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Aromatic Solvent Effect on Polarity and Proton-Transfer Equilibrium in Phenol –Triethylamine Systems

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Dipole moments of hydrogen-bonded complexes of 4-nitrophenol–triethylamine and 2,4,6-trichlorophenol–triethylamine have been determined in various aromatic solvents. On this basis, the Gibbs energy ΔG_{PT} of the proton-transfer equilibrium has been estimated. The aromatic solvent effect on the proton transfer has been discussed in terms of two solvation contributions, arising from a local complex-aromatic molecules interaction and a long-range dielectric effect. The microstructure of the solvent near a complex has been taken into account, utilizing a dielectric model of two spherical solvent layers. The crucial effect of the size of the aromatic solvent molecules on ΔG_{PT} has been simulated by variation of the thickness of the first solvation layer.

Key words: phenol–triethylamine complexes, dipole moment, proton-transfer equilibrium, aromatic solvent effect

Complexes of 4-nitrophenol and 2,4,6-trichlorophenol with triethylamine belong to that group of systems with hydrogen bonds, where the location of the proton in the hydrogen bridge may be presented by a tautomeric (protomeric) equilibrium:

$$\underset{\text{(HB)}}{\text{O–H}\cdots\text{N}} \overset{K_{PT}}{\rightleftarrows} \underset{\text{(PT)}}{\text{O}^{\ominus}\cdots\text{H–N}^{\oplus}} \tag{I}$$

where HB is the molecular hydrogen-bonded complex and PT is the hydrogen-bonded ion pair. The appearance of the tautomeric equilibrium can be observed by almost all of the available spectroscopic techniques [1–8]. The proton-transfer constant K_{PT} can be determined also relatively simply from the dipole moment measurement [9–11].

Of the many factors that influence the position of the protomeric equilibrium (I), the effect of environment is one of the most important and least predictable. Both the polar properties of the solvent [12], as well as its specific proton-donating properties [13–16], influence the population of the proton transfer state. Environmental effects exert a drastic influence on K_{PT}, when specific hydrogen bonds between the complex and neighbouring molecules of the solvent or additional molecules of phenol are formed [15–18]. In such cases co-operative hydrogen-bonding effects give a polarization-assisted and/or charge transfer-assisted enhancement of the O–H···N hydrogen bond strength and markedly promote the proton transfer.

Less attention has been paid to the effect of aromatic solvents. In our previous report [13] on the solvent influence on the dipole moment and proton-transfer equilibrium in the 4-nitrophenol–triethylamine system, an anomalous behaviour of the aromatic solvents has been found. The dipole moment of the complex and K_{PT} do not correlate with the dielectric permittivity of the solvent. On the other hand, aromatic solvents induce the proton transfer much more than isodielectric non-aromatic ones [14,16]. This observation has been explained as due to a π-π type charge-transfer interaction.

Abnormal solvation behaviour of aromatic solvents is well known. While discussing their effect on conformational equilibria it was found that aromatic solvents quite frequently seem to be much more polar than it would result from their bulk dielectric permittivity [19–21]. This is particularly evident in benzene and an effective dielectric permittivity of benzene, equal to 7.5 instead of 2.3, is even proposed to describe its electrostatic solvation ability [20–21].

Aromatic solvent-induced shifts (ASIS) in ^{1}H NMR spectroscopy have been widely investigated [22,23]. Numerous attempts of explaining the ASIS phenomenon have been given [24–29], but the most accepted approach seems to be a solute/solvent cluster model [30]. In this model ASIS results from an orientation of aromatic solvent molecules around the dipolar sites of the solute molecule. In the original paper [30], the nature of this solute-solvent interaction is not discussed. The interaction may be both electrostatic (dipole-induced dipole, dipole-quadrupole) and electron donor-acceptor in origin. An important feature of this approach is that the solvent parameters can be rationalized in terms of solvent molar volume and electronic effects, the latter caused by substituents in the aromatic molecules.

