



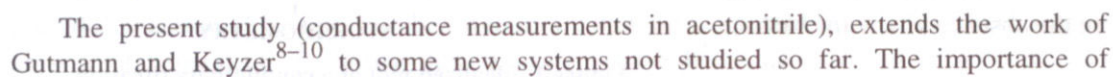
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Conductometric method has been used to investigate electron donor-acceptor complex formation between anthracene (AN), naphthalene (NA) and hexamethylbenzene (HMB) as electron donors and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), chloranil (CA), bromanil (BA) and 1,4-benzoquinone (BQ) as electron acceptors in acetonitrile. The results indicate the formation of 1 : 1 complexes. Effects of concentration, temperature, solvent polarity, ionization potential of donors and electron affinity of acceptors on σ_p , ($\sigma_p - \sigma_o$) and $\alpha\sigma_m$ values have been examined and discussed in detail.

Electron donor-acceptor (EDA) complexes are of current interest because of their diverse applications in non-linear optics¹⁻³ and in solar energy storage⁴. They also play an important role in the reactions of living organisms^{5,6}.

The basic theory of EDA complexes is due to Mulliken⁷. According to this theory, the bonding in an EDA complex is postulated to arise from the partial or complete transfer of an electron from donor (D) to acceptor (A). Mulliken pointed out that when the interaction between the donor and acceptor is very strong, the EDA complex (DA) formed between D and A may undergo dissociation into ions in solvents of sufficiently high dielectric constant giving rise to appreciable electrical conductivity according to the general scheme:



conductometric studies of molecular complexes is increasing rapidly on account of their use as semiconductors^{11,12}. Further, the donors and acceptors chosen for the present work are biologically, analytically and industrially important¹³.

The solvent chosen was acetonitrile because it has a high dielectric constant (37.5) and all the chosen donors and acceptors are soluble in it.

EXPERIMENTAL

1,4-Benzoquinone¹⁴ and bromanil¹⁵ were prepared in the laboratory from hydroquinone and all other donors and acceptors were obtained commercially and purified by standard methods. LR grade acetonitrile (Qualigens) was treated with calcium hydride followed by repeated distillation over P₂O₅ until the conductivity was less than 0.1 μ mho. Carbon-tetrachloride (BDH, AR) was dried and distilled before use.

Equimolar stock solutions of donors and acceptors were prepared freshly in acetonitrile on the day of the experiment and thermostated to a constant temperature. 10 mL of donor solution was taken in a conductivity cell and acceptor was added in 2 mL portions and vice versa. The mixture was stirred after each addition and conductivity (σ) was measured on a digital type direct reading conductivity meter (Control Dynamics Model APX – 185) after five minutes, the usual period required for attaining a constant conductivity value. Plots have been drawn between the measured conductivity and mole fraction of the donor.

According to Gutmann and Keyzer⁸ a non-linear relation, especially appearance of a maximum in the conductivity versus concentration plot is a clear indication of complex formation and molar ratio of donor and acceptor at the position of the maximum in the plot would represent the stoichiometry of the EDA complex (Fig 1). $\alpha\sigma_m$ values were calculated using the Gutmann equation⁹

$$\alpha\sigma_m = \frac{(\sigma_p - \sigma_0)}{M\sigma_0}$$

where α is the dissociation constant of the complex, M is the molar concentration of titrant (either the donor or acceptor) at the conductivity peak, where $\sigma = \sigma_p$ and σ_0 is the background conductivity (i.e.) conductivity in the absence of any interaction.

