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Articles

Solvation Effect on the Proton Transfer Complex Formation between 2,4-Dinitro-1-naphthol and Amines

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The equilibrium constants for the proton transfer complex formation K_{eq} of 2,4-dinitro-1-naphthol (DNN) with some amines in benzene–dimethylformamide, ethyl acetate, dioxane, and acetonitrile mixed solvents were measured. The sharp increase in K_{eq} for the reaction of DNN with primary and secondary amines suggests the formation of a hydrogen bond between the amine hydrogen(s) and the electron-donating solvents. A linear correlation between K_{eq}, for the DNN–DEA reaction, and Taft's β parameter is found except for dioxane. The increase in the equilibrium constants between DNN and TEA is explained on the grounds of a long-range solvation effect. It is shown that K_{eq} in these systems is qualitatively related to the dielectric constant (ϵ) and Taft's π parameters of the solvents used. It is found that the short-range solvation effect increases K_{eq} more sharply than the long-range one.

Introduction

The solvation effect on reaction is either long range or short range in nature. The long range effect is the result of solvent polarity and is described in such units as the dielectric constant or Taft's π scale, which relates to the ease with which charge separation may occur in solutes (Kamlet *et al.*, 1983). The short-range effect results from direct interaction between solute and solvent molecules with formation of hydrogen bonds and is expressed in such units as Taft's α or β values (Kamlet *et al.*, 1979, 1981, 1983). The α scale of solvent HBD (hydrogen bond donor) acidities describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond (Kamlet and Taft, 1976, 1979), while the β scale of HBA (hydrogen bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond (Kamlet and Taft, 1976; Yokohama *et al.*, 1976).

The two classes of solvation effect have been recognized by several techniques such as NMR, IR, and electronic spectra (Berman *et al.*, 1987; Ganguly and Banejee, 1982). It was found that the amine–solvent hydrogen bond increased the amine basicities (Ye *et al.*, 1988; Khan and Scott, 1988). This was indicated in the increase in equilibrium constants K_{eq} for proton transfer complex formation of phenol–amine (Berman *et al.*, 1987; Scott *et al.*, 1968; Scott and Vinogradov, 1969) and carboxylic acid–amine systems (Khan and Scott, 1988) when HBD or HBA solvents were added.

We report here the equilibrium constants K_{eq} for the formation of proton transfer complexes between 2,4-dinitro-1-naphthol (DNN) and benzylamine (BnA), diethylamine (DEA), morpholine (Mo), and triethylamine (TEA) in benzene containing different proportions of electron-donating solvents such as dimethylformamide (DMF), ethyl acetate (EA), dioxane, and acetonitrile (AN). The work investigates the effect of hydrogen bond formation between these solvents and amines on the measured equilibrium constants in benzene.

Experimental Section

2,4-Dinitro-1-naphthol was prepared as previously reported (Hudgson and Smith, 1935). Benzene, dimethylformamide, dioxane, ethyl acetate, and acetonitrile were of spectroscopic grade. Triethylamine, diethylamine, morpholine, and benzylamine were dried over potassium hydroxide and distilled through a 25 mL fractionating column shortly before use and stored in brown bottles.

The spectra were recorded on a 160-A Shimadzu UV–vis recording spectrophotometer using 1 cm matched silica cells at the wavelength range between 200 and 500 nm. The benzene solution of DNN (1×10^{-4} M) containing different proportions of electron-donating solvent and concentrations of amines under investigation (1×10^{-5} to 1 M) were measured at 25 °C. The proton transfer equilibrium constants K_{eq} for 1:1 complexes (Habeeb *et al.*, 1995) were calculated by the minimum–maximum method (Albert and Serjeant, 1962).

Results and Discussion

Equilibrium constants were obtained for the formation of proton transfer complexes between DNN and benzylamine, diethylamine, morpholine, and triethylamine in a range of benzene–dimethylformamide and benzene–ethyl acetate mixed solvents.

In benzene, DNN reacts with TEA, DEA, Mo, or BnA to form a proton transfer complex, displaying equilibrium constants of 15 488, 1690, 478, and 96 M^{-1}, respectively (Habeeb *et al.*, 1995). This order of equilibrium constants is also found when 2,4-dinitrophenol is reacted with TEA, DEA, Mo, and *n*-butylamine (Ye *et al.*, 1988). On the basis of the inductive effect of the alkyl groups which raises the electron density of the amine nitrogen, we would expect the tertiary amine to be the most reactive and the primary amine to be the least.

