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Investigating the Thermodynamics of Charge-Transfer Complexes

A Physical Chemistry Experiment

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Charge-transfer complexes and reactions are of great interest in chemistry (1–3) as evidenced by femtosecond studies of the dynamics of charge-transfer complexation in the gas phase and in solution (4–6) as well as ab initio calculations on these systems (7–9). Significant studies of charge transfer in biological systems such as DNA and bacterial photosynthesis also have been reported (10–13). In spite of the intense research interest in and the importance of charge-transfer complexes, only a few articles on this topic have been published in this *Journal* (14–20). None of these articles describe a student experiment involving the determination of the changes in enthalpy (ΔH), entropy (ΔS), and Gibbs energy (ΔG) associated with the formation of a charge-transfer complex.

The colorful charge-transfer complexes described in this experiment have been a topic of investigation for many years. Benesi and Hildebrand (21) observed that when aromatic hydrocarbons and iodine are present in nonpolar solvents, such as heptane and carbon tetrachloride, an absorption band appears in the ultraviolet region that is not present in the spectrum of either solute. They also developed a spectroscopic method for measuring the equilibrium constant for such complexes. Since that time, equilibrium constants and thermodynamic properties for these iodine complexation reactions (22–32) as well as others involving complexation of aromatic hydrocarbons with chloranil (33–36) have been studied in detail.

A few years after the Benesi and Hildebrand article was published, Mulliken (37–39) depicted the electronic structure of these systems in terms of a so-called “no-bond” wave function $\psi(A, D)$ and a dative (charge-transfer) wave function $\psi(A^+ - D^-)$, where A is the electron acceptor and D is the electron donor. Using perturbation theory, Mulliken described the ground state as a resonance hybrid composed mostly of the no-bond wave function with a small quantity of the dative wave function. The excited state was mostly made up of the dative wave function with a little of the no-bond wave function. Later, McGlynn (40) presented a similar treatment of these systems in terms of the variation method. The color of these complexes is interpreted as being caused by a charge-transfer absorption band associated with an electronic transition from the ground state to the charge-transfer state. According to Mulliken’s theory, the energy of this charge-transfer band is given by

$$h\nu_{CT} = IE_D - EA_A - W \quad (1)$$

where h is Planck’s constant, ν_{CT} is the frequency of the charge-transfer transition, IE_D is the ionization energy of the donor, EA_A is the electron affinity of the acceptor, and W is the Coul-

ombic attraction energy of the complex. It has been shown by Mulliken that this equation works well in predicting the trends in the iodine–alkylbenzene systems as well as other charge-transfer systems.

A few experiments involving the application of spectroscopy to the determination of thermodynamic properties have been published in this *Journal*. These studies involve hydrogen bonding complexation (41), cyclodextrin inclusion (42), DNA duplex formation (43), protonation reactions (44), and a photochromic isomerization (45). Only two articles involving the thermodynamics of charge-transfer complexes have appeared in this *Journal*, both more than 40 years ago. The first article (14) contained a clear presentation of the theory of charge-transfer complexation based on McGlynn’s variational approach (40) but did not have a thermodynamic emphasis (ΔG only). The second article (15) was a suggestion of a charge-transfer system for study (only ΔH) and contained no experimental details.

A major objective of the experiment described herein is to give students an understanding of the nature of charge-transfer complexes. Another objective is to illustrate how UV–vis spectroscopic methods can be used to determine the equilibrium constants and the other thermodynamic quantities for complexation reactions. The original spectroscopic Benesi–Hildebrand method (21) is used to measure the equilibrium constants of charge-transfer complexation between an electron acceptor (I_2 , chloranil) and an electron donor (methyl-substituted benzenes, alcohols) over a range of temperatures. A van’t Hoff plot is used to obtain ΔH , ΔS , and the ΔG value at 298 K (determined from the associated equilibrium constant). Calorimetric techniques cannot be used for these studies because the reactions do not go to completion. Given the importance of charge-transfer interactions, this experiment should provide a significant contribution to the undergraduate curriculum.