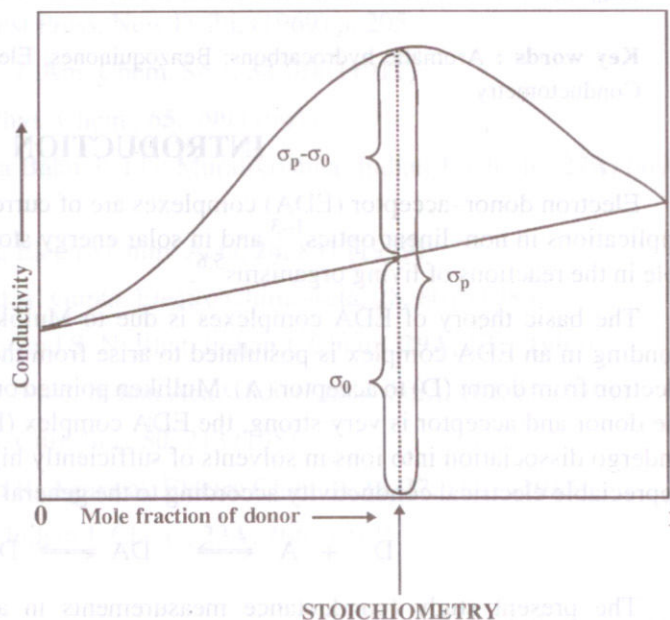


Figure 1. Idealized plot of a conductivity titration

The cell was a closed one with fixed cell constant and fitted with a pair of smooth bright platinum electrodes. It was standardized every day with 0.01N KCl using Lind, Zwolenik and Fuoss constants¹⁶. Care was taken to avoid moisture in the cell. All the measurements were made in a thermostat where temperature was controlled to $\pm 0.05^\circ\text{C}$.

RESULTS AND DISCUSSION

Stoichiometry: Plots were drawn between $(\sigma - \sigma_0)$ values and concentration of the donor/acceptor (Figs. 2–4). All the systems exhibit a well-developed maximum at the molar ratio of 1 : 1; thereby establishing the formation of EDA complex with 1 : 1 stoichiometry. This observation is in agreement with the earlier reports^{8–10}, 17–20 on the stoichiometry of complexes of quinones as 1 : 1.

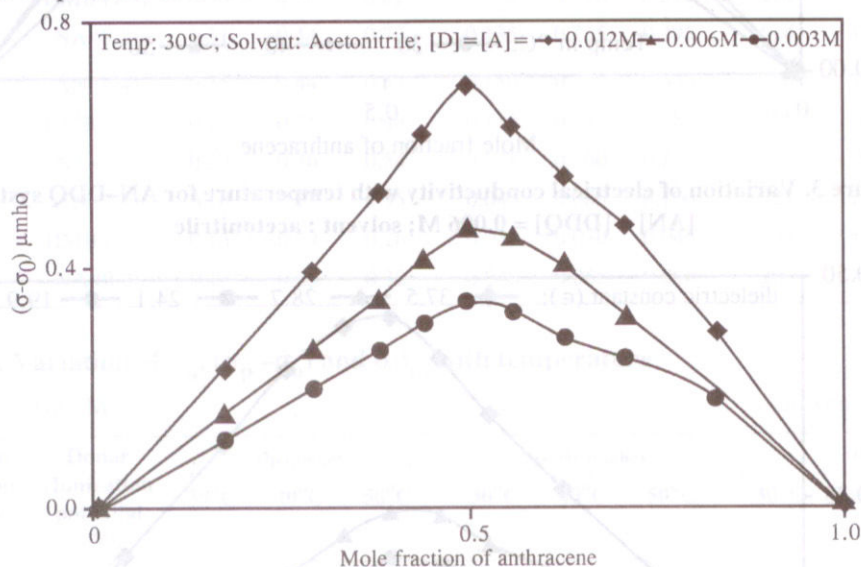


Figure 2. Variation of electrical conductivity with concentration of donor and acceptor for AN-DDQ system

Effect of concentration: In all the systems, as the concentration of the components increases from 0.003M to 0.012M (Table 1), both σ_p and $(\sigma_p - \sigma_0)$ values increase. The increase in conductivity with the increase in concentration of donor/acceptor may be due to an increase in the number of charge carriers. Similar effect of concentration has been reported earlier.^{20,21} However, in all cases, $\alpha\sigma_m$ values decrease with an increase in concentration. This may be due to $\alpha\sigma_m$ value being inversely proportional to the molar concentration of the titrant⁹.

