

it is necessary to allow for the change in density of the solution. For the very dilute solutions used in the present work, adequate correction is obtained by multiplying the optical density by the relative volume of the solvent referred to some standard condition. Such a correction has been applied to the measurements shown in Figure 1.

Table I gives the wavelength of the CT maximum, λ_{CT} , and the energy shift of it at 3040 bars ($\delta\nu$ in cm^{-1}), as well as the equilibrium constants and absorption coefficients found at 1 bar and the volume change derived from the pressure variation of K , for the different complexes we have examined.

Table I: Equilibrium Constants, Absorption Coefficients, and CT Maxima of EDAC in Solution

Complex (solvent)	Temp, °K	λ_{CT} , nm	$\delta\nu$ (3040 bars), cm^{-1}	K , (mole fraction) $^{-1}$	ϵ , $\text{mol l.}^{-1} \text{cm}^{-1}$	ΔV , $\text{cm}^3 \text{mol}^{-1}$
MMPI (acetone)	265.2			2680 ^a		
	275.2			4180 ^a		
	293.2	427	416	3600	1060	
	303.2	429	590	3200	930	+16
	313.2	434	660	3000	1710	
MMPI (<i>i</i> -BuOH)	303.2	372	220	43000	910	+17
I ⁻ -TNB (MeOH)	298.2	360	0	87	390	0
I ⁻ -TNB (<i>i</i> -BuOH)	318.2		0	27	940	
I ⁻ -TNB (<i>i</i> -BuOH)	298.2	365	0	1540	575	
TRP ⁺ -HMB (CH_3CN)	308.2		0	550	340	
TRP ⁺ -HMB (CH_3CN)	303.2	417 ± 3	0	165	455	0
MCP ⁻ -TNB (CH_3CN)	313.2	413 ± 2	0	52	1180	
MCP ⁻ -TNB (MeOH)	303.2	382	0	194	1260	0
MCP ⁻ -TNB (MeOH)	313.2	385	0	73	2620	

^a From ref 3.

Figure 2 is a plot of the values of $\log K^p/K^1$ as a function of pressure and includes¹ the neutral complex TNB-HMB for comparison. Figure 3 shows the values of $\delta\nu$ found for the complexes at various pressures. Values for TNB-HMB are again included. The pressure shift is zero within the accuracy of the measurements for all the ion-neutral EDAC and only the TRP⁺-HMB complex is shown.

We shall discuss the individual systems first and then draw some general conclusions.

MMPI. The spectra of this salt were measured in acetone at three temperatures, and in *i*-BuOH at one temperature, at five pressures between 1 and 3040 bars. The concentration range was 5 to 80×10^{-5} mole fraction MMPI.¹² The absorption band in *i*-BuOH was found at a shorter wavelength and showed less pressure shift than the band in acetone. The great sensitivity of the MMPI/CT band to solvent polarity has been attributed by Kosower² to a "dipole flip" of the complex during excitation which, due to the Franck-Condon

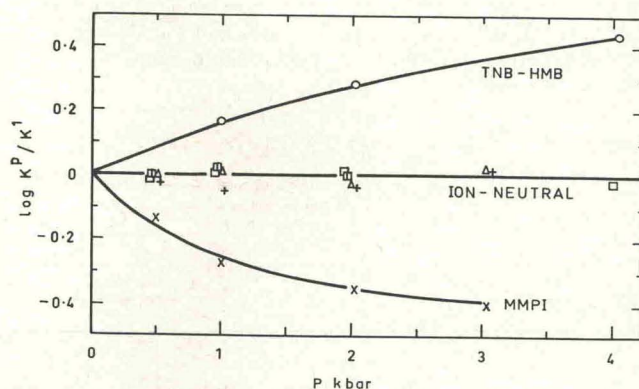


Figure 2. Effect of pressure on the relative stability of various EDAC.

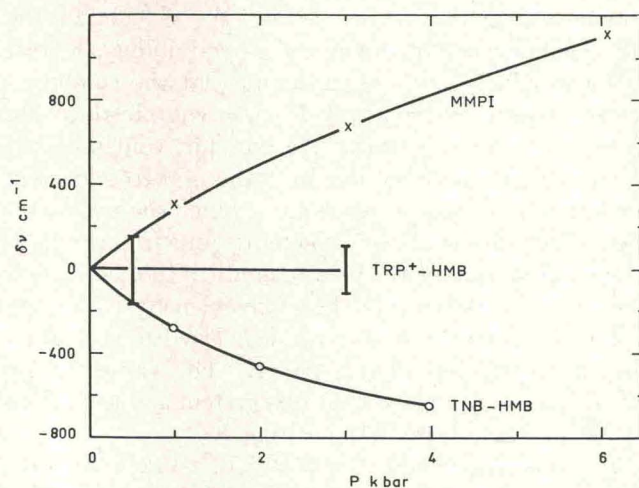


Figure 3. Effect of pressure on the energy of the CT transition of various EDAC.

effect, leads to a mismatch between the dipole field of the excited complex and the reaction field of the solvent around it. This destabilizes the excited state relative to the ground state and leads to a blue shift of the absorption band when the solvent interaction is increased by increase of pressure.