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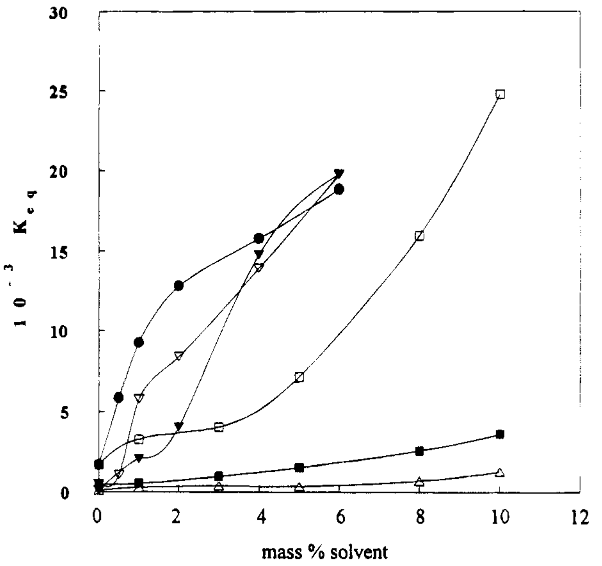

Figure 1. Equilibrium constants for proton transfer complex formation between 2,4-dinitro-1-naphthol and various amines in different benzene–solvent mixtures: ●, DEA–DMF; ▽, Mo–DMF; ▼, BnA–DMF; □, DEA–EA; △, BnA–EA; ■, Mo–EA.

Table 1. Equilibrium Constants for Proton Transfer Complex Formation between DNN and DEA and Mo and BnA in Benzene–DMF and Benzene–Ethyl Acetate Mixed Solvents

	benzene + DMF			benzene + ethyl acetate		
	K_{eq}					
solvent mass %	DEA	Mo	BnA	DEA	Mo	BnA
0.0	1690	478.6	96.5	1690.0	478.6	96.5
0.5	5836	1056.0				
1.0	9243	5763.0	2046.0	3257.6	517.6	276.0
2.0	12802	8388.3	4026.0			
3.0				4015.0	964.0	387.0
4.0	15800	13931.0	14800.0			
5.0				7137.3	1521.6	352.0
6.0	18830	17756.0	19765.0			
8.0				15960.6	2561.8	689.0
10.0				24784.0	3602.6	1297.0

The data presented in Table 1 show that BnA has a lower K_{eq} value when reacting with DNN in benzene containing DMF lower than 4.0 mass %. Meanwhile, DEA showed a higher K_{eq} than Mo and BnA under similar conditions, Table 1. This behavior can be explained on the grounds that the effect of two alkyl groups and one hydrogen bond with DMF intensifies the lone pair of the amine nitrogen in secondary amines more than does the effect of the single alkyl group and one hydrogen bond with DMF in primary amines.

Beyond 4.0 mass % DMF, BnA shows a greater increase in K_{eq} than Mo and DEA, Figure 1. This may be attributed to the formation of two hydrogen bonds between the two hydrogens of BnA protons and DMF molecules during the formation of the PT complex, which stabilize the positive charge developed on the amine nitrogen atom and so promote the complex formation. On the other hand, secondary amines may undergo self-association (Coetzee and Padmanbhan, 1965) rather than hydrogen bonding with DMF molecules, resulting in a decrease in their equilibrium constants, Table 1.

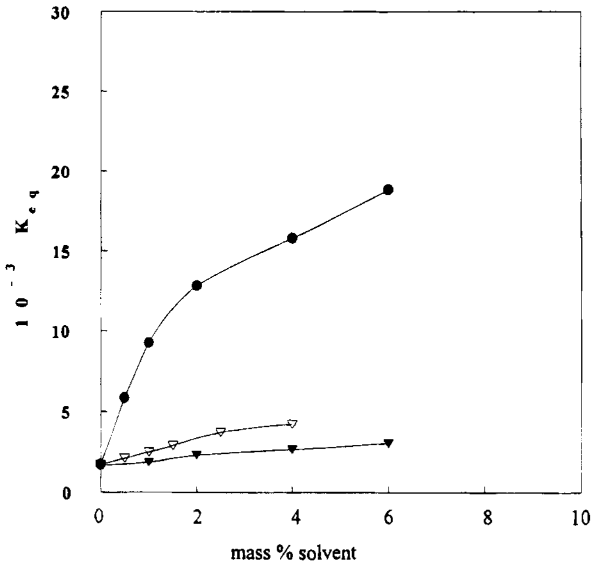

Figure 2. Equilibrium constants for proton transfer complex formation between 2,4-dinitro-1-naphthol and diethylamine in different benzene–solvent mixtures; ●, dimethylformamide; ▽, acetonitrile; ▼, dioxane.

