

Physical Chemical Study of the Distribution of Some Amine Salts Between Immiscible Solvents II

Complexation in the Organic Phase

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The apparent partition coefficients of some amine salts of four aromatic sulfonic acid dyes are reported. The effect of adding complexing molecules to the organic layer has been studied. The binding number and over-all stability constant for the complexation has been determined. The results indicate that the acid strength of the complexing agent and the van der Waals forces of attraction are important considerations in partition studies. The results also indicate that the analyst should consider the use of proton donor molecules to aid in an efficient extraction of amine salts of dyes.

IN THE preceding paper the apparent partition coefficients of some amine salts of tropaeolin OO were related to the molecular weight and branching of the aliphatic amine, the relative concentrations of the amine and dye, and the dielectric constant of the solvent (1). Methylene chloride, chloroform, and carbon tetrachloride were the solvents used. In a discussion of the choice of suitable solvents, Mukerjee suggested that the dielectric constant of the solvent was a factor which determined the amount of salt extracted (2). However, Higuchi suggested that the complexation of the salt with the solvent was a more predominating factor than was the dielectric constant (3). Therefore, we continued the investigation and now report the studies of complexation of certain azobenzenesulfonic-type acid salts with some halogenated solvents and aliphatic alcohols in a benzene rich solvent system.

EXPERIMENTAL

Reagents.—The sulfonic acid dyes used included methyl orange (Eastman Kodak), tropaeolin O (Eastman Kodak), tropaeolin OO (National Aniline), and sodium azobenzenesulfonate (Gallard Schlesinger Mfg. Corp.). The primary alcohols were purchased from Allied Chemical; the methylene chloride, chloroform, and ethylene dichloride were purchased from Baker and Adamson and Matheson Coleman and Bell.

Preparation of Solutions.—Methods of preparation were similar to those described in the first communication (1). Stock solutions of the sulfonic acid dyes and amine solutions were prepared so that 2 μ m. of the acid or base were present in 5 ml. of solution. The pKa of methyl orange was sufficiently high so that the stock solution had to be buffered at a pH of 6.0 with phosphate buffer (potassium acid phosphate 0.001%, potassium phosphate 0.007%). The phosphate buffer was not added to

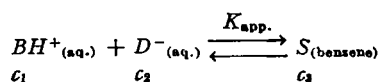
the stock solutions of the other dyes. The pH of the final solution mixtures was such that hydrolysis of the amine dye salt in the aqueous phase was at a minimum.

The benzene solutions were prepared by adding given volumes of the complexing agent to 100 ml. of benzene. The molality (*m*) of the solutions was then calculated. The desired molalities were prepared after previously determining the necessary concentrations for measurable extractions of the dye salt. The complexing agents used included the normal amyl, hexyl, octyl, and lauryl alcohols as well as methylene chloride, chloroform, and ethylene dichloride.

Procedure.—The procedures previously described were modified (1). Specific volumes of the stock solution of the dye and amine were mixed in 4-ounce amber bottles and brought to a final aqueous volume of 40 ml. with distilled water. Usually 3 μ m. each of the dye and amine were added. A 40-ml. quantity of the organic solvent was added to the 40 ml. of aqueous solution. Blank solutions were prepared also. All bottles were then shaken for 1 hour in an Eberbach horizontal shaker. Following the shaking the liquids were transferred to glass-stoppered separators, and the nonpolar and aqueous phases were separated.

Analysis.—The spectra of the aqueous solutions of the sulfonic acid dyes were scanned using the Cary model 15. The Beckman DU spectrophotometer was used for determining the absorbance of the dye salts in the aqueous extracts. The absorbance of the tropaeolin O solutions was determined after the solutions were made strongly basic with sodium hydroxide (pH > 12.5).