Experimental Method

A variety of systems including toluene, *p*-xylene, mesitylene, hexamethylbenzene, or *t*-butanol as donors with iodine or chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone) as acceptors have been examined. Stock solutions of the donor and the acceptor in heptane are available to the students. The students prepare six heptane solutions by precisely mixing various quantities of the donor and the acceptor. Using a standard UV–vis spectrophotometer, a set of survey spectra (acceptor alone, donor alone, acceptor and donor together) is followed by sets of spectra involving four different donor–acceptor concentration ratios at three different temperatures. The time required is 3–4 hours.

Hazards

The organics used in this experiment (toluene, *p*-xylene, mesitylene, hexamethylbenzene, *n*-butanol, chloranil, and heptane) are volatile and should be handled with caution. All of the chemicals can cause skin and respiratory irritation. Iodine is corrosive, causes burns, and may be harmful by inhalation and through skin absorption. Gloves should be worn when handling these chemicals. A fume hood should be used in the preparation of the solutions and the filling of spectrophotometer cells.

Results

For the iodine–mesitylene system the appearance of a new absorption band associated with the formation of a charge-transfer complex is first established by comparing the spectra of solutions containing just iodine, just mesitylene, and both iodine and mesitylene (Figure 1). The spectrum of the iodine solution shows a weak peak at 520 nm corresponding to the absorption of molecular iodine. The solution with mesitylene shows no significant absorption except a tail starting at about 310 nm. The solution containing both iodine and mesitylene shows a slightly shifted visible absorption band as well as a new band with a λ_{max} at 330 nm. Because neither iodine nor mesitylene alone absorb at this wavelength, this absorption band is interpreted as being due to the charge-transfer absorption band of the mesitylene– I_2 complex. Increasing concentrations of mesitylene also have the effect of enhancing the charge-transfer band and blue shifting the visible absorption band of iodine (Figure 2). The charge-transfer absorption band at 330 nm was used to obtain the equilibrium constant.

The chloranil–mesitylene charge-transfer system provides a second and more colorful example than the previous one. The absorption spectra associated with this system are shown in Figure 3. The spectrum of the solution containing chloranil with no mesitylene (spectrum a) shows a weak UV absorption band ($\lambda_{\text{max}} = 360 \text{ nm}$) that tails into the visible. This solution is pale yellow in color. Increasing concentrations of mesitylene result in a stronger absorption band with a λ_{max} at 412 nm. These solutions become progressively pinker in color as the concentration of mesitylene increases. To determine the equilibrium constant for this system, the absorbance associated with the band at 412 nm is utilized.

The complexation equilibrium reaction involving an acceptor A such as iodine and a donor D such as mesitylene is



and the equilibrium constant expression is

$$K = \frac{[\text{DA}]}{[\text{D}][\text{A}]} \quad (3)$$

The initial concentrations of the donor and acceptor in the solution before equilibrium is established can be represented by $[\text{D}]_0$ and $[\text{A}]_0$, respectively. The concentration of the complex after equilibrium is established is $[\text{DA}]$. If $[\text{D}]_0 \gg [\text{A}]_0$, the concentration of the donor at equilibrium will be essentially the same as before equilibrium or $[\text{D}] = [\text{D}]_0$, and that of the