In order to gain more information on the influence of aromatic solvents on the proton-transfer equilibrium in 4-nitrophenol–triethylamine complex (PNP·TEA), we have determined its dipole moment in more alkylated benzenes, such as isopropylbenzene and tert-butylbenzene. The previously published results [13] of PNP·TEA were recalculated according to the uniform procedure. New measurements for the 2,4,6-trichlorophenol–triethylamine complex (TCP·TEA) have been performed. The experimental study of the protomeric equilibrium (I) in the phenol–trialkylamine system is hindered by the presence of a competing equilibrium, that is the 2:1 (phenol:trialkylamine) complex formation. Thus, in our measurements the high excess of triethylamine in ternary solutions has been used. Furthermore, in solvents of low dielectric permittivity, aggregation of the polar 1:1 complex can cause some difficulties. For this reason, the measurements have been carried out at low concentrations of phenol.

We discuss the solvation effect as being composed of two contributions: short and long-range effects. Short-range solvation effect results from a specific interaction of the complex molecule with the solvent molecules. As a result, an ordered region with a specific microstructure in the vicinity of the dipole is formed. The extent of this region is determined, in the first approximation, by the size of solvent molecules. A long-range effect reflects the influence of the bulk dielectric permittivity.

The Gibbs energies ΔG_{PT} of the proton-transfer, computed from the dipolar data, are discussed in terms of the above-mentioned solvent parameters – its size and bulk dielectric permittivity. To describe quantitatively the influence of both factors, a simple dielectric model of two spherical solvent layers [31] is employed. This model has been successfully applied to investigate the inhomogeneity of the medium in the vicinity of ions [32]. The thickness of the first solvation layer, in which the local dielectric permittivity is lower than the bulk value, is allowed to vary with the molecular volume of the solvent. Finally, to analyse the solvent dependence of ΔG_{PT} we look towards empirical solvent parameters. Among the various existing scales [33], the Kamlet-Taft π^* [34] and the Swain *et al.* [35] *A* parameters offer an explanation of our results.

EXPERIMENTAL

The dielectric permittivity was measured by the superheterodyne beat method at 2 MHz in a Dipolmeter, model DM 01. The refractive index for the sodium D line was measured with the Abbe' refractometer and the density was determined pyknometrically. All the measurements were performed at 25±0.02°C. 4-Nitrophenol and 2,4,6-trichlorophenol were crystallized from 0.01 M HCl and petroleum ether, respectively. Triethylamine and aromatic solvents were purified and dried by the standard methods [36].

Calculations: The molar dipole polarization P of the 1:1 complex (AHB) has been determined in the presence of a large excess of triethylamine (B) ($10 < x_B/x_{AH} < 100$) and at rather low concentrations of phenol (AH) ($8\times10^{-4} < x_{AH} < 6\times10^{-3}$). Under these conditions one can assume that a complex of 1:1 stoichiometry predominates and its polarization can be determined from

$$\frac{P - P_S x_S}{x_B^*} = P_B + P_{AHB}\frac{x_{AH}}{x_B^*} \tag{1}$$

where P, P_S, P_B and P_{AB} are molar dipole polarizations of solution, solvent, amine and complex, and $x_B^*\left(x_B^* = x_B - x_{AH}\right)$ and x_{AH} are molar fractions of amine and phenol, respectively. In each of the solvents tested the polarization of triethylamine was also independently determined. The conformity of P_B, obtained from (1), and P_B, determined in a binary solution, was a criterion for the assumptions made as to the composition of the complex and complete binding of phenol. The Onsager local field model [37] was used to calculate P, according to

$$P = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2}V \tag{2}$$

where ε, n and V are the dielectric permittivity, refraction index, and molar volume of solvent or solution. The molar polarization of triethylamine in binary solution was determined according to the above model, using an analytical extrapolation up to infinitely high dilution [38]. Typical dependencies of $(P - P_S x_S)/x_B^*$ on x_{AH}/x_B^* for the PNP·TEA system in benzene, toluene, and tetralin are shown in Figure 1.

