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Effects of Temperature and Pressure on the Charge-Transfer Complex Formation through Hydrogen Bonding and Ionization Reactions between 2,6-Dibromo-4-[(3,5-dibromo-4-hydroxyphenyl)(2-ethoxycarbonylphenyl)-methylene]-2,5-cyclohexadien-1-one and Amines

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The effects of temperature and pressure on the formation of charge-transfer (CT) complexes between 2,6-dibromo-4-[(3,5-dibromo-4-hydroxyphenyl)(2-ethoxycarbonylphenyl)methylene]2,5-cyclohexadien-1-one (TBPE) and amines in nonpolar solvents have been studied, and the thermodynamic parameters estimated. It was found that the heat of formation (ΔH°) as well as the reaction volume (ΔV°) are largely negative, compared with those for ordinary CT complex formation. The electronic spectra in the visible region due to the outer CT complexes are well-characterized for primary and secondary amines in nonpolar solvents that have no proton-donating/-accepting nature. In other cases, the CT spectra are broad. Ionization of TBPE in polar solvents takes place as evidenced by the electronic spectrum of TBPE anion. However, ΔH° as well as ΔV° are unusually small. When Proton Sponge is used in nonpolar solvents, ion pairs are formed. In this case, ΔH° and ΔV° are largely negative as expected.

In 1954, Davis and Hetzer[1] found that when a benzene solution of 2,6-dibromo-4-[(3,5-dibromo-4-hydroxyphenyl)(2-ethoxycarbonylphenyl)methylene]2,5-cyclohexadien-1-one (TBPE) was poured to solid tribenzylamine, the yellow solution of TBPE acquired a slightly pink tinge which disappeared on heating but returned on cooling. Sakai and co-workers have shown that the thermochromic nature of the TBPE–amine systems in 1,2-dichloroethane (DCE) could be applied to the selective determination of antihistamine drugs.[2–6] They suggested that TBPE associates with amines to form a kind of charge-transfer (CT) complex through hydrogen bonding.

In a preliminary paper,[7] we have shown that the complexes formed between TBPE and triethylamine (TEA) and between TBPE and *N*,*N*-dimethy-2-(diphenylmethoxy)ethylamine (DHA) are of a new type of CT complex as characterized by their strong CT band in the visible region, large equilibrium constant, and large negative values of the heat of reaction and reaction volume.

In this paper, we report the thermodynamic quantities for the CT complex formation between TBPE and primary, secondary, and tertiary aliphatic amines, together with those for the ion-associate formation between TBPE and *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine (Proton Sponge, PS).

Experimental

Materials. Reagent grade potassium salt of TBPE was dissolved into an H_2O-EtOH mixture. An aqueous solution of oxalic acid was added slowly to the mixture until the blue color of the solution changed to orange red. TBPE as a free phenol, was extracted by chloroform and the solution evaporated to dryness. Recryctallization of TBPE was made by adding hexane dropwise to its chloroform solution, mp 215—217 °C (lit,[8] 210—215 °C). Reagent grade Proton Sponge was recrystallized from a cyclohexane–petroleum ether mixture. Triethylamine (TEA), dipropylamine (DPA), and propylamine (PA) were dried over potassium hydroxide and distilled under a reduced pressure. Solvents were purified in the usual manner.

Procedures. Spectra of the CT complex and the ion-associate at 0.1 MPa were recorded on a Union SM-401 spectrophotometer. The measurement temperature was regulated within ±0.1 °C by circulating thermocontrolled water. A high-pressure vessel with a water jacket for temperature control was used for spectral measurements.[9] It was set in a cell compartment of a Hitachi 100-50 double-beam spectrophotometer. Using available data, the changes of solvent density with temperature and pressure were taken into account. The equilibrium constants for the formation of the CT complex and the ion-associate were determined from the Benesi–Hildebrand (B–H) plot[10] with the base in great excess over TBPE. The enthalpy and entropy of formation were determined from the variation of the equilibrium constants with temperature according to the van't Hoff equation.

