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A STUDY OF SOME CHARGE-TRANSFER COMPLEXES INVOLVING N-METHYLACETAMIDE AND OTHER AMIDES

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Abstract—Spectral studies of solutions of tetracyanoethylene and various amides indicate that charge-transfer complexes are formed. It is postulated that these complexes are the n,π donor–acceptor type and that formation occurs through the carbonyl oxygen of the amide since benzamide, in which there is conjugation of the aromatic ring and CO group is the only amide for which no CT band is observed.

Complexes between N-methylacetamide (NMA) and nitrobenzene, *m*-dinitrobenzene, 2,4,6 trinitrobenzene and benzaldehyde as acceptors have also been observed in carbon tetrachloride solutions. Formation constants for these complexes of 0·97,1·14, 1·55 and 2·00, respectively, have been calculated from the UV spectra, with a possible error in these calculations of about 15%. Complexes between N-methylacetamide and *m*-dinitrobenzene have also been studied in solvents having a range of dielectric constants from 2·23 (CCl_4) to 32·63 (MeOH). The values of the complex formation constants vary inversely with the dielectric constant of the solvent. A study of NMA complexes of anthraquinone and *p,p'*-dinitrobenzyl in chloroform solutions indicate that charge-transfer complexes are formed with both rings of the 2-ring compounds. Spectra of *p*-nitrotoluene are compared with those of 4,4'-dinitrobibenzyl and it is found that both compounds have similar absorption peaks at 310 mμ. The dinitrobibenzyl complex also has an absorption peak at 393 mμ for which the NMA concentration dependence is the same as that of the 308 mμ peak. A complex formation constant of 0·49 is calculated in each instance. Osmotic coefficients of 4,4'-dinitrobibenzyl in NMA as determined by freezing-point depression are greater than unity for dilute solutions. This had been observed previously only for solutions of anthraquinone and its sulfonated salts.

INTRODUCTION

IT HAS has been demonstrated[1–3] that N-methylacetamide (NMA) serves as a solvent for a variety of different types of solutes. It is, for example, one of the few substances which is miscible in all proportions with both water and benzene. It is virtually insoluble, however, in aliphatic hydrocarbons. It was postulated[2] that two types of solvation were responsible for this behavior. For solutes as water, alcohols, carbon tetrachloride, etc., the solvation is probably accomplished by the formation of solute–solvent hydrogen bonds. The solvation of aromatic hydrocarbons and substituted aromatic hydrocarbons was stated to arise from the formation of a charge-transfer complex with NMA as the electron donor.

Complexes of the electron donor–acceptor type (EDA complexes) are well known and Briegleb[4] has published a rather complete summary of work appearing in this area before 1961. These complexes are characterized by CT absorption bands in the UV or visible region which are in general broad, unsymmetrical and have no fine structure even at low temperatures. The complexes usually produce colored solutions. Spectral measurements thus appeared to be the most convenient method of identification and this work was initiated to verify the second type of amide solvation and to measure the formation constants for several typical complexes.

RESULTS AND DISCUSSION

A. *Complexes between amides and tetracyanoethylene*

In previous measurements of colligative properties of NMA, it appeared that complexes occurred when aromatic solutes were used and that they were stronger when ring substituents were electron-withdrawing groups. This induced the belief that they were π acceptors. It was also believed that NMA was an n donor but few data are available for amides. A strong π acceptor, TCNE, was chosen since amides probably form weak complexes, and a solvent of low dielectric constant, 50–50 volume percent chloroform and methylene chloride was used. When amides, with the exception of benzamide, were added to the solutions of TCNE, they became colored and a new broad band appeared at 400–420 mμ. It was noted that the presence of groups adjacent to the CO group or N atom which delocalized the electrons tended to reduce the intensity of the visible absorption. Although the absence of a band in solutions of benzamide, in which the aromatic ring is conjugated with the CO group, is not conclusive evidence, it is a further indication that the complexes are of the n,π type with the non-bonded CO electrons being involved. Positions of CT absorption maxima are given in Table 1.