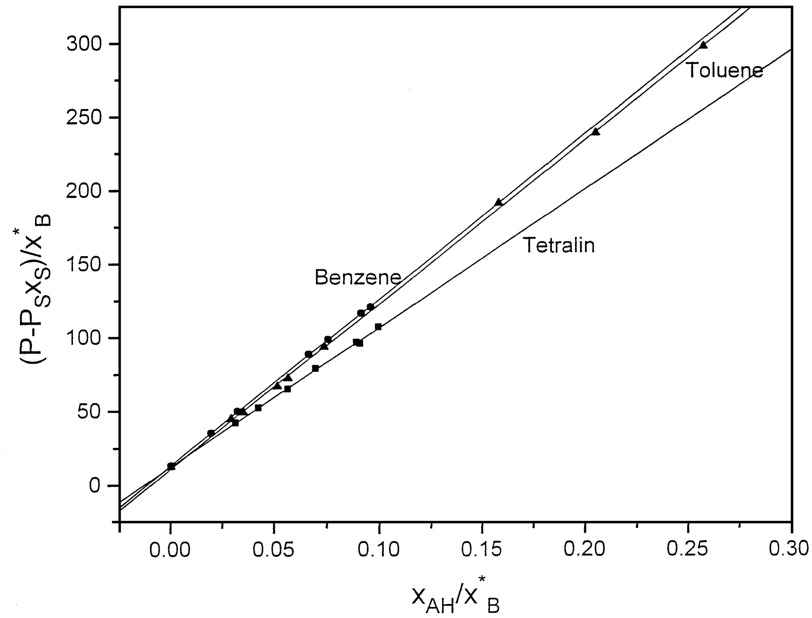

Figure 1. Dielectric polarization $(P - P_Sx_S)/x^*_B$ plotted against the x_{AH}/x^*_B ratio according to eq. (1); 4-nitrophenol–triethylamine system in benzene (●), toluene (▲), and tetralin (■).

The dipole moments μ_{AHB} of the complex ($\mu_{AHB} = 0.21986 \cdot P^{1/2}_{AHB}$ in 298 K) in a given solvent make it possible to determine the fraction of the proton-transfer form x_{PT}, according to

$$\mu^2_{AHB} = \mu^2_{HB} + (\mu^2_{PT} - \mu^2_{HB})x_{PT} \tag{3}$$

where μ_{HB} and μ_{PT} are the dipole moments of the two protomeric forms (see equilibrium I). The estimated dipole moments of both forms are: $\mu_{HB} = 6.3$ and $\mu_{PT} = 14.2$ D for PNP·TEA and $\mu_{HB} = 2.8$ D and $\mu_{PT} = 11.2$ D for TCP·TEA. In order to calculate these moments it was assumed that a 1:1 complex with a linear hydrogen bridge is formed and that the induction and charge-transfer effects bring about an increase in the dipole moment of the O–H···N bond by 0.8 D [11]. The proton transfer effect increases the polarity of the hydrogen bridge by 9.3D [9]. Having determined x_{PT}, the Gibbs energy $\Delta G_{PT}[\Delta G_{PT} = -RT\ln(x_{PT}/x_{HB})]$ can be calculated and will be discussed in the next section.

The procedure applied in determining the apparent molar volume of the 1:1 complex was identical to that used in the determination of P_{AHB}. The apparent molar volume was determined according to

$$\frac{V - V_Sx_S}{x^*_B} = V_B + V_{AHB}\frac{x_{AH}}{x^*_B} \tag{4}$$

where V and V_S are molar volumes of the solution and the pure solvent, respectively.

RESULTS AND DISCUSSION

Tables 1 and 2 present the results of the dipole moment measurements of PNP·TEA and TCP·TEA in aromatic solvents.

Table 1. Dipole moments of the 4-nitrophenol–triethylamine complex in aromatic solvents.