Determination of Apparent Partition Coefficient.—The apparent partition coefficient was derived in the previous paper knowing that the dye salt existed as the ion-ion pair in the organic phase and that the cation and anion were completely dissociated in the aqueous phase (1). The same approach was used in these studies in determining the apparent partition coefficient. The following chemical equation was used



where K_{app} is the apparent partition coefficient,

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TABLE I.—APPARENT PARTITION COEFFICIENTS OF SOME DYE SALTS

Dye Salt	Apparent Partition Coefficient (L./mole)
Di-iso-amylamine salt of tropaeolin OO	1.5×10^{-3}
Di-iso-amylamine salt of methyl orange	2.3×10^{-4}
Di- <i>n</i> -octylamine salt of methyl orange	3.35×10^{-4}
Di- <i>n</i> -octylamine salt of tropaeolin O	1.3×10^{-4}
Di- <i>n</i> -octylamine salt of azobenzenesulfonic acid	2.5×10^{-4}

BH^+ (c_1) is the amine cation in the aqueous layer, D^- (c_2) is the sulfonic acid anion in the aqueous layer, and S (c_3) is the dye salt in the benzene layer. Therefore, the apparent partition coefficient was calculated using

$$K_{app} = \frac{c_3}{c_1 c_2} \quad (\text{Eq. 1})$$

The validity of Eq. 1 was checked in the manner previously reported. Various concentrations of amine cation and sulfonic acid dye were mixed in aqueous solution and partitioned with the organic solvent; the concentrations c_1 , c_2 , and c_3 were then determined. When c_3 was plotted against the product of c_1 and c_2 , a straight line intercepting the origin was obtained. In addition, we worked with concentrations low enough knowing that dissociation of the dye salt in the aqueous phase was greater than 90%.

The di-iso-amylamine was the preferred amine for determination of the equilibrium constants using tropaeolin OO and methyl orange, whereas di-*n*-octylamine was used in the tropaeolin O and azobenzenesulfonic acid studies. Previously reported studies indicated that the mechanism of extraction of these two amine salts of tropaeolin OO was the same. The apparent partition coefficients (using aqueous and benzene solvents), calculated from eight or more determinations using various concentrations, are presented in Table I.

TABLE II.—OVER-ALL STABILITY CONSTANTS FOR INTERACTION OF COMPLEXING AGENTS WITH DYE SALTS IN BENZENE SOLUTIONS

Complexing Agent (A)	Dye Salt (S)	Binding No. Complexing Agent (n)	Over-all Stability Constant (K_c)
Amyl alcohol	Di- <i>n</i> -octylamine azobenzenesulfonate	2.23	3.5×10^2
Hexyl alcohol		2.30	4.72×10^2
Lauryl alcohol		2.23	6.69×10^2
Hexyl alcohol	Di-iso-amylamine salt of methyl orange	1.78	8.8×10^1
Octyl alcohol		1.78	9.4×10^1
CH ₂ Cl ₂		1.15	5.5×10^{-1}
CHCl ₃		1.11	5.4×10^{-1}
Cl(CH ₂) ₂ Cl		0.96	4.2×10^{-1}
CH ₂ Cl ₂		1.20	1.54×10^{-1}
Amyl alcohol		3.16	4.74×10^1
Octyl alcohol	Di-isoamylamine salt of tropaeolin O	3.00	8.42×10^1
Amyl alcohol	Di-iso-amylamine salt of tropaeolin OO	1.89	0.99×10^2
Hexyl alcohol		1.85	1.37×10^2
Octyl alcohol		1.81	1.67×10^2
Lauryl alcohol		1.84	1.80×10^2
CH ₂ Cl ₂		1.68	1.24×10^{-1}
CHCl ₃		1.97	1.21×10^{-1}
Cl(CH ₂) ₂ Cl		1.88	1.01×10^{-1}

Determination of Binding Number and Over-all Stability Constant.—The complexing tendencies of primary alkanols and halogenated solvents with some dye salts are presented in Table II. The binding power of the complexing agent with the dye salt and the over-all stability constant for the complexation are also recorded. The data presented are obtained from six or more sample determinations.