TABLE 1. ABSORPTION MAXIMA OF COMPLEXES OF TETRACYANOETHYLENE IN 50–50 CHLOROFORM, METHYLENE CHLORIDE SOLUTIONS

Donor	λ_{max} (mμ)
N,N-Dimethylacetamide	302
N,N-Dimethylformamide	302
N-Methylacetamide	307
Dimethyl urea	324
N-Methylformamide	328
N,N-Diphenylacetamide	325 to 330
N-Ethylacetanilide	358
Acetamide	443, 470 (doublet)
α-Phenylacetamide	443, 470
Formamide	448, 471 (doublet)
Acetanilide	458
Benzamide	none

B. *Complexes between NMA and substituted aromatic compounds in carbon tetrachloride solution*

Spectra were recorded for solutions of at least three different concentrations of nitrobenzene, *m*-dinitrobenzene, 2,4,6 trinitrobenzene and benzaldehyde and for solutions of these substances in which NMA concentrations ranged from 0·016M to saturation. Charge-transfer complex constants were calculated for the reaction

$$\text{NMA} + \text{acceptor} = \text{complex}$$

from absorbances at several wave lengths on the broad CT bands and for various concentrations of donor and acceptor. The equilibrium constant for this reaction may be represented as

$$K = \frac{[\text{complex}]}{[\text{NMA}][\text{acceptor}]}$$

The results are shown in Figs 1–4 as a plot of K as a function of the initial concentration of NMA. It may be observed that in all systems, the values of K become larger as the concentration of NMA decreases. No such systematic behavior is observed when the concentration of the acceptor molecule is varied. It is believed that this

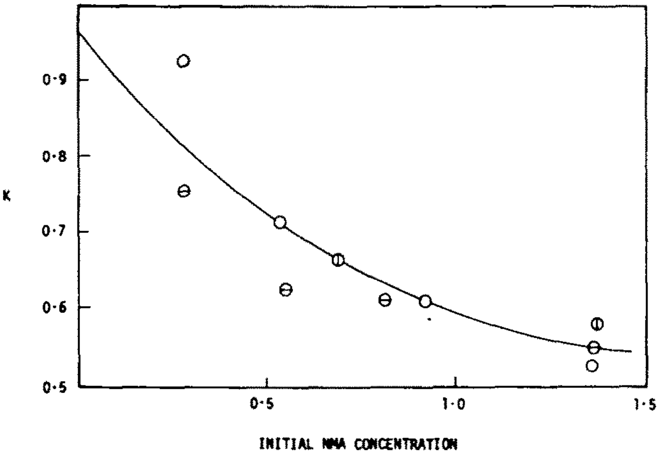

FIG. 1 Nitrobenzene–NMA charge-transfer complex constants

○ 0·0501M nitrobenzene } $\lambda = 305$ mμ
⊖ 0·0250M nitrobenzene }
⦶ 0·0125M nitrobenzene $\lambda = 285$ mμ

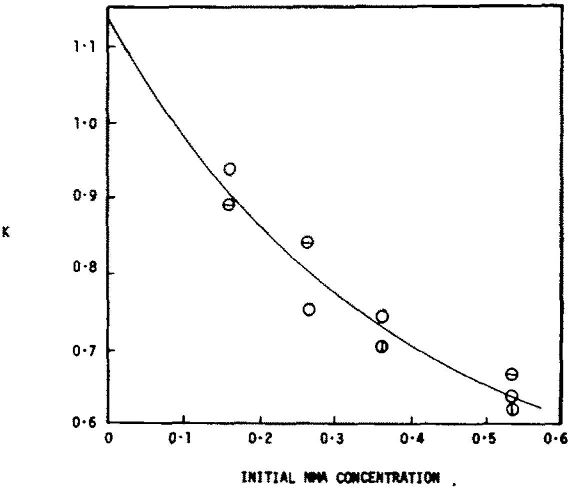

FIG. 2 *m*-Dinitrobenzene–NMA charge-transfer complex constants.