Solvent	P_{AHB} (cm^3)	P_B (cm^3)	μ_{AHB} (D)	$V_{AHB}\left(\frac{cm^3}{mol}\right)$
Benzene	1133.1	13.4 (13.2)	7.40±0.02	244.4
Methylbenzene (Toluene)	1110.4	12.3 (12.5)	7.33±0.02	223.8
1,2-Dimethylbenzene (o-Xylene)	1001.7	12.3 (11.5)	6.96±0.07	222.5
1,4-Dimethylbenzene (p-Xylene)	1051.8	12.4 (12.5)	7.12±0.06	221.1
1,3,5-Trimethylbenzene (Mesitylene)	931.0	11.8 (11.9)	6.71±0.04	221.4
Isopropylbenzene	1042.7	12.2 (12.0)	7.10±0.02	224.9
tert-Butylbenzene	995.9	13.0 (13.1)	6.94±0.04	228.0
1,2,3,4-Tetrahydronaphthalene (Tetralin)	946.8	12.5 (12.6)	6.77±0.02	229.5
Chlorobenzene	1286.5	23.1 (24.5)	7.88±0.06	217.0

Table 2. Dipole moments of the 2,4,6-trichlorophenol–triethylamine complex in aromatic solvents.

Solvent	P_{AHB} (cm^3)	P_B (cm^3)	μ_{AHB} (D)	$V_{AHB}\left(\frac{cm^3}{mol}\right)$
Benzene	1051.3	14.9 (13.2)	7.13±0.03	241.9
Methylbenzene	1015.8	13.5 (12.5)	7.01±0.05	233.9
1,4-Dimethylbenzene	945.7	11.6 (11.7)	6.76±0.02	227.6
1,3,5-Trimethylbenzene	912.9	12.2 (11.9)	6.64±0.05	234.7
Chlorobenzene	1075.9	24.9 (24.5)	7.21±0.02	238.3

For comparison, the polarizations of triethylamine determined in binary solution are also given in brackets. First, let us compare the influence of aromatic solvents on both complexes. There is a satisfactory linear correlation between the dipole moments according to

$$\begin{array}{ll} \mu(\text{PNP}\cdot\text{TEA}) = -4.14 + 1.61\mu(\text{TCP}\cdot\text{TEA}) & (N = 5) \\ \qquad\qquad\qquad (\pm 2.48)\ (\pm 0.36) & (R = 0.94) \end{array} \tag{5}$$

where N is the number of solvents and R refers to the correlation coefficient. However, the most interesting result is that the dipole moments do not correlate with the bulk dielectric permittivity ε (see Table 4) of the solvent. An increase in ε should stabilize the polar PT form, thus increasing the effective dipole moment of the complex. By comparing benzene with isodielectric mesitylene we can see that the dipole moment in the latter solvent is distinctly lower. A similar result was obtained previously for the 2,6-dichlorophenol–triethylamine complex [14]. A moderate increase in the dipole moments in polar chlorobenzene ($\varepsilon = 5.62$) also deserves consideration.

A starting point for a discussion of the aromatic solvent effect is the assumption that the solvation effect falls into two contributions. Short-range solvation effects result from specific, local interactions between complex and solvent molecules. This interaction depends on the microscopic parameters of the solvent molecule and on the steric crowding around the solute molecule. We believe that it is not appropriate to speak about a definite stoichiometry of the complex-aromatic molecule system. Here, we are rather dealing with a time-averaged 1:n cluster formation. However, it seems that the active site of the complex molecule is the polar O–H···N bridge with a negatively charged oxygen atom. The interaction in the first solvation shell stabilizes a complex molecule. It was shown previously [16] that the solvation Gibbs energies of the TCP·TEA complex in benzene and bromobenzene are about 2 kJ/mol more negative comparing with ΔG in isodielectric non-aromatic solvents.

The second solvation contribution arises from a long-range effect caused by the dielectric permittivity. However, because of the orientation of solvent molecules in the vicinity of solute, the nearest region (cybotactic region) is characterized by a local ε, which is lower than the bulk ε. The size of the cybotactic region for a given solute depends on the size and shape of the solvent molecule.

The influence of aromatic solvents on proton transfer shall be now discussed in terms of the Gibbs energy, ΔG_{PT},of this process. In Tables 3 and 4 the values of ΔG_{PT} are presented.

Table 3. Gibbs energies of the proton transfer and electrostatic interaction in the 2,4,6-trichlorophenol–triethylamine system.