The system has been the subject of a detailed conductometric investigation³ and this led to association constants which were rather different (Table II) from those found spectroscopically and given in Table I. According to Prue's "optical marker" argument¹⁹ the two methods could give the same association constant even if not all the associated species give a CT absorption; the ϵ derived from spectroscopic measurements on such systems, on the other hand, is a weighted average of the absorption coefficient of the different associated species. We therefore carefully analyzed our present results to see whether the difference between them and the earlier results is significant.

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Table II: MMPI Association Constants at 1 bar Found Conductometrically (from Ref 3 Converted to (mole fraction)⁻¹ Units)

Temp, °K	265.2	275.2	293.2	303.2	313.2
	—In acetone—				
$K_\gamma \times 10^{-3}$	2.68	4.18	8.11	8.56	13.3
	—In <i>i</i> -BuOH—				
$K_\gamma \times 10^{-3}$	52.1	...

We used a computer to map out the standard deviation in the fit of eq 2 as a function of K and ϵ . This showed the minimum to lie in a long, narrow, approximately hyperbolic valley, along which the value of the standard deviation varies little. We calculated the 90% confidence limits for K and ϵ by applying a χ^2 test to the residual variance and found that the conductometric association constant K_γ was contained within these limits in every case. We therefore conclude that the difference between K_γ and the spectroscopically determined K_s is *not significant*. Since the conductometric measurements are inherently much more accurate ($\pm 10\%$),³ K_γ is the best estimate of the association constant in this system. For convenience we quote in Table II the values from ref 3, converted to mole fraction units as used in this paper. The values of $\log K^p/K^1$ shown in Figure 2 for this system and the values of ΔV in Table I are derived from K_γ .

The positive values of ΔV are in marked contrast with the contractions found for the EDAC formed from neutral molecules and indicate the important role of desolvation when the EDAC is formed from the component ions. The magnitude of ΔV is not as great as one would expect for completed desolvation of a pair of ions (30–40 cm³/mol, from kinetic measurements²⁰) and this, together with the solvent sensitivity of the CT energy, indicates that the EDAC is still solvated.

I⁻-TNB. The color produced when iodide solutions are added to TNB solutions has been attributed to the formation of EDAC.^{21–23} Briegleb, *et al.*,²¹ found the absorption maximum to be solvent dependent and measured the formation constant and absorption coefficient in a series of solvents using different salts as sources of I⁻ ions. He showed by infrared studies that the complexes differed from "Meisenheimer" complexes, and we confirmed this by nmr measurements.

In our measurements NaI was used as the source of I⁻ and for the measurements in methanol the concentrations ranged from 250 to 1000 $\times 10^{-5}$ mole fraction I⁻, and from 5 to 9 $\times 10^{-5}$ mole fraction TNB. In *i*-BuOH the solutions darken in the course of a few hours,²¹ but this effect can be suppressed by the addition of a small amount (*ca.* 10⁻⁴ M) of glacial acetic acid. The concentration of I⁻ in this solvent was 15 to 300 $\times 10^{-5}$ mole fraction and that of TNB 3 to 30 \times

10⁻⁵ mole fraction. The CT band was observed as a shoulder on the TNB absorption and the spectra had to be corrected for this absorption.

NaI is known to be almost completely dissociated in MeOH^{24,25} and the EDAC formation is therefore not complicated by any ion pair equilibrium. Our results show the CT energy and the equilibrium constant to be unchanged by pressure, but ϵ_{\max} was found to increase slightly with pressure.

In *i*-BuOH only 75% of NaI is dissociated³ and two different complexes can be formed, one between free I⁻ and TNB and therefore carrying a negative charge, and the other from an ion pair and TNB and carrying no charge. These cannot be distinguished in the present experiments. The results in this solvent are similar to those in MeOH except for larger values of K and a decrease of ϵ with rising temperature. This last effect could occur if the charged EDAC had a larger ϵ than the uncharged complex, since with rising temperature the ion pairing in *i*-BuOH increases³ and the observed average ϵ would thus decrease.

In both solvents K is independent of pressure and $\Delta V = 0$. Comparison between the negative ΔV found for neutral complexes¹ and the positive value for MMPI suggests that the contraction due to the formation of the CT bond is just balanced by the reduced electrostriction of the solvent due to the spreading of the ionic charge.

TRP⁺-HMB. The tropylium halides do not give stable solutions and are therefore not suitable for lengthy measurements. The tetrafluoroborate is stable in acetonitrile and was used in these measurements at concentrations between 15 and 150 $\times 10^{-5}$ mole fraction. The π - π complex formed by TRP⁺ with mesitylene²⁶ has $K = 13$ and in order to measure a larger K we used HMB as the donor at concentrations between 25 and 140 $\times 10^{-5}$ mole fraction. The solid brown complex could be obtained by evaporating the solutions and gave an ir spectrum equal to an intimate mixture of the components and a uv spectrum, as a mull, similar to the EDAC in solution.

The EDAC has a very broad CT band at 417 nm and the position has been found to be solvent independent.²⁷ The pressure measurements showed that K is independent of P ($\Delta V = 0$), but ϵ increases slightly with increasing pressure. A rise in temperature caused a decrease in K and an increase in ϵ .

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