○ 0·01135M dinitropenzene
⊖ 0·00681M dinitrobenzene
⦶ 0·00454M dinitrobenzene.

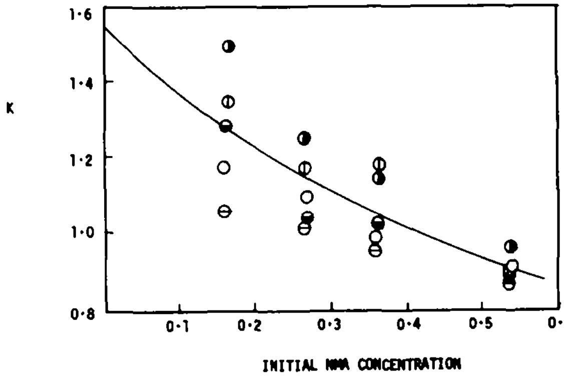

FIG. 3 2,4,6-Trinitrobenzene–NMA charge-transfer.

○ 0·00930M trinitrobenzene
⊖ 0·00465M trinitrobenzene
⦶ 0·00233M trinitrobenzene
$\lambda = 280$ mμ

◒ 0·00465M trinitrobenzene
◑ 0·00233M trinitrobenzene
$\lambda = 270$ mμ.

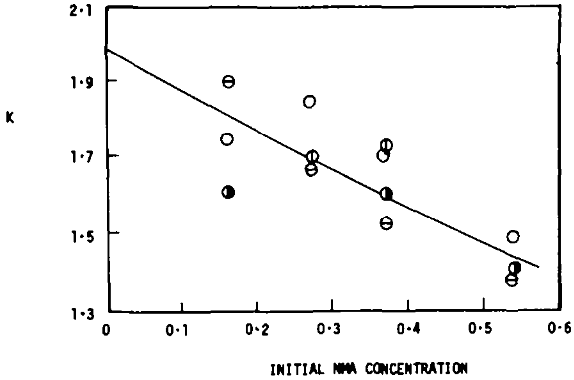

FIG. 4 Benzaldehyde–NMA charge-transfer complex constants.

○ 0·197M benzaldehyde
⊖ 0·0985M benzaldehyde
◑ 0·0492M benzaldehyde
⦶ 0·0246M benzaldehyde.

behavior is due in part to the decrease in the length of the chain of hydrogen-bonded NMA molecules with dilution. Lin and Dannhauser[5] have shown that NMA is a highly associated liquid, consisting of "polymer chains" of varying lengths. It would be expected that NMA would still exhibit some degree of "polymerization" in the more concentrated solutions for which spectra were recorded. A second cause of this behavior, which will be dealt with in more detail in the next section of this paper, is the variation in dielectric constant of the solvent medium as the concentration of NMA is varied.

The four equilibrium constants (Table 2), which have been obtained by extrapolation of the K vs. [NMA] curves to infinitely dilute NMA, appear to have an uncertainty of

TABLE 2. TABLE OF CHARGE-TRANSFER FORMATION CONSTANTS IN CARBON TETRACHLORIDE SOLUTIONS

Acceptor	K	Wave Length at which calculated (mμ)
Nitrobenzene	0·97	305, 285
m-Dinitrobenzene	1·14	275
2,4,6-Trinitrobenzene	1·55	280, 270
Benzaldehyde	2·00	297

perhaps 15% which is usual for this type of measurement. They are in the expected order for the three nitrobenzenes. The values of K increase with the addition of nitro groups to the aromatic ring causing it to become more electron deficient. The large value of the formation constant when benzaldehyde is the acceptor atom appears to be somewhat anomalous and, although no exact interpretation will be attempted, two relevant observations should be noted. Foster[6] has indicated that steric effects can play an important role in the formation of charge-transfer complexes. The observations of Olah[7] are of perhaps even greater significance. He differentiates between π-complex formation and σ-complex formation as the rate-determining step in aromatic substitution and shows that the Hammett-Brown treatment is not applicable when the former mechanism is dominant. It is reasonable to expect, therefore, that formation constants of the n,π type complexes should not necessarily follow the order of the Hammett σ constants.