Solvent	ΔG_{PT} (kJ/mol)	$\delta\Delta G_{PT}^{(exp)}$ (kJ/mol)	$\delta\Delta G_{PT}^{(el)}$ (kJ/mol)	
			$b - a = R$	$b - a = r$
Benzene	1.37	–	–	–
Methylbenzene	1.52	0.15	0.11	0.17
1,4-Dimethylbenzene	1.85	0.48	0.30	0.63
1,3,5-Trimethylbenzene	2.00	0.63	0.39	0.83
Chlorobenzene	1.26	–0.11	–0.85	–2.83

Table 4. Gibbs energies of the proton transfer and electrostatic interaction in the 4-nitrophenol–triethylamine system.

Solvent	ε	R (10^8 cm)	ΔG_{PT} (kJ/mol)	$\delta\Delta G_{PT}^{(exp)}$ (kJ/mol)	$\delta\Delta G_{PT}^{(el)}$ (kJ/mol)	
					b – a = R	b – a = r
Benzene	2.274	6.57	5.77	–	–	–
Methylbenzene	2.372	6.98	5.84	0.07	0.10	0.17
1,2-Dimethylbenzene	2.572	7.28	7.09	1.32	0.12	0.11
1,4-Dimethylbenzene	2.260	7.32	6.49	0.72	0.30	0.65
1,3,5-Trimethylbenzene	2.270	7.62	8.38	2.61	0.39	0.86
Isopropylbenzene	2.383	7.64	6.56	0.79	0.34	0.69
tert-Butylbenzene	2.354	7.90	7.18	1.41	0.43	0.92
1,2,3,4-Tetrahydronaphthalene	2.766	7.58	8.01	2.24	0.15	0.11
Chlorobenzene	5.621	6.87	4.57	–1.20	–0.87	–2.66

Spectroscopic studies of proton transfer in PNP·TEA and TCP·TEA complexes in aromatic solvents are scare. The electronic spectra of PNP·TEA in chlorobenzene [39] show that the protomeric equilibrium is strongly shifted towards the molecular HB form in agreement with our result. The value $\ln K_{PT} = -0.70$ obtained from infrared data for TCP.TEA in chlorobenzene [5] is close to $\ln K_{PT} = -0.51$ yielded by the dipole moment measurements. According to the suggested model of the complex-solvent interaction, the Gibbs energy is partitioned into three parts:

$$\Delta G_{PT} = \Delta G_{PT}^{o} + \Delta G_{PT}^{(sp)} + \Delta G_{PT}^{(el)} \tag{6}$$

where ΔG_{PT}^{o} is the Gibbs energy of PT in the isolated complex. The electrostatic Gibbs energy $\Delta G^{(el)}$ is very often assessed on the ground of the continuum dielectric models. Commonly Onsager's model [12,40,41] is used, according to which the electrostatic contribution to the proton-transfer equilibrium is given by:

$$\Delta G_{PT}^{(el)} = -N_A \frac{\mu_{PT}^2 - \mu_{HB}^2}{a^3} \frac{\varepsilon - 1}{2\varepsilon + 1} \tag{7}$$

where „a" is the radius of the solvent spherical cavity and ε is the bulk dielectric permittivity. Even a rough inspection of Tables 3 and 4 show this model to be doomed to fail. The radii of spherical cavities calculated from molar volumes in the solvents under investigation are: a (PNP·TEA) = 4.46 Å and a (TCP·TEA) = 4.54 Å. Hence, knowing μ_{HB} and μ_{PT} estimated earlier, transfer of the PNP·TEA complex from non-polar benzene to chlorobenzene is accompanied by a reduction of ΔG_{PT} by 16.2 kJ/mol, whereas the experimental lowering is only 1.2 kJ/mol. The reason of this is, as mentioned before, the local orientation of the solvent molecules around the complex.