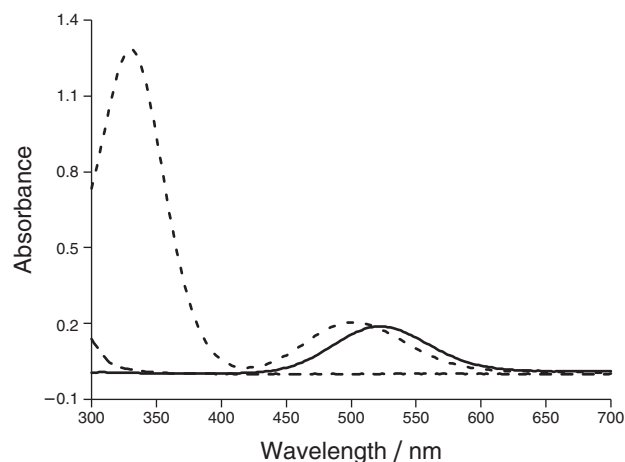


Figure 1. Absorption spectra of iodine ($2.14 \times 10^{-4} \text{ M}$) in heptane (—), mesitylene (2.14 M) in heptane (---), and both iodine ($2.14 \times 10^{-4} \text{ M}$) and mesitylene (2.14 M) in heptane (- -).

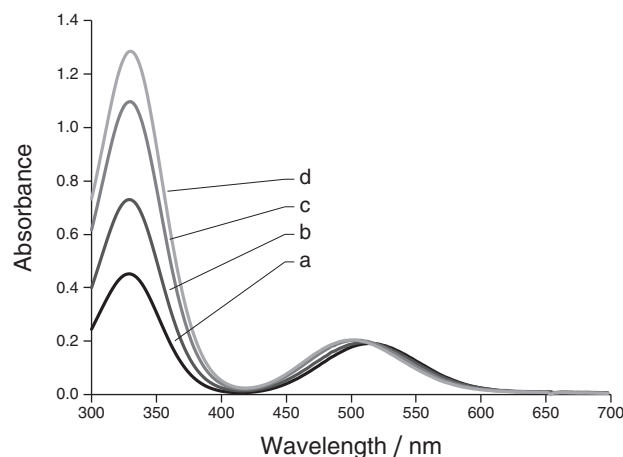


Figure 2. Absorption spectra of iodine ($2.14 \times 10^{-4} \text{ M}$) in heptane with various concentrations of mesitylene. The concentrations of mesitylene for solutions a through d are 0.362 M , 0.711 M , 1.42 M , and 2.14 M , respectively.

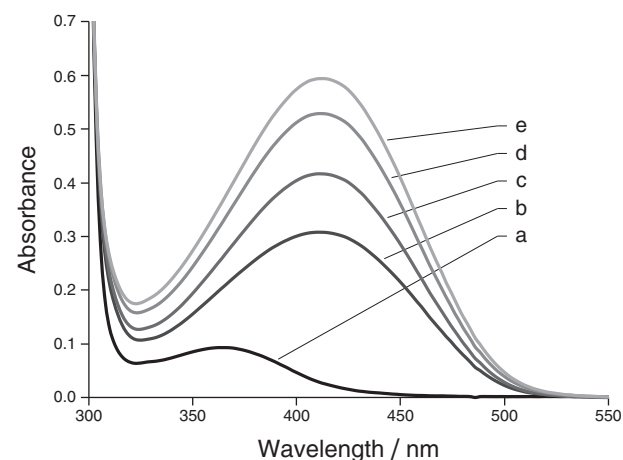


Figure 3. Absorption spectra of chloranil ($3.64 \times 10^{-4} \text{ M}$) in heptane with various concentrations of mesitylene. The concentrations of mesitylene for solutions a through e are 0.0 M , 0.363 M , 0.719 M , 1.43 M , and 2.15 M , respectively.

acceptor will be $[A] = [A]_0 - [DA]$. Therefore,

$$K = \frac{[DA]}{[D]_0 ([A]_0 - [DA])} \quad (4)$$

The concentration of the DA complex is related to the measured absorbance of the charge-transfer absorption band through the Beer–Lambert law,

$$a = \epsilon_{DA} b [DA] \quad (5)$$

where a is the absorbance of the charge-transfer band at the wavelength of maximum absorption, ϵ_{DA} is the molar absorptivity