Effect of temperature and solvent polarity: Temperature as well as polarity of the solvent should affect the extent of ionization of the EDA complex appreciably. The σ_p values (which provide a measure of the total number of ions) are therefore expected to be temperature as well as solvent dependent. To verify this, σ_p values have been measured in acetonitrile and

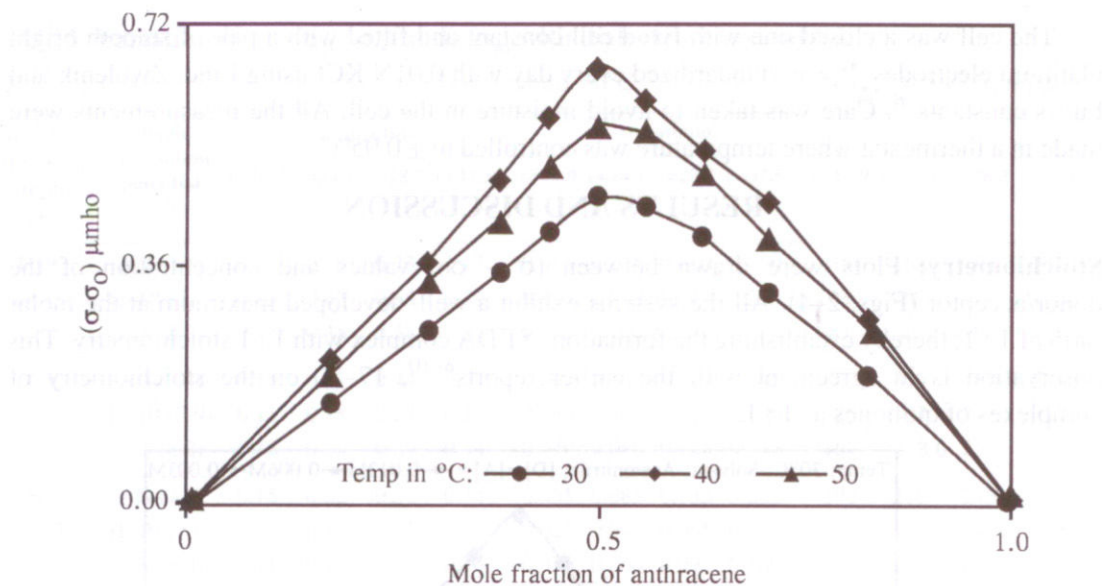


Figure 3. Variation of electrical conductivity with temperature for AN-DDQ system
 $[\text{AN}] = [\text{DDQ}] = 0.006 \text{ M}$; solvent : acetonitrile