C. *Effect of solvent*

The original interest of the authors was in the formation of NMA-aromatic charge-transfer complexes with NMA as the solvent. Although verification of the formation of such complexes has been spectroscopically achieved in the preceding section, the two constituents are the minor components in a solution in which carbon tetrachloride is the solvent. Since a diluent is necessary for the measurement of these formation constants because of the large molar absorptivities of the complexes, it was thought advisable to observe the effect of the solvent on this reaction. The *m*-dinitrobenzene–NMA complex was chosen because the absorbance varies only slightly with wave length over a range of several millimicrons.

Spectra were recorded for at least two concentrations *m*-dinitrobenzene in each of five solvents. From the results shown in Table 3 it is apparent that the strength of the

TABLE 3. TABLE OF FORMATION CONSTANTS FOR THE N-METHYLACETAMIDE-*m*-DINITROBENZENE CHARGE-TRANSFER COMPLEX

Solvent	Dielectric constant	K
MeOH	32·63	0·09+
CH_2Cl_2	9·08	0·35
$CHCl_3$	4·81	0·55
Et_2O	4·34	0·63
CCl_4	2·23	1·14

complex decreases as the dielectric constant of the solvent becomes larger. This is possibly the result of two effects which may reinforce one another. It might be expected that a solvent having a higher dielectric constant would be more effective in the separation of an electron "source" and an electron "sink" just as it enhances ionization and decreases dipole–dipole interactions. It is probable also that NMA is solvated to a greater extent by the more polar solvents and that this solvent shell must be removed when the complex is formed. The solvation effect must be the smaller of the two effects, however, since there is a uniform variation of K with the reciprocal of the dielectric constant (Fig. 5) and one would expect stronger hydrogen bonds between NMA and the oxygens of MeOH and Et_2O than would be the case with CCl_4, CHI_3 or CH_2Cl_2 as the solvent.

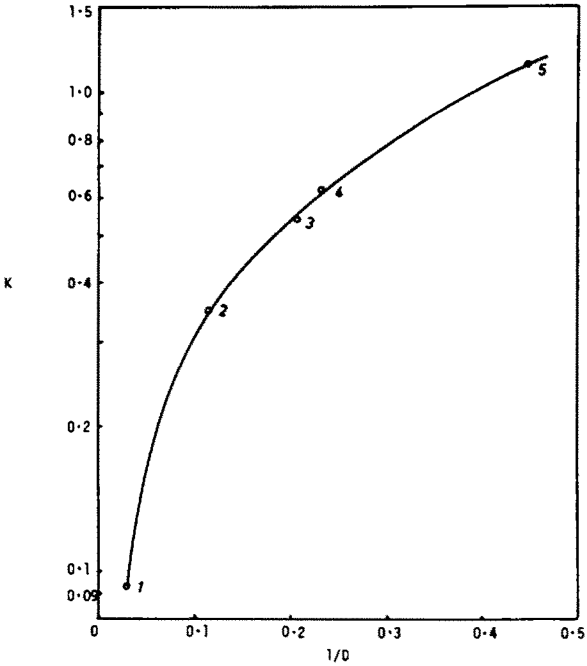

FIG. 5 m-Dinitrobenzene–NMA charge-transfer complex constants in several solvents.
1. MeOH 2. CH_2Cl_2 3. $CHCl_3$ 4. Et_2O 5. CCl_4.