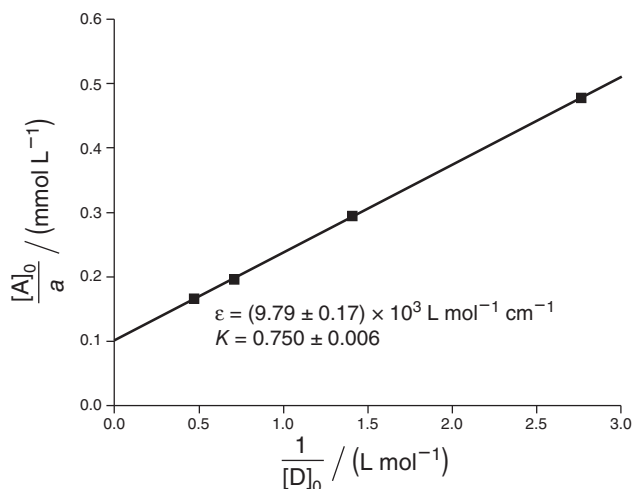


Figure 4. Benesi–Hildebrand plot for the charge-transfer complexation between mesitylene and I_2 in heptane at 25.0 °C. The equilibrium constant and the molar absorptivity at 330 nm were determined from the measured slope and intercept according to eq 6.

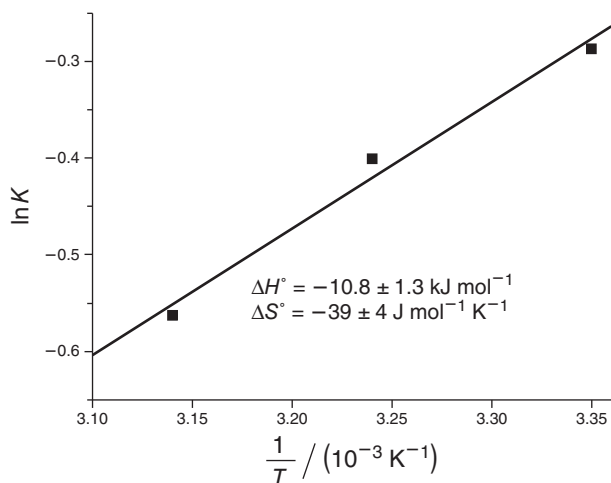


Figure 5. $\ln K$ versus $1/T$ plot for the complexation reaction between mesitylene and I_2 in heptane. The thermodynamic quantities were obtained from the slope and intercept according to eq 8.

ity at this wavelength, and b is the path length (1.00 cm cell). Substituting eq 5 into eq 4 and rearranging terms leads to the Benesi–Hildebrand equation:

$$\frac{[A]_0}{a} = \frac{1}{\epsilon_{DA} b} + \frac{1}{K \epsilon_{DA} b} \left(\frac{1}{[D]_0} \right) \quad (6)$$

A plot of $[A]_0/a$ versus $1/[D]_0$ should yield a straight line, and ϵ_{DA} and K can be obtained from the intercept and slope. Such a plot for the mesitylene– I_2 system is shown in Figure 4. The equilibrium constant (0.75) reported here for the mesitylene– I_2 system in heptane compares with literature values of 0.74 (26) and 1.00 (28) in hydrocarbon solvent and values ranging between 0.43 and 0.82 in carbon tetrachloride (21, 22, 25, 27, 31), all at 25 °C. The average of 18 student values is 0.71 ± 0.06 .

It should be noted that systems in which the donor or the acceptor absorption overlaps with that of the complex can also be analyzed. For example, in the chloranil–mesitylene system, the “ a ” in eqs 5 and 6 above should be replaced by $a - a_0$ where a_0 is the absorbance of chloranil at the wavelength in question without any mesitylene present.