The equilibrium constant in logarithmic scale was plotted against external pressures, and the plots were fitted to the following quadratic equation by means of a computer program.

$$\ln K_p/K_0 = ap^2 + bp + c \tag{1}$$

where K_p and K_0 are the equilibrium constants at p and 0.1 MPa, respectively. The volume of reaction extrapolated at atmospheric pressure (ΔV°) was calculated by

$$bRT = -\Delta V^\circ - \Delta n\, \kappa_T RT \tag{2}$$

where κ_T denotes the isothermal compressibility of solvents, and Δn the difference in the number of molecules between products and reactants. The second term arises from the translational energy loss associated with reaction.[11]

Results

The temperature dependence of the absorption spectrum in the visible region is shown in Fig. 1. The

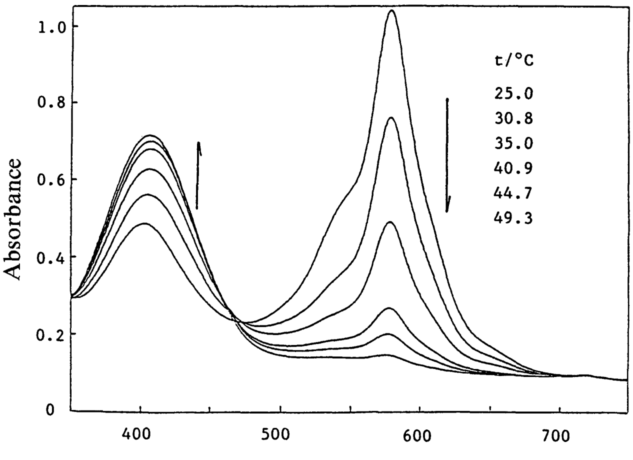


Fig. 1. Temperature dependence of the absorption spectrum in benzene; $[\mathrm{TBPE}]_0=6.04\times10^{-5}$ mol dm^{-3}, $[\mathrm{PA}]_0=2.08\times10^{-4}$ mol dm^{-3}.

absorption band at ca. 580 nm can be ascribed to the CT complex and the band at ca. 400 nm to TBPE. As the temperature raises, the CT band decreases, while the TBPE band increases but less rapidly and shifts toward a longer wavelength side. Thus the band at ca. 400 nm must involve some contribution of the CT complex. The B–H plots were performed using the absorbance of the CT band for this reason. The shape and the position of the CT band depend on the combination of amines and solvents. This is shown in Figs. 2 and 3. It was found that each B–H plot for the CT complex formation is linear. Representative B–H plots are shown in Fig. 4. Remarkable pressure effects on the equilibrium were observed. By the aid of Eqs. 1 and 2, the reaction volumes were estimated. The thermodynamic parameters are given in Table 1. When TBPE

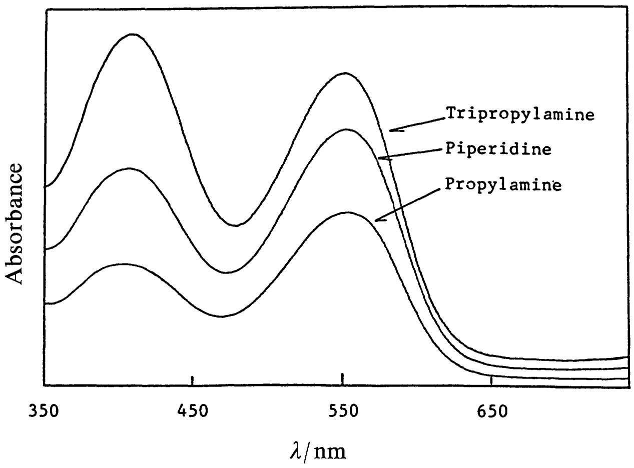


Fig. 2. Absorption bands of TBPE in 1,4-dioxane in the presence of primary, secondary, and tertiary amines.