Table 2. Equilibrium Constants for Proton Transfer Complex Formation between DNN and DEA in Benzene–Dioxane and Benzene–Acetonitrile Mixed Solvents

	K_{eq}			K_{eq}	
solvent mass %	benzene + dioxane	benzene + AN	solvent mass %	benzene + dioxane	benzene + AN
0.0	1690.0	1690.0	2.0	2267.0	
0.5		2082.0	2.5		3698.0
1.0	1832.0	2469.5	4.0	2642.5	4225.0
1.5		2857.0	6.0	3018.0	

The interaction of DNN and DEA in benzene–DMF mixed solvent shows a region of sharply increasing K_{eq} on first addition of solvent (0–1 mass % DMF gives a 5-fold increase in K_{eq}) followed by a reduced rate of K_{eq} increase as more DMF is added (1–6 mass % DMF gives a 2-fold increase). The same pattern is found with Mo (0–1 mass % DMF shows a 12-fold increase in K_{eq} while 1–6 mass % DMF gives a 3.4-fold increase in K_{eq}). Also, BnA shows a sharp initial rise in K_{eq}; 0–1 mass % DMF gives a 21-fold increase, followed by a 9.7-fold increase in K_{eq} by increasing DMF from 1 to 6 mass % DMF, Table 1. This demonstrates that K_{eq} is largely affected in 0–1 mass % DMF. The above findings can be interpreted by both short- and long-range solvation in 0–1 mass % DMF and by exclusive long-range solvation beyond this region where the DMF concentration increases in solution.

Equilibrium constants obtained for the formation of proton transfer complexes between DNN and DEA and Mo and BnA in a range of benzene–ethyl acetate mixed solvents are given in Table 1. DEA shows K_{eq} values greater than Mo and BnA at all concentrations. This can be attributed to the lower value of the β parameter which inhibits the hydrogen bond between the second hydrogen of BnA and EA, and the low dielectric constant which prevents the self-association of DEA. On the other hand, Mo alternates between the two above factors, Table 1. No area of decreasing slope is observed in this system.

We now consider the relative effectiveness of other electron-donating solvents such as AN and dioxane in generating a short-range solvation effect. The equilibrium constants for proton transfer complexes between DEA and DNN in benzene–dioxane and benzene–AN mixed solvents are collected in Table 2 and Figure 2, where a region of decreasing slope is found in both systems. The equilibrium constants for DEA at 1 mass % electron-donating solvents correlate reasonably with Taft's β parameter for that solvent with the exception of dioxane, Tables 2 and 3 and Figure 3. The obvious common feature differentiating

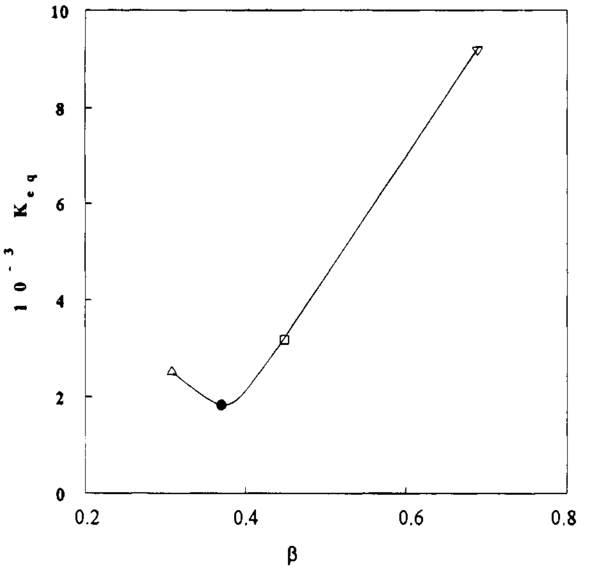

Figure 3. Taft parameters (β) versus equilibrium constants for proton transfer complex formation between 2,4-dinitro-1-naphthol and diethylamine in 1 mass % of different solvents; △, acetonitrile; ●, dioxane; □, ethyl acetate; ▽, dimethylformamide.

Table 3. Equilibrium Constants for Proton Transfer Complex Formation between DNN and DEA in 1 mass % Benzene–Electron-Donating Mixed Solvents and Solvent Parameters

solvent	K_{eq}	β	π	ε
dioxane	1832.0	0.37	0.55	2.21
acetonitrile	2469.5	0.31	0.75	38.8
ethyl acetate	3257.6	0.45	0.55	6.02
DMF	9243.0	0.69	0.88	37.2

Table 4. Equilibrium Constants for Proton Transfer Complex Formation between DNN and TEA in Benzene–DMF and Benzene–Ethyl Acetate Mixed Solvents

	K_{eq}			K_{eq}	
solvent mass %	benzene + EA	benzene + DMF	solvent mass %	benzene + EA	benzene + DMF
0.0	15 488.0	15 488	5.0	20 477.7	
0.5		27 143	6.0		41 345
2.0		38 002	10.0	25 358.6	
3.0	19 242.5				

dioxane from other solvents studied is the presence of two oxygen atoms and the relatively high proton affinity ($PA_{dioxane} = 193$). This hinders the interaction with DNN, reflecting lower K_{eq} than those of the other solvents, Table 2.