Once the equilibrium constants at different temperatures are determined, one can then calculate the other thermodynamic quantities using the equations

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

$$\ln K = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (8)$$

A plot of $\ln K$ versus $1/T$ should yield a straight line whose slope and intercept are $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. Such a plot for the mesitylene– I_2 system is shown in Figure 5 along with ΔH° and ΔS° values of $-10.8 \text{ kJ mol}^{-1}$ and $-39 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. These values are representative of the average student values of $-12.1 \pm 2.3 \text{ kJ mol}^{-1}$ and $-43.5 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. They compare well with published values in hydrocarbon solvent of $-12.6 \text{ kJ mol}^{-1}$ and $-42.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, reported by Holmen (28) and with more recent values in carbon tetrachloride solvent of $-12.5 \text{ kJ mol}^{-1}$ and $-48.9 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, reported by Joens (31).

Discussion

This experiment provides the opportunity to incorporate interesting discussion questions that lead the students to a deeper understanding of complex formation. Could mixing solutions of the two reactants in a calorimeter and measuring the temperature change determine the heat of reaction? The students calculate that only 62% of the acceptor undergoes complexation in the iodine–mesitylene solution with the highest concentration of the donor, based on the value of their equilibrium constant at 25 °C and on the initial concentrations of the donor and acceptor. Because the reaction does not go to completion, ΔH cannot be determined calorimetrically.

The students are asked to comment on the sign and the magnitude of the enthalpy change. As expected, the formation of the charge-transfer complex is an exothermic process. Given

that the solvent is nonpolar and should not interact strongly with the reactants and products, the formation of a complex should release heat. Would the same necessarily be true for a more polar solvent? The students compare the magnitude of their measured values with the enthalpy change associated with chemical bond formation and with hydrogen bond formation so that they recognize that the enthalpy change for the reaction is rather low.

The students are also asked to discuss the sign of the entropy change. The entropy change for these complexation reactions is negative. This is usually the case whenever two molecules come together to form a complex. The process results in a decrease in freedom and an increase in order. Exceptions should only occur if solvent effects are important, which should not be the case when the solvent is a hydrocarbon.

The magnitude of the equilibrium constant is a measure of the stability of the complex. Complexes with large equilibrium constants are said to be stronger complexes than those with small equilibrium constants. The Gibbs energy for complexation is related to K by eq 7. The students are asked to comment on whether the enthalpy and entropy factors are complementary or opposing in their effect on stability. It is interesting to note that studies show that systems with more negative enthalpy changes also have more negative entropy changes (46). This may be true because stronger complexes are more ordered. It is found that systems with more negative enthalpy changes also have larger equilibrium constants and thus more negative Gibbs energy changes. For these systems, the enthalpy factor is more important in stabilizing the complex than the entropy factor is in destabilizing it. These issues have been discussed more fully by Person (46). The aromatic- I_2 complexes are weak with small equilibrium constants and positive Gibbs energy changes, so the entropy factor is more important than the enthalpy factor in the complex formation.

To extend their understanding of charge-transfer complexation, the students are given a set of literature data for various iodine-methylbenzene charge-transfer systems and asked to plot the data according to eq 1. Although the resulting plot shows some scatter, it does illustrate that the frequency of the charge-transfer absorption band increases with the ionization energy of the donor. The students are also asked to comment on the magnitude of ϵ , the molar absorptivity of the charge-transfer band ($\sim 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$). The value of ϵ is large because the transition of an electron from the HOMO of the donor to the LUMO of the acceptor produces a large transition moment (i.e., a large rearrangement of the electron density occurs with the absorption of light).

Conclusion

This experiment serves the dual purpose of introducing students to charge-transfer complexes and to a spectroscopic technique for measuring the thermodynamic properties of chemical systems at equilibrium. Each year students in the course consistently rank this experiment near the top of the experiments they do. Students enjoy working with the colorful solutions and the relative ease of making the measurements compared to using bomb and solution calorimeters. The results allow students to consider the relative importance of enthalpy and entropy changes in determining the stability of the complexes. Although

molecular interactions such as hydrogen bonding and polar and van der Waals forces are discussed in lecture, this experiment is the only coverage of charge transfer. The students recognize that charge-transfer complexes involve a different, but important, type of interaction. We are in the process of developing a follow-up computational exercise that should provide even more insight into the nature of these charge-transfer interactions.

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