Two modifications of Onsager's model provide a chance to allow for spatial variation of the dielectric permittivity, which is small near the dipole and is large at the long distance from it. The Block-Walker modification [42] was applied with some success to explain the effect of polar non-aromatic solvents on the proton-transfer equilibria [14–16,43]. However, Block-Walker's reaction field model cannot mimic the dielectric permittivity variation with the molecular volume of the solvent. Such dependence is a crucial point that we expect in the case of aromatic solvent effect. Therefore, we will try to employ the Beveridge-Schnuelle model of a two concentric dielectric continua [31]. In this simple model the polar molecule is treated as a point dipole in the centre of a spherical cavity of radius a and $\varepsilon = 1$. The cavity is surrounded by two concentric continua with some local permittivity ε_{loc} and a bulk dielectric permittivity ε. The local layer has a thickness (b-a). Although it is still a continuum dielectric model and the molecularity of the medium is completely ignored, it serves the possibility of simulation of the (b-a) thickness with the size of the solvent molecule. According to above model the electrostatic Gibbs energy is given by relation [31,44]:

$$\Delta G_{PT}^{(el)} = -N_A(\mu_{PT}^2 - \mu_{HB}^2)\left[\frac{\varepsilon_a - 1}{(2\varepsilon_a + 1)a^3} + \frac{\varepsilon_b - 1}{(2\varepsilon_b + 1)b^3}\left(1 - \frac{1 - \varepsilon_a}{2\varepsilon_a + 1}\right)\right] \tag{8}$$

where ε_a and ε_b depend on ε_{loc} and ε as follows:

$$\varepsilon_b = \frac{\varepsilon}{\varepsilon_{loc}} \qquad \text{and} \qquad \varepsilon_a = \varepsilon_{loc}\left[1 + \frac{2(1-\varepsilon_{loc})(1-\varepsilon_b)a^3}{(2\varepsilon_b + 1)b^3}\right]^{-1} \tag{8.1}$$

To calculate $\Delta G^{(el)}$ it is necessary to choose the numerical values of the parameters (b-a) and ε_{loc}. The thickness of the layer depends on the solvent molar volume and in calculations of $\Delta G^{(el)}$ it was taken as the solvent radius r or diameter R. It is a reasonable assumption, because the number of solvent molecules in the first layer is rather small. It is very difficult to decide what is the local dielectric permittivity. We have modulated the decrease of ε in the vicinity of the complex molecule taking ε as equal to 1, 1.5, and 2.25.

The magnitudes of $\Delta G_{PT}^{(el)}$ calculated assuming (b-a) = r as well as (b-a) = R and ε_{loc} = 1 are shown in Tables 3 and 4. Tables 3 and 4 compare the experimental and calculated Gibbs energies $\delta\Delta G_{PT}^{(el)}$ of transfer of a complex from benzene to a given solvent. It is seen that for the TCP·TEA system the two concentric layers model explains quite well the decrease of the proton-transfer degree with increasing the size of the solvent molecule. The dependence of $\delta\Delta G_{PT}^{(exp)}$ on the calculated Gibbs energies $\delta\Delta G_{PT}^{(el)}$ for PNP·TEA in the series of mono- substituted and 1,4-di-substituted benzenes is shown in Fig. 2. Good, although not linear, relations can be seen. However, the deviations from above relations are observed in o-xylene, mesitylene and tetralin. It must be