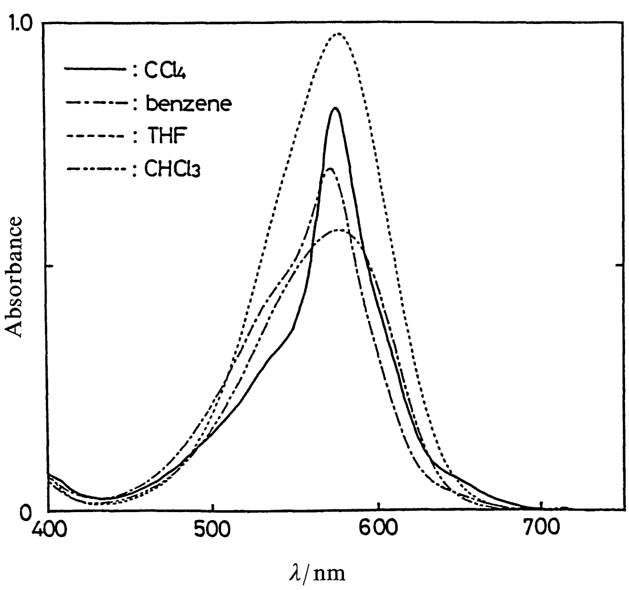


Fig. 3. Absorption bands of a mixture of propylamine and TBPE in $\mathrm{CCl_4}$, benzene, $\mathrm{CHCl_3}$, and THF.

Table 1. Thermodynamic Quantities for the Reaction

TBPE + Amines $\rightleftarrows$ CT Complex

Amine	Solvent[a]	$K(25\,°\mathrm{C})$[b]	$\Delta H°$	$\Delta S°$	$\Delta V°(30\,°\mathrm{C})$
		dm^3 mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	cm^3 mol^{-1}
TEA	$\mathrm{CHCl_3}$	26000	−58±6	−110±20	−23.2
	Toluene	26000	−64±3	−130±20	−24.9
	DX	2500	−43±3	−79±10	−22.3
DPA	CB	29000	−100±9	−250±30	−31.1
	DE	27000	−70±3	−150±9	−35.3
	DX	2300	−55±1	−120±5	−23.1
PA	Benzene	6000	−114±7	−310±20	−31.5
	CB	520	−96±7	−270±25	−31.2
	DE	1100	−68±4	−170±15	−34.8
	DX	2300	−55±1	−120±5	−31.9

a) DX: 1,4-dioxane, CB: chlorobenzene, DE: 1,2-dichloroethane. b) Interpolated values from the van't Hoff plot.

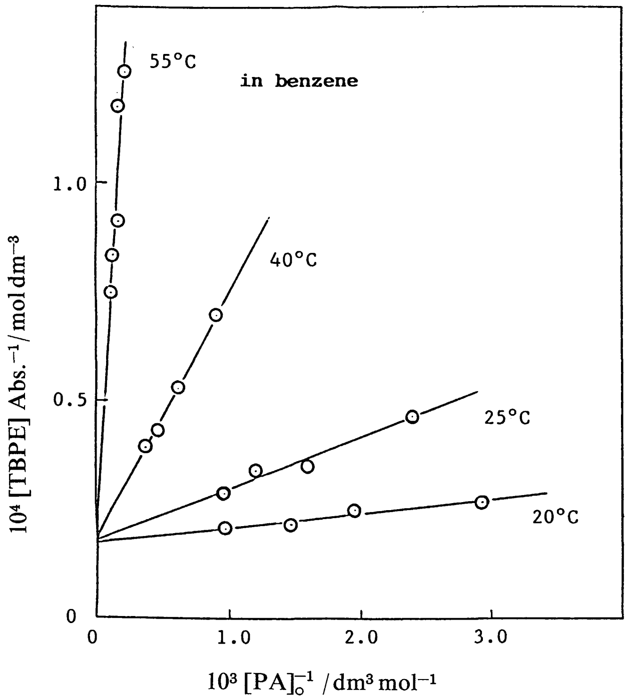


Fig. 4. B–H plots for the TBPE–PA system at various temperatures.