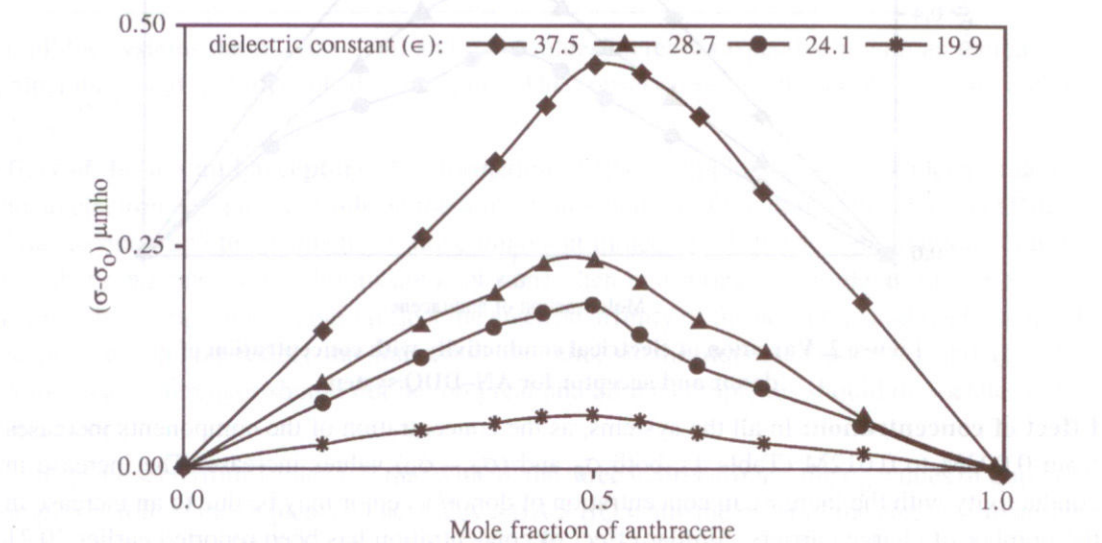


Figure 4. Variation of electrical conductivity with dielectric constant (ϵ) of solvent mixtures for
 AN-DDQ system $[\text{AN}] = [\text{DDQ}] = 0.006 \text{ M}$; Temp. 30°C; Solvent: Acetonitrile–
 carbon tetrachloride mixtures

acetonitrile–carbon tetrachloride mixtures (dielectric constants of 37.5, 28.7, 24.1 and 19.9) at three different temperatures (30, 40 and 50°C). From Tables 2 and 3, it is interesting to note that

Table 1. Variation of σ_p , ($\sigma_p - \sigma_o$) and $\alpha\sigma_m$ with concentration

Solvent: Acetonitrile

Temp: 30°C

[D] = [A]

Acceptor (Electron affinity eV)	Donor (Ionization potential eV)	σ_p (μmho)			$\sigma_p - \sigma_o$ (μmho)			$\alpha\sigma_m$		
		0.003 M	0.006 M	0.012 M	0.003 M	0.006 M	0.012 M	0.003 M	0.006 M	0.012 M
DDQ (1.95)	AN (7.4)	0.87	1.17	1.64	0.340	0.460	0.695	428	216	123
	HMB (7.9)	0.66	0.89	1.29	0.135	0.205	0.380	171	100	70
	NA (8.2)	0.67	0.95	1.35	0.145	0.260	0.425	184	126	77
CA (1.37)	AN (7.4)	0.42	0.57	0.80	0.240	0.345	0.455	889	511	220
	HMB (7.9)	0.30	0.39	0.62	0.125	0.190	0.310	476	317	167
	NA (8.2)	0.31	0.44	0.72	0.135	0.235	0.395	514	382	203
BA (1.37)	AN (7.4)	0.35	0.44	0.67	0.180	0.220	0.340	706	333	172
	HMB (7.9)	0.28	0.35	0.48	0.115	0.155	0.185	465	265	90
	NA (8.2)	0.29	0.36	0.54	0.125	0.160	0.230	505	267	124
BQ (0.77)	AN (7.4)	0.18	0.27	0.35	0.045	0.085	0.100	222	153	67
	HMB (7.9)	0.15	0.19	0.26	0.020	0.030	0.045	103	63	35
	NA (8.2)	0.17	0.23	0.32	0.040	0.065	0.090	206	131	65

Table 2. Variation of σ_p , ($\sigma_p - \sigma_o$) and $\alpha\sigma_m$ with temperature