The formation of the complex in the benzene solution may be expressed by $S + nA \rightleftharpoons SA_n$, where S is the dye salt in the benzene phase, A is the complexing agent in the benzene phase, n is the binding number of the complexing agent, SA_n is the complex in the benzene phase, and K_c is the over-all stability constant. The mathematical expression for the over-all stability constant is

$$K_c = \frac{SA_n}{(S)(A)^n} \quad (\text{Eq. 2})$$

Equation 2 may be rearranged and expressed in the logarithmic form as

$$\log K_c + n \log A = \log \frac{SA_n}{S} \quad (\text{Eq. 3})$$

The concentration of A is expressed as the molality (m) of the complexing agent in the benzene layer. The amount of the dye which is not complexed in the benzene solution (referred to as S or as c_3 in Eq. 1) is calculated by (a) utilizing Eq. 1, (b) using the apparent partition coefficient listed in Table I, and (c) determining the concentrations of the cation and anion in the aqueous phase. Any additional increase in solubility of dye salt in the benzene solution will be attributed to complexation with the complexing agent present in the benzene. The complexed dye in the benzene solution (SA_n) is equal to the total dye salt in the organic layer minus the concentration of S . The total dye salt in the organic layer is equal to the concentration loss in the aqueous layer (1). The complexation number (n) of the complexing agent is the slope of the line obtained by plotting $\log (SA_n/S)$ versus $\log A$. The complexation numbers for the various dye salts in benzene are listed in Table II. The plots of some of the data are presented in Figs. 1-5.

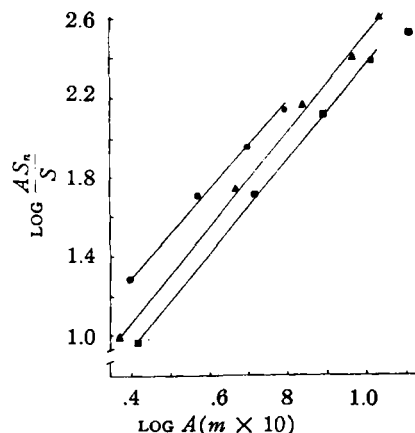
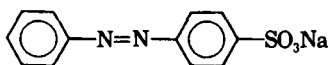


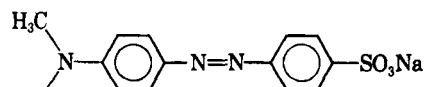
Fig. 1.—Log-log plot of the complexed (SA_n) and noncomplexed (S) amine salt of azobenzenesulfonic acid to the molality of the complexing agent. Key: ●, lauryl alcohol; ▲, hexyl alcohol; ■, amyl alcohol.

DISCUSSION

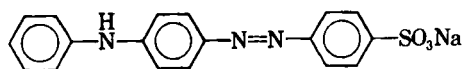
The sulfonic acid dyes were chosen because of the difference in functional groups attached to the azobenzenesulfonic acid nucleus. They were also chosen possibly to correlate the complexation of the alcohol or halogenated solvent to the structure. The formulas are



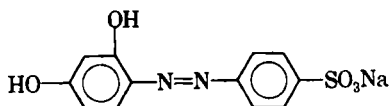
Sodium azobenzenesulfonate



Methyl orange



Tropaeolin OO



Tropaeolin O

Complexation with Primary Alkanols.—Alcohols are capable of being both acceptor and donor molecules in hydrogen bonding; the molecule or ion that serves as the proton acceptor may be termed the base (4). Pearson and Levine have stated that alcohols are "outstandingly efficient extractors of organic acids from water solution" (5). They also suggested that the sulfonate anion present in the aqueous phase would have little tendency to complex with any other structure than that of a hydrogen donor such as an alcohol.