D. *Complexes of NMA with two-ring aromatic compounds*

In studies of the colligative properties of NMA solutions,[2] only three solutes were found which gave negative deviations from Raoult's law. These were anthraquinone, 2-sodium anthraquinone-sulfonate and 2,7 disodium anthraquinonedisulfonate. In all instances these were 2-ring aromatic compounds and it was speculated that the rings solvated independently by the formation of charge-transfer complexes with NMA. The spectra of NMA complexes of these substances are difficult to obtain because of solubility problems. Only chloroform and solvents of high dielectric constant can be used and in high dielectric solvents the complex formation constants are too small to be determined accurately. Spectra of the anthraquinone complex may be measured in solutions of chloroform containing moderate amounts of NMA

TABLE 4. TABLE OF CHARGE-TRANSFER FORMATION CONSTANTS IN CHLOROFORM SOLUTIONS

Acceptor	K	Wave lengths of absorption peaks (mμ)
Anthraquinone	0·54	350, 283
p-Nitrotoluene	0·49	310
4,4'-Dinitrobibenzyl	0·49	393, 310

and two absorption peaks are observed at 350 and 283 mμ. It was not possible to use saturated solutions of NMA to obtain spectra in which essentially all of the anthraquinone was complexed since these quantities of NMA caused precipitation of the complex. Approximate values were obtained, however, by extrapolation procedures and a complex formation constant of 0·54 was calculated. This value is approximately that which would be expected in this solvent.

It is of interest that new bands appear with λ_{max} at 281 mμ in N-methylformamide-anthraquinone solutions, 273 mμ in N,N-dimethylformamide-anthraquinone solutions and at 287 mμ and 355 mμ in N,N-dimethylacetamide-anthraquinone solutions.

It is believed that these data indicate the formation of NMA complexes with both rings of this compound since only one absorption maximum was observed for all of the one-ring compounds studied previously.* Because of the solubility difficulties, though, it was felt that further verification would be desirable. It was found that solutions of 4,4'-dinitrobibenzyl and *p*-nitrotoluene in chloroform yielded excellent spectra and that the charge-transfer formation constants are of such a magnitude that they can be accurately determined. These compounds are of unusual interest since the 4,4'-dinitrobibenzyl can be considered a dimer of *p*-nitrotoluene. A comparison of their spectra (Fig. 6) furnishes the following information.

(a) Both compounds from complexes with NMA which have an absorption maximum at 310 mμ.

(b) The molar absorptivities of the two complexes are identical since the intensities at this wave length are the same when identical molar concentrations of NMA and acceptor are used.

(c) The 4,4'-dinitrobibenzyl complex has an additional absorption maximum at 393 mμ which is assumed to be due to the second ring.

(d) Complex formation constants calculated for both compounds have identical values of 0·49 as calculated from the 310 mμ band. No value has been calculated for the second band.

(e) The isosbestic points occurring between the two peaks appear to be further evidence that complexes are formed by both rings of the two-ring compound.

At this point it was felt that a study of the colligative properties of solutions of 4,4'-dinitrobibenzyl in NMA would be an appropriate conclusion to these investigations.

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* Briegleb (Ref. 4, p. 48) lists four conditions under which CT bonds may have two distinct absorption maxima, only one of which appears applicable to this system. It is the case in which two stable configurations of the complex in solution are possible, resulting in two different values for the couloumbic energy.