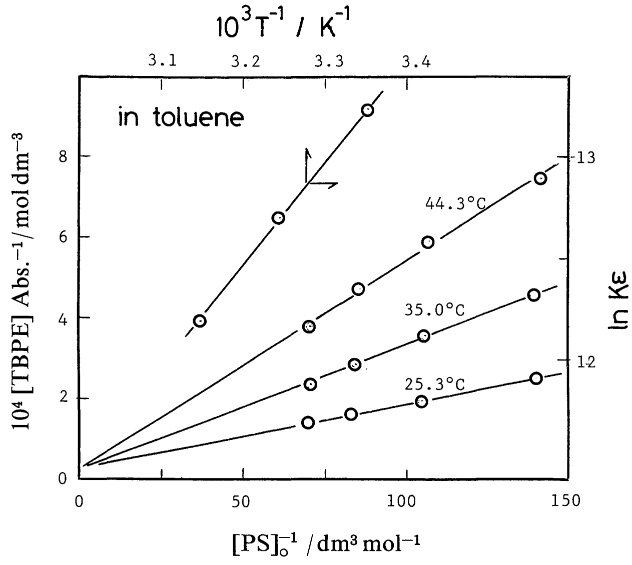


Fig. 5. B–H and van't Hoff plots for the TBPE–PS system.

was mixed with PS in nonpolar solvents, a band appeared at ca. λ_{max}=620 nm. This band can be assigned to the TBPE anion, since both the position and the spectral pattern agreed with those of the potassium salt of TBPE. Remarkable temperature and pressure dependences on the equilibrium were observed in this case, too. Figure 5 shows the B–H plot. The thermodynamic quantities for the formation of the ion-associate in some nonpolar solvents were estimated and are given in Table 2.

Table 2. Thermodynamic Quantities for the Reaction
TBPE + PS $\rightleftarrows$ Ion Pair[a]

Solvent	K(25 °C)[b]	ΔH°	ΔS°	ΔV°(25 °C)
	dm^3 mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	cm^3 mol^{-1}
Benzene	19	−44±4	−125±15	−35.4
Toluene	22	−39±2	−105±20	−35.8
$CHCl_3$	470	−57±4	−140±40	−38.5
1-Chloro-butane	110	−46±1	−115±40	−30.7

a) Molar absorptivity estimated from the B–H plot is 36000±1500 dm^3 mol^{-1} cm^{-1}. b) Interpolated values from the van't Hoff plot.

Discussion

Charge-Transfer Complex Formation Reaction. We have reported[7] that the tertiary amines such as TEA react with TBPE to form a new type of CT complex in nonpolar solvents, and that the system exhibits a remarkable thermochromism as well as piezochromism. We proposed that the origin of the strong CT band could be ascribed to the canonical electronic structures of the following type.

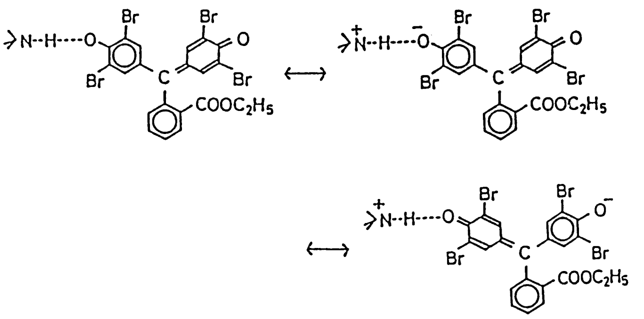
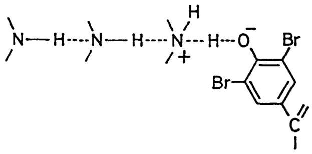


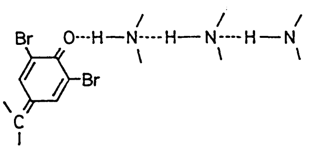
Figure 1 shows a remarkable thermochromic nature for the TBPE–propylamine system, too. From the B–H plot, the equilibrium constants were estimated. By means of the van't Hoff plot, the heat of reaction and the entropy of reaction were estimated (Table 1). The reaction volumes are between −22 and −35 cm^3 mol^{-1}. These (absolute) values are remarkably greater than those for ordinary CT complex formation (0—−15 cm^3 mol^{-1}).[12] Therefore, due to the predominant contribution of the dative structures (vide supra), the present CT complex must be more "tight" than the ordinary one.