[D] = [A] : 0.006M

Solvent : Acetonitrile

Acceptor (Electron affinity eV)	Donor (Ionization potential eV)	σ_p (μmho)			$\sigma_p - \sigma_o$ (μmho)			$\alpha\sigma_m$		
		30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
DDQ (1.95)	AN (7.4)	1.17	1.41	1.60	0.460	0.565	0.655	216	223	231
	HMB (7.9)	0.89	1.10	1.26	0.205	0.275	0.330	100	111	118
	NA (8.2)	0.95	1.18	1.33	0.260	0.350	0.400	126	141	143
CA (1.37)	AN (7.4)	0.57	0.66	0.75	0.345	0.410	0.470	511	547	560
	HMB (7.9)	0.39	0.49	0.57	0.190	0.260	0.305	317	377	384
	NA (8.2)	0.44	0.54	0.63	0.235	0.305	0.365	382	433	459
BA (1.37)	AN (7.4)	0.44	0.54	0.65	0.220	0.295	0.370	333	401	440
	HMB (7.9)	0.35	0.41	0.49	0.155	0.185	0.225	265	274	283
	NA (8.2)	0.36	0.45	0.53	0.160	0.220	0.265	267	319	333
BQ (0.77)	AN (7.4)	0.27	0.32	0.36	0.085	0.105	0.125	153	163	177
	HMB (7.9)	0.19	0.24	0.27	0.030	0.040	0.050	63	68	76
	NA (8.2)	0.23	0.29	0.33	0.065	0.090	0.110	131	150	167

Table 3. Variation of σ_p , $(\sigma_p - \sigma_0)$ and $\alpha\sigma_m$ with dielectric constant (ϵ)

[D] = [A] :0.006M

Temperature: 30°C

Solvent : CH₃CN + CCl₄ mixture

Acceptor (Electron affinity eV)	Donor (Ionization potential eV)	σ_p (mmho)				$\sigma_p - \sigma_0$ (mmho)				$\alpha\sigma_m$			
		$\epsilon=19.9$	$\epsilon=24.1$	$\epsilon=28.7$	$\epsilon=37.5$	$\epsilon=19.9$	$\epsilon=24.1$	$\epsilon=28.7$	$\epsilon=37.5$	$\epsilon=19.9$	$\epsilon=24.1$	$\epsilon=28.7$	$\epsilon=37.5$
DDQ (1.95)	AN (7.4)	0.27	0.56	0.73	1.17	0.065	0.185	0.260	0.460	106	164	184	216
	HMB (7.9)	0.22	0.43	0.55	0.89	0.035	0.080	0.110	0.205	63	76	83	100
	NA (8.2)	0.23	0.45	0.58	0.95	0.045	0.100	0.140	0.260	81	95	106	126
CA (1.37)	AN (7.4)	0.16	0.31	0.44	0.57	0.060	0.165	0.245	0.345	200	379	419	511
	HMB (7.9)	0.11	0.18	0.27	0.39	0.030	0.060	0.105	0.190	125	167	212	317
	NA (8.2)	0.12	0.20	0.29	0.44	0.040	0.080	0.125	0.235	167	222	253	382
BA (1.37)	AN (7.4)	0.15	0.22	0.32	0.44	0.055	0.085	0.135	0.220	193	210	243	333
	HMB (7.9)	0.10	0.15	0.22	0.35	0.025	0.040	0.065	0.155	111	121	140	265
	NA (8.2)	0.11	0.17	0.25	0.36	0.035	0.060	0.095	0.160	156	182	204	267
BQ (0.77)	AN (7.4)	0.12	0.16	0.22	0.27	0.025	0.040	0.060	0.085	88	111	125	153
	HMB (7.9)	0.08	0.11	0.15	0.19	0.005	0.010	0.020	0.030	22	33	51	63
	NA (8.2)	0.09	0.12	0.17	0.23	0.015	0.025	0.040	0.065	67	88	103	131

for all the systems the σ_p , $(\sigma_p - \sigma_0)$ and $\alpha\sigma_m$ values increase respectively with an increase in temperature and polarity of the medium. This observation is in harmony with earlier reports.^{18–24}

Effect of donors and acceptors: The formation of EDA complex between an electron donor and an electron acceptor depends on the ionization potential of the donor, the electron affinity of the acceptor and the geometry of the component molecules. If the solvent, the temperature and other experimental conditions are kept same, then in a series of complexes (a) for a fixed electron donor, σ_p values should reflect the electron affinity of the acceptors and (b) for a fixed acceptor, σ_p should reflect the ionization potential of the donors. Under (a) and (b), the geometrical differences should not be too great and all the complexes should dissociate to the same extent.