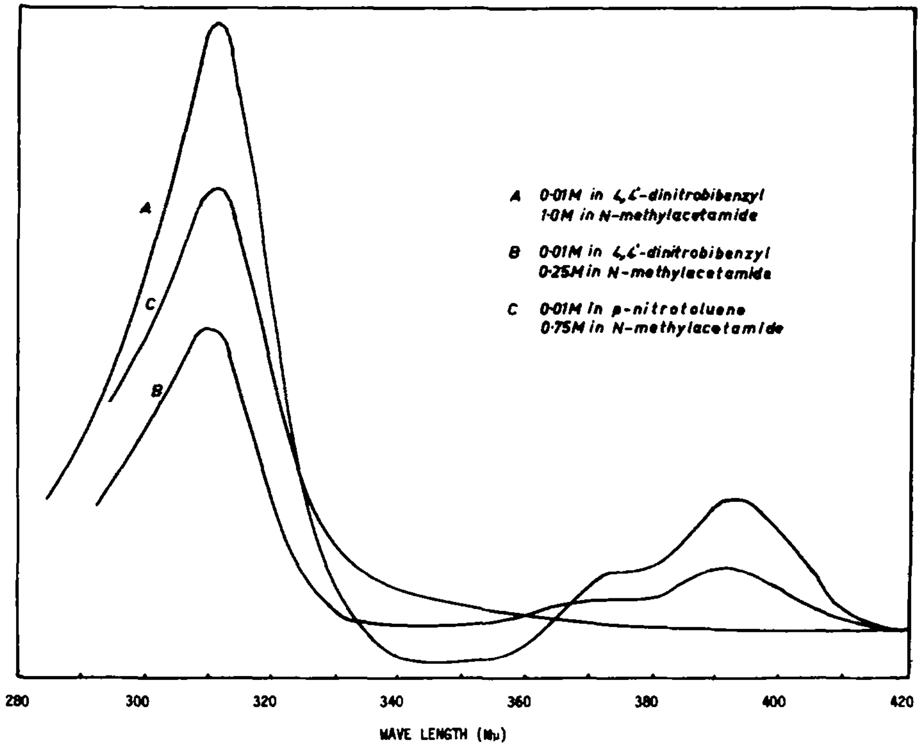

FIG. 6 Charge-transfer complex spectra in chloroform.

The data of Table 5, in which osmotic coefficients greater than unity are observed in dilute solutions, are similar to those of the systems in which anthraquinone and its sulfonate salts were solutes. It is believed that this combination of spectral and thermodynamic evidence confirms the conclusions reached earlier[2] about the structure and solvation of NMA.

TABLE 5. TABLE OF OSMOTIC COEFFICIENTS OF 4,4-DINITROBIBENZYL IN N-METHYLACETAMIDE

m	ϕ
0·00478	1·035
0·00968	0·968
0·01994	0·967

EXPERIMENTAL

A. *Purification of materials*

Solvents. Reagent grade solvents were used and in all instances were twice distilled with the middle fraction being used. Drying precautions were also taken such as distillation of MeOH from Mg and passage of CCl_4 through activated alumina prior to distillation.

Solutes. Tetracyanoethylene (TCNE) was sublimed under vacuum and immediately dissolved in dry $CHCl_3$. Solns containing 0·1% TCNE were colorless. All amides except NMA were twice recrystallized from EtOH and dried under vacuum. Reagent grade aromatic compounds were used. Solids were, in general, recrystallized from an appropriate solvent. Benzaldehyde was distilled at 20 mm press under an atmo of N_2 just prior to use. The nitrobenzene was repeatedly washed with conc Na_2CO_3 aq and distilled water. It was then passed through a column of alumina and distilled under reduced press.

N-Methylacetamide was vacuum distilled and zone refined.[1] Solns of NMA in the various solvents were spectroscopically transparent at the wave lengths used in the calculation of the complex constants.

B. *Spectral measurements*

All spectra were recorded using a Cary Model 14M spectrophotometer. The experimental procedures were similar to those reported in recent spectral investigations of similar systems.[8–10] complex formation constants have been calculated from data at several wave lengths for some of the systems as was done by Jurinski and Popov *et al.*[8–10] The correction for the absorbance of the acceptor molecule at the wave lengths used to determine the complex concentrations was accomplished in a different manner. Drago[9] reports complexes between substituted anilides and I_2 and states that the absorption of the complex was corrected by subtracting the absorbance measured for I_2 in solns having the same I_2 concentration. In our studies spectra of complexed and uncomplexed solns having the same stoichiometric concentration of the acceptor were compared *directly* in the double beam instrument. In order to determine the fraction of the aromatic acceptor which was complexed in the dilute solns a spectrum was recorded in each system of solns which were saturated with NMA and the absorbance of the 100% complexed acceptor was obtained by extrapolation. The use of essentially pure NMA as a solvent caused no shift in absorption bands. This is in agreement with previous reported observations.[11,12]

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