In 1,4-dioxane (DX) and tetrahydrofuran (THF), the spectral pattern of the CT band is very similar to each other, irrespective of primary, secondary and tertiary amines (Fig. 2). The spectral pattern of the TBPE–TEA system in benzene, chloroform, and THF is also the same as that in Fig. 2. On the other hand, when primary or secondary amines are used, the spectral pattern changes remarkably, depending on the nature of solvents (Fig. 3). With auxiliary experiments, it has been confirmed that the CT spectrum is sharp and exhibits a "structure" (shoulder) only when TBPE and primary or secondary amines are dissolved in nonpolar solvents that have no proton donating/accepting ability.

According to our view, hydrogen bonding is playing an important role. There are some possible combinations of hydrogen bonding. In DX and THF, the hydrogen-bond formation between TBPE and these solvents will disfavor the CT complex formation. The situation will be the same for the hydrogen bonding between primary/secondary amines and DX/THF. The comparatively small values of the equilibrium constants in DX may be ascribed to this reason. Primary and secondary amines can donate as well as accept the hydrogen atom that can form hydrogen bond. In benzene and CCl_4, they will form a kind of (dynamic) cluster through hydrogen bonding. The amine cluster taking part in the formation of CT complex would give rise to its enhanced effective mass, resulting in a less mobile conformation (see type A indicated below). Hydrogen bonding of the type B is also possible.



Type A



Type B

It is likely that either or both of the above types of hydrogen bonding are responsible for the well-characterized CT band. Meanwhile, the formation of cluster is disfavored in DX due to the predominant hydrogen bonding between primary/secondary amines and excessively existing DX. It is evident that the cluster formation is impossible for tertiary amines in any kinds of solvents. The above idea would explain the spectral patterns in Figs. 2 and 3.

In order to obtain evidence for supporting the cluster formation, the shift of the CT band with solvent was examined. In Fig. 6, $\bar{\nu}_{max}$ is plotted against the E_T-value, a solvent polarity parameter. For the TBPE–TEA system, a fairly well correlation may be seen (line A). For the TBPE–PA system, solvents that have hydrogen-bonding ability seem to fall on the same line. Judging from the chemical shift of ^1H NMR of chloroform (δ=7.25 ppm vs.TMS, 60 MHz ^1H NMR), chloroform could, be regarded to this group of solvents. The position of diethyl ether is rather critical. On the other hand, solvents that have no hydrogen-bonding ability seem to constitute an other group (line B). The shift is less remarkable, and this is in harmony with the assumption of cluster formation, proposed in the foregoing paragraph. That is, the formation of amine cluster will disfavor the access of solvent molecules to the CT complex, resulting in the small red shift.

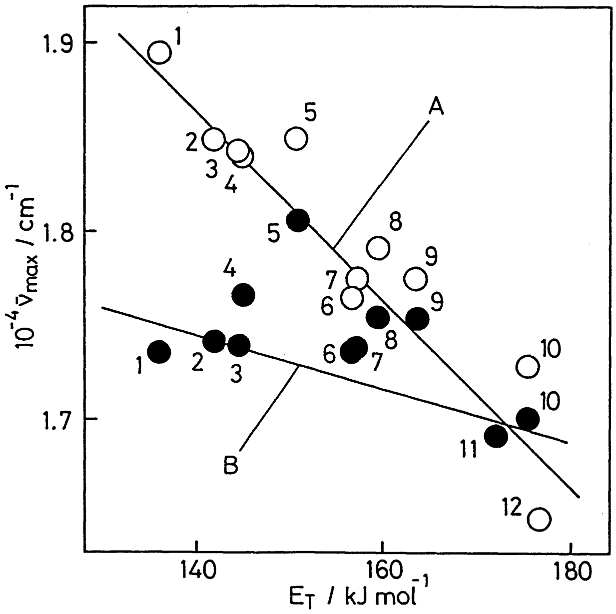
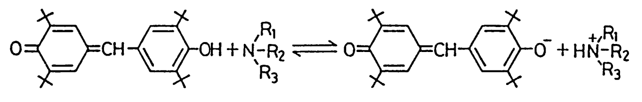