It can be seen from Tables 1–3 that with all the three hydrocarbons, the σ_p values of quinone complexes follow the sequence DDQ > CA > BA > BQ while the order of the electron affinities of these quinones is DDQ > CA = BA > BQ. As expected based on E_A values, with a given donor complexes of DDQ and BQ, respectively have maximum and minimum σ_p values. The observed difference in the σ_p values of the complexes of chloranil and bromanil may be attributed to the difference in electronegativity between chlorine and bromine atoms. Further, complexes of bromanil are expected to have less mobility because of their bulky nature. It is observed that both σ_p and $(\sigma_p - \sigma_0)$ values have good linear correlation with the electron affinity of acceptors as well as their polarographic reduction potential (Fig. 5). However, in all

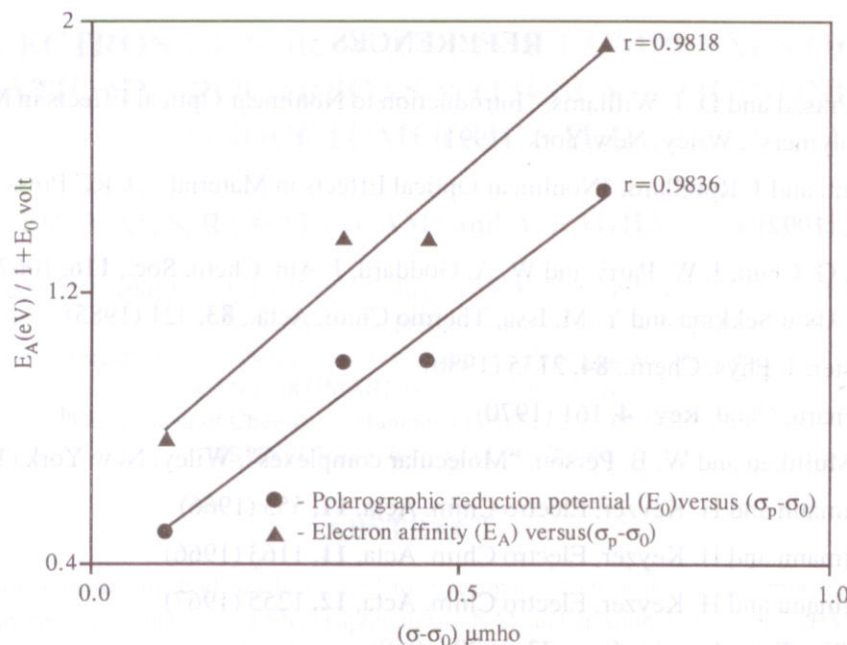


Figure 5. Variation of electrical conductivity with electron affinity / polarographic reduction potential of acceptors for Anthracene – Benzoquinones systems
[Anthracene] = [Quinone] = 0.012M; Temp 30°C; Solvent: Acetonitrile

the systems the $\alpha\sigma_m$ values exhibit no definite order with the EA of acceptors. Similar trend has been noted in earlier works^{18,23} also.

As expected because of ionization potential of donors, the σ_p , $(\sigma_p - \sigma_o)$ and $\alpha\sigma_m$ values of anthracene complexes are higher than the values of naphthalene and hexamethylbenzene complexes. However, the complexes of hexamethylbenzene with all the quinones have lower σ_p , $(\sigma_p - \sigma_o)$ and $\alpha\sigma_m$ values than the corresponding complexes of naphthalene. Although the magnitude of ionization potential is of importance, the formation of a stable dative structure is also sensitive to steric factors and such interactions determine the extent to which the complex will ionize in a given solvent. The low σ_p values of hexamethylbenzene–quinone complexes may be attributed to the steric factors because of the six bulky methyl groups present in a hexamethylbenzene molecule.

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