The relation between K_{eq} values at the area of decreasing slopes (Figure 2) with ε and π parameters shows qualitative agreement. Meanwhile, the K_{eq} value in the presence of DMF is higher than those in the presence of AN and dioxane, suggesting that DMF molecules promote long-range solvation more than the other solvents, Table 3.

The K_{eq} values for proton transfer complex formation between DNN and TEA in a range of benzene–DMF and benzene–EA mixed solvents are given in Table 4, where K_{eq} increases with increasing DMF and EA concentrations in the ranges 1.5×10^4 to 4.1×10^4 and 1.5×10^4 to 2.5×10^4, respectively. Without an amine nitrogen proton, there is no site for hydrogen bonding with DMF, so such an increase in K_{eq} as occurs is ascribed to the long-range solvent effect. The increase in K_{eq} for benzene–DMF is higher than that for benzene–EA, which is attributed to the difference in the dielectric constant (ε) between DMF (37.2) and EA (6.02). The relationship between K_{eq} and the mass percent of DMF and EA gave a linear correlation for all EA mass percents and for small mass percents of DMF, Figure 4. A deviation at higher DMF mass percents is attributed to the increase of the medium polarity, leading to the formation of a TEA-solvated hydrogen-bonding complex which reverses the proton transfer process (Hudson *et al.*, 1972).

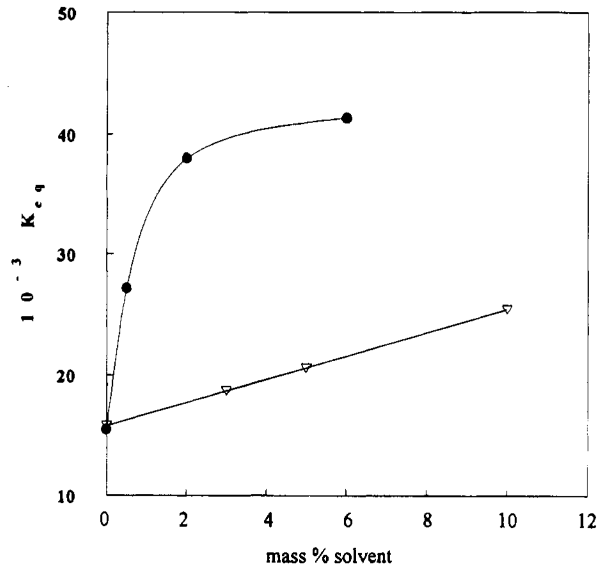

Figure 4. Equilibrium constants for proton transfer complex formation between 2,4-dinitro-1-naphthol and triethylamine in dimethylformamide (●) and ethyl acetate (▽).

Our data reveal that the change in K_{eq} of DNN with DEA, Mo, BnA, and TEA in 1 mass % benzene–DMF mixed solvent is greater than that in benzene for that amine (5, 12, 21, and 1.7 times, respectively). The same pattern is also found in 1 mass % benzene–ethyl acetate mixed solvent. This indicates that the effect of a hydrogen bond between the primary or secondary amines and electron-donating solvents increases the basicity of the amine nitrogen atom more than does the inductive effect of alkyl groups in tertiary amines (Ye *et al.*, 1988).

Conclusions

(1) Short- and long-range solvation effects are operating for primary and secondary amines in the range 0–1 mass % DMF, while the long-range solvation effect is exclusively operative beyond this range. (2) The long-range solvation effect for tertiary amines manifests itself at all DMF concentrations. (3) The long-range solvation effect is detected from the area of decreasing slopes in reactions of DNN with DEA in benzene–DMF, benzene–AN, and benzene–dioxone mixed solvents. (4) The hydrogen bond formation between the solvent and the second hydrogen of a primary amine depends on the dielectric constant of the solvent. (5) The β parameter successfully describes the short-range solvation effect in our systems except in benzene–dioxane mixed solvents due to the formation of a sterically hindered complex between dioxane and DEA molecules. (6) The ε parameter successfully describes the long-range solvation effect in our system. (7) The short-range solvation effect increases K_{eq} more than the inductive effect of the alkyl substituents of amines.

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