Fig. 6. Relationship between $\bar{\nu}_{max}$ (CT band) and E_T-value for the TBPE–TEA (○) and TBPE–PA (●) systems. Entry number: 1, CCl_4; 2, toluene; 3, benzene; 4, Et_2O; 5, DX; 6, THF; 7, chlorobenzene; 8, ethyl acetate; 9, $CHCl_3$; 10, DE; 11, dichloromethane; 12, acetone.

When ordinary aromatic amines of low basicity are used, the formation of CT complex was not observed in the usual conditions. Hence the equilibrium would be related to the amine basicity. The value of pK_a for TEA and PA are 11.01 and 10.71, respectively. Although the value of pK_a for DPA is not available, it would be very near to that of TEA, referring to the pK_a of diisopropylamine (10.96). Although the above pK_a-values are those in water, the equilibrium constants for the TBPE–PA system is, as a whole, smaller than those for the other two; this may be ascribed to the difference in the pK_a value. The solvent effects on the thermodynamic data in Table 1 seem to be entangled, and it is difficult to find a definite trend. Perhaps the complication could be ascribed to the intervention of various types of hydrogen-bond formations, the steric factor, and the amine basicity etc., and further study is neccesary.

Ionization Reaction. It is generally known that ionization is enhanced by temperature and pressure. The observation of considerable volume decrease has been interpreted in terms of electrostriction. The electrostriction becomes pronounced when the ion is small, the charge large and localized, and the solvent nonpolar. Typical ionization of phenols is accompanied by the volume change from −4 to −30 $cm^3\,mol^{-1}$.[13] When TBPE alone or TBPE and small amount of aliphatic amine was dissolved in polar solvents, the formation of TBPE anion was observed. We examined the temperature dependence on the equilibrium and found that the equilibrium scarcely shifts with temperature in acetonitrile, acetone, and methanol. This indicates that the heat of ionization is near zero and the entropy change so small. In agreement with our observation, Sakai[2)] also reported that the temperature dependence on the equilibrium between TBPE anion/quaternary ammonium ion-associates and its nonionized components in 1,2-dichloroethane is negligibly small. The effect of pressure on the equilibrium was also examined in acetone and methanol. The approximate ΔV°-value estimated by means of Eqs. 1 and 2 was 1.0 ± 1.0 cm^3 mol^{-1} in acetone and negligibly small in methanol. The above findings are unusual in view of normal ionization reactions where remarkable enthalpy, entropy, and volume decreases are observed.

A possible cause might be due to the symmetrical structure of TBPE anion; the electric charge will be delocalized over the molecule, and this might give rise to the small temperature effects. Free phenol corresponding to galvinoxyl (so-called "hydrogalvinoxyl", see below) could be regarded as a model compound for examining the above presumption. We expected that the temperature effects for the following equilibrium



"hydrogalvinoxyl"

will be similar, since the anion has symmetrical electronic structures similar to those of TBPE anion. However, remarkable temperature dependence was observed for this system. The estimated values of the heat of formation were -29 kJ mol^{-1} in acetone and -46 kJ mol^{-1} in acetonitrile.[14)] Although the reason is not clear, this temperature/pressure-insensitive nature seems peculiar to the ionization of TBPE in polar solvents.

