–5.57	–5.95	–4.42	–4.94 (–5.15)

^a In kilocalories per mole. ^b Values in parentheses are those of Briegleb *et al.* (14, 15).

teraction) is equal to the net solute–solvent interaction lost on complexation.

RESULTS

Cavity Term—The surface areas of the interacting planes of the various molecules were calculated using the standard van der Waal radii (7) and the values shown in Table I. The r represents the mean radius, from the center of the molecule, in two different directions, corresponding to the maximum and minimum values for r . The surface areas of the various methylbenzenes were calculated using a value of 5.47 \AA^2 per methyl group. The surface tension and Eotvos constant of carbon tetrachloride at 20° were taken to be 26.75 dynes/cm (8) and 2.21 (9), respectively. The surface area lost on complexation was taken to be the sum of the interacting planar surface areas of the two complexing molecules.

Tables II–IV show the solvent contribution to the energy of complexation for the complexes of fluoranil, chloranil, and tetrachlorophthalic anhydride. In these tables, γ/γ_0 represents the ratio of the curvature-corrected surface tension to the surface tension of a planar surface. The radius of the cavity for the complex was taken to be the mean of the radii of the two complexing molecules. The terms $E_{SS'}$ and E_{SS} are the solvent terms with and without curvature correction. These results indicate a significant contribution of the solvent to the increase in complex strength with increasing methyl substitution. In all cases the solvent term alone contributes 2–3 kcal/mole to the increase in the complex strength of hexamethylbenzene over the corresponding benzene complex.

the donor and acceptor molecules from which they are displaced on complexation (Eq. 9). These values represent the difference in the solute–solvent interaction when the solute is free and complexed, *i.e.*, $E_{AS}(\text{complex}) - E_{AS}(\text{free})$, assuming one molecule of carbon tetrachloride is displaced from the planar surface of the solute. The tabulated values refer to the absolute interaction energy at the potential energy minima, and the results are shown in Tables V and VI¹. The interactions are mainly dispersive and, of the acceptor molecules, chloranil shows the strongest interaction with the solvent. The donor–solvent interactions increase with each additional methyl substitution, with the planar face of hexamethylbenzene showing a 1.5 kcal/mole stronger interaction with the solvent than benzene.

DISCUSSION

These results can now be combined with those of the preceding paper (1) to provide an overall quantitative picture of complexation in the solvent carbon tetrachloride.

Table VII compares the experimental (10) and theoretical results for the complexes of fluoranil with the methylbenzenes. The experimental value in all cases lies between the two theoretical estimates. In Table VIII the differences in the various energy terms for the benzene *versus* hexamethylbenzene complexes with fluoranil are presented. The absolute interaction energy term, E_{AB} ,

¹ More complete potential energy maps are available from the author upon request.

Table XI—Summary of Results^a for the Tetrachlorophthalic Anhydride Complexes in Carbon Tetrachloride

Tetrachlorophthalic Anhydride Complex	E_{AB}	E_{SS}	E_{SS}'	E (Donor- CCl_4)	E_{th}	E_{th}'	E_{exp}
Hexamethylbenzene	-7.75	-12.67	-10.49	-5.57	-8.01	-5.83	-5.75 ^b
Benzene	-7.06	-9.97	-7.87	-4.06	-6.13	-4.03	-4.19

^a In kilocalories per mole. ^b From Ref. 16.

the solvent terms, E_{SS} and E_{SS}' , and the donor-solvent term, E (donor- CCl_4), all increase with increasing methyl substitution. The increase in the donor-solvent term nearly cancels the increase in the absolute interaction energy term (Eq. 1). While this grouping of the terms is somewhat arbitrary (note also the paralleling of the two terms in Table VII), it is suggestive of the important role of even the nonpolar solvent carbon tetrachloride. The overall theoretical estimate still underestimates the experimental increase in the complex strength per methyl group. However, since the experimental values were determined by a plot of $\log K$ versus $1/T$, this difference may not be significant due to experimental uncertainties (1).

The results for the chloranil-methylbenzene complexes are shown in Tables IX and X. The agreement between theory and experiment is again good. The large increase in the absolute interaction term for a given methylbenzene complex with chloranil over fluoranil is essentially canceled by the larger acceptor-solvent term for chloranil. Thus, the theoretical estimate of the solution heat of complexation is nearly the same in the two series and is in line with the experimental values. Again, the solvent term is significant, with the donor-solvent and absolute interaction terms approximately canceling.

The tetrachlorophthalic anhydride complexes with benzene and hexamethylbenzene provide examples where the molecular sizes of the complexing systems are significantly different. The theoretical and experimental values agree quite well and, again, the solvent term is a predominant factor (Table XI).

Within the context of the cavity model, both the solvent contribution to the heat of complexation, E_{SS} , and the solute-solvent terms, E_{AS} and E_{BS} , depend on the surface area change on complexation. This would suggest that for complexes with little surface area change on complexation, the gas phase and solution heats of complexation would be nearly the same. This prediction is supported by data on the diethyl sulfide-iodine and benzene-iodine complexes (11) in which the solution and gas phase ΔH° 's are approximately equal.

The solvent contribution, E_{SS} , also depends on the surface energy of the solvent, E^S ; for solvents with a high E^S , the solvent term may well be the largest energy term. For example, since the E^S of water is about two to three times larger than that of carbon tetrachloride, the contribution of the solvent term to the energy of complexation would be correspondingly larger. Therefore, this may be the basis for the good correlations of ΔG° of complexation with surface area (12) and for the decreasing complex strength in mixed solvents of lower surface energy. The principle of maximum overlap of areas can also be justified by considering the absolute energy term, E_{AB} , since this term is also likely to be at a maximum when the areas of overlap are maximized. Thus, for planar-type complexes in solution, both terms that lower the energy of the complex relative to the independent molecules are likely to be maximized when the area of overlap is maximized. Since, for a given complex,

many structures may be consistent with the maximum overlapping of areas while having different absolute energies, the actual structure of the complex will be determined by the relative absolute energy terms. This is probably the reason for some of the deviations observed in plots of complex strength versus maximum overlap area (13).

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ACKNOWLEDGMENTS AND ADDRESSES

Received December 12, 1973, from the *College of Pharmacy, University of Michigan, Ann Arbor, MI 48104*

Accepted for publication May 3, 1974.

The author thanks Dr. W. I. Higuchi, Dr. M. Tamres, Dr. J. Hoyland, Dr. L. B. Kier, and Mr. R. Pearlman for helpful discussions during this work. The support of the National Science Foundation, Public Health Service, and the University of Michigan Computing Center is gratefully acknowledged.

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