Consequently, the presence of the amino or hydroxy group on the azobenzenesulfonate nucleus could affect the degree of complexation in the organic phase and could affect the apparent partition coefficient. In addition, the azo group may be considered to accept the hydrogen donor molecule since it is a basic functional group (6).

The binding number of the alcohols in the organic phase was determined using Eq. 3. The experimental data were plotted as shown in Figs. 1–5. The amine salt of azobenzenesulfonic acid complexed with 2 moles of the primary alcohol in benzene. Having determined this, the alcohol complexation was determined with the dyes having a substituted amine group, *i.e.*, methyl orange and tropaeolin OO. The salts of both dyes complexed with 2 moles of alcohol also. This may appear to be surprising, particularly for the salt of methyl orange, since one might predict 3 moles of alcohol to complex with the dye salt in benzene when compared to the azobenzenesulfonic acid studies. However, it is possible that the dimethylamino group hydrates, thereby carrying water into the organic layer. Investigations are now underway to determine if this does occur. Hydration has been found to occur in the partitioning of dibasic acids (7). Examination of the structure of tropaeolin O shows the presence of two phenolic groups. These groups had a positive effect in complexation with alcohol. Under the conditions of the experiments 3 moles, not 4 moles, complexed with tropaeolin O. Two moles of alcohol also complexed with the amine salt of tropaeolin OO. In considering the over-all stability constant and the apparent partition coefficient, it must be concluded that tropaeolin OO is the choice of the four dyes studied for amine salt extraction.

The presence of the phenolic groups had an over-all effect of reducing the apparent partition coefficient of the dye salt between benzene and water, whereas the dimethylamino group had a positive effect on the apparent partition coefficient.

It is significant to note that the over-all stability constants of the alcohol complexes of the dye salts increased with an increase in the molecular weight of the alcohol. This is demonstrated by examination of the values in Table II or the plots in Figs. 1, 2, 4, and (in particular) Fig. 5. The acid strength of aliphatic alcohols should not be expected to increase with an increase in molecular weight (4, 8). Therefore, the increase in the over-all stability constant for the complexation may be attributed to increased van der Waals forces of attraction as the chain length of the alcohol is increased. It is also possible that micelle formation may contribute to the over-all stability constant. Studies are underway to deter-

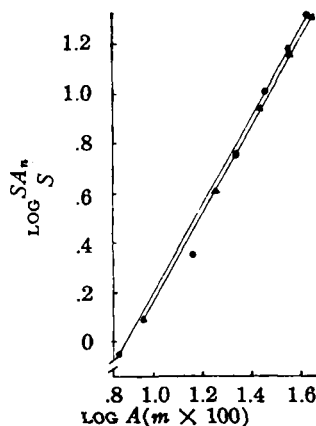


Fig. 2.—Log-log plot of the complexed (SA_n) and noncomplexed (S) amine salt of methyl orange to the molality of the complexing agent. Key: ●, octyl alcohol; ▲, hexyl alcohol.

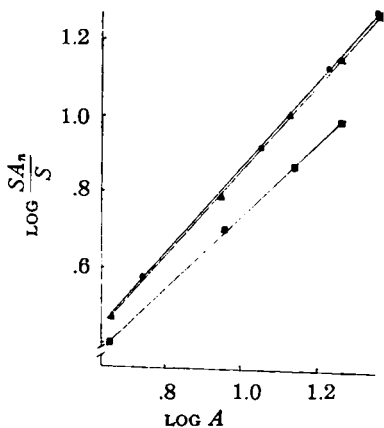


Fig. 3.—Log-log plot of the complexed (SA_n) and noncomplexed (S) amine salt of methyl orange to the molality of the complexing agent. Key: ●, methylene chloride; ▲, chloroform; ■, ethylene dichloride.