When TBPE and PS were mixed in nonpolar solvents, the proton from TBPE was trapped by PS to form ion pairs, as evidenced by the appearance of well-characterized spectrum of TBPE anion in the vicinity of 600 nm. In contrast to the case of the CT complex, the pattern of the spectrum does not change with solvent at all. Substantial temperature and pressure effects were observed. The thermodynamic data are given in Table 2. The volumes of reaction for the formation of ion-pair are between -30 and -39 cm^3 mol^{-1} as expected in the ordinary ion-pair formation reactions. The enthalpy and entropy changes are those usually observed. Using the data in Tables 1 and 2, we tentatively plotted ΔH° against ΔS° (Fig. 7). In spite of the intervention of a various types of hydrogen bonding, it seems that the approximate linear free energy relationship[15)] holds for both the CT complex and ion-pair formations. Figure 8 shows the relation between $\bar{\nu}_{\max}$ and E_T-value. For solvents of smaller E_T-values, a small but clear red-shift trend may be seen, as usually observed for π-π^* transitions. In contrast, a rather blue-shift trend may be seen for solvents of larger E_T-values, indicating that the ground state of the anion is a little more stabilized than the excited state. A good correlation between $\bar{\nu}_{\max}$ and E_T-values for a series of alcohols suggests a substantial role of hydrogen bonding. The comparatively small solvatochromic shift over a wide E_T range is in accord with our expectation, since the dipole moment of the ion pair in the ground state will not be so different from that in the excited state.

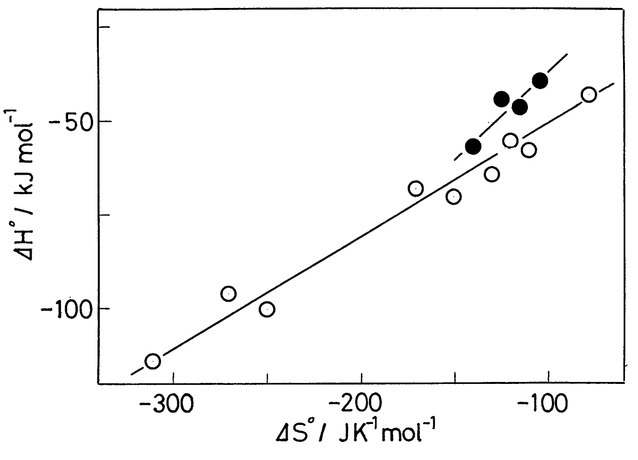


Fig. 7. Linear free energy relationship for CT complex formation (○) and ion-pair formation (●).

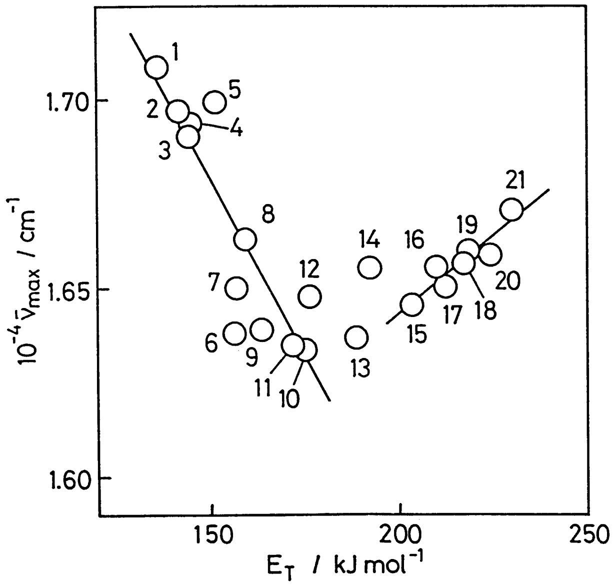


Fig. 8. Plot of $\bar{\nu}_{\max}$ against E_T-value for the TBPE–PS system. Entry number: 1—12, same as in Fig. 6; 13, DMSO; 14, CH_3CN; 15, 2-propanol; 16, 1-butanol; 17, 1-propanol; 18, EtOH; 19, 2-methoxyethanol; 20, EtOH/H_2O=80/20 vol-%; 21, MeOH.

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