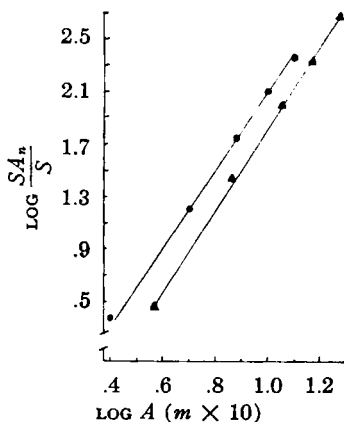


Fig. 4.—Log-log plot of the complexed (SA_n) and noncomplexed (S) amine salt of tropaeolin O to the molality of the complexing agent. Key: ●, octyl alcohol; ▲, amyl alcohol.

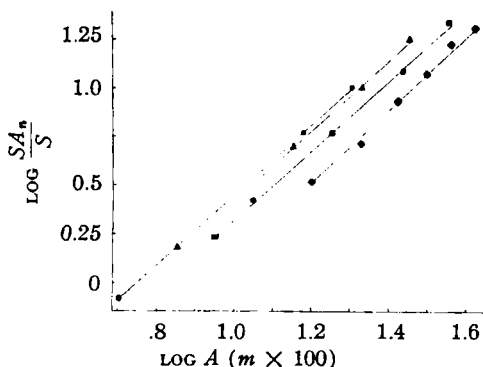


Fig. 5.—Log-log plot of the complexed (SA_n) and noncomplexed (S) amine salt of tropaeolin OO to the molality of the complexing agent. Key: ●, lauryl alcohol; ▲, octyl alcohol; ■, hexyl alcohol; ◆, amyl alcohol.

mine the thermodynamic properties (ΔF , ΔH , and ΔS) of the complexation.

When Mitchell and Clark developed a suitable method for the determination of quaternary ammonium compounds, they utilized the dye brom-

phenol blue. They used ethylene dichloride as the water immiscible extracting solvent. To minimize any possibility of adsorption of the dye salt from the organic solvent onto the glass surface, the investigators added 1.5% isoamyl alcohol by volume (9). As a result of our studies, one has a greater understanding of the use of isoamyl alcohol. All of the evidence provided should prove more beneficial to the analyst.

Complexation with Halogenated Hydrocarbons.—The halogenated solvents may be considered solvents whose acid strengths are less than those of the primary alcohols. Investigators recently have presented their research measuring the effectiveness of the C—H group in the halogenated solvents as a proton donor (10, 11). Complexation with these solvents is possible, but the over-all stability constant for the complexation would be less than the value for the alcohol complexation. This, as shown in Table II, was found to be true; the over-all stability constants with the halogenated solvents were about a thousandfold less than the values for the alcohol complexation. Complexation of the halogenated solvents with the dye salts of azobenzenesulfonic acid and tropaeolin O was so small that the over-all stability constant could not be determined.

The three halogenated solvents complexed with the amine salts of methyl orange and tropaeolin OO. Two moles of the hydrocarbon complexed with 1 mole of the tropaeolin OO salt. With this knowledge it was surprising to find that a 1:1 complex formed with the methyl orange salt and the hydrocarbon solvents. To verify the 1:1 complex formed with the di-iso-amylamine salt of methyl orange, studies were repeated using di-*n*-octylamine. As recorded in Table II, the di-*n*-octylamine salt of methyl orange also formed the 1:1 complex with the halogenated hydrocarbon in benzene.

The data obtained using the di-iso-amylamine salt of methyl orange are plotted in Fig. 3. On the molality basis, methylene chloride and chloroform are equally effective in extracting the dye salt. Similar results were obtained using tropaeolin OO. Since the over-all stability constants are the same or nearly so, it is quite possible to conclude that the acid strength of these halogenated hydrocarbons is the same, or the polar and nonpolar influences of the three solvents balance out to give the same over-all stability constant. These results then question the opinions of Mukerjee (2) and the authors as reported in our previous report (1) concerning the reliance on the dielectric constant in choosing a suitable solvent.

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