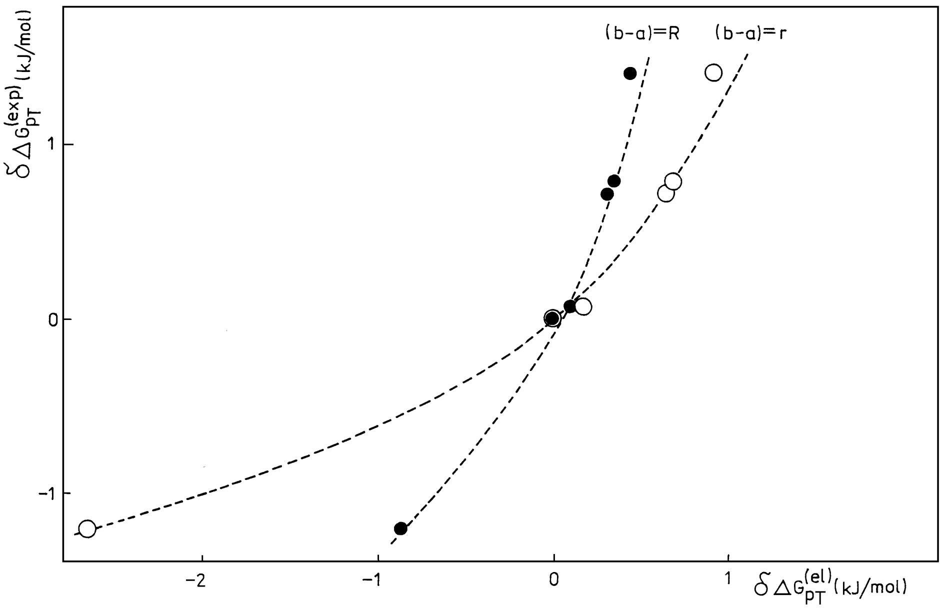

Figure 2. Relation between the experimental and calculated Gibbs energies for the PNP·TEA complex.

remembered that the $\Delta G_{PT}^{(sp)}$ term in (7) was allowed to be constant. It can be valid in a series of structurally similar solvents. However, the dipole- induced dipole and charge-transfer interactions, which seem to be the main factors for ordering the solvent molecules, can be different in these three solvents. The reasons of their different behaviour are anisotropy of the polarizability and steric requirements for the most effective interaction.

In previous papers [14–16] we have attempted to correlate the ΔG_{PT} values with empirical solvent parameters. A proper choice of such parameters allows to describe contribution of both specific and electrostatic solvation effects to the proton transfer. Unfortunately, the aromatic solvents are only meagrely represented in the existing polarity scales. Nevertheless, the Kamlet-Taft dipolarity/polarizability term π^* [34] decreases in the order: chlorobenzene > benzene > toluene > p-xylene > mesitylene. The π^* scale is a measure of the solvent ability to interact with solute molecule by dipole/dipole, dipole/induced dipole and dispersion interactions. The following correlations are found between ΔG_{PT} and the π^* parameter:

$$\Delta G_{PT}(\text{PNP·TEA}) = \underset{(\pm 1.61)}{11.66} - \underset{(\pm 2.94)}{10.17}\,\pi^* \qquad \begin{array}{l}(N = 5)\\(R = 0.98)\end{array} \qquad (9)$$

$$\Delta G_{PT}(\text{TCP·TEA}) = \underset{(\pm 0.26)}{3.81} - \underset{(\pm 0.48)}{4.37}\,\pi^* \qquad \begin{array}{l}(N = 5)\\(R = 0.98)\end{array} \qquad (10)$$

It is worth noting that hydrogen-bond accepting (electron-donating) properties of the solvent revealed in the β Kamlet-Taft parameter are not important for the solvent influence on ΔG_{PT}; β decreases in the opposite order than π*. The electron-accepting abilities represented by α parameter are not distinguished in the group of solvents discussed and are equal to zero [33,34]. Good correlations are also obtained with the Swain *et al.* [35] *A* parameter:

$$\Delta G_{PT}(\text{PNP}\cdot\text{TEA}) = \underset{(\pm 0.44)}{7.44} - \underset{(\pm 3.04)}{13.10}\,A \qquad \begin{matrix}(N = 4)\\(R = 0.98)\end{matrix} \qquad (11)$$

$$\Delta G_{PT}(\text{TCP}\cdot\text{TEA}) = \underset{(\pm 0.08)}{2.09} - \underset{(\pm 0.57)}{4.35}\,A \qquad \begin{matrix}(N = 4)\\(R = 0.98)\end{matrix} \qquad (12)$$

The *A* parameter represents the bulk solvent properties involved in the solvation of negatively charged sites in the solute. In our case it is the oxygen atom in the hydrogen bonded OH group. It can be believed that the *A* parameters include both the electrostatic and specific (for example charge-transfer) interactions and their steric modification.

Summing up, one can state that the formal splitting of the solvation effect into a local and long-range dielectric contributions allows to explain the abnormal aromatic influence on the protomeric equilibria studied in this work. On one hand, the aromatic solvent molecules stabilize specifically the hydrogen-bonded ion pair, on the other hand, the long-range effect is weakened, due to the decrease of the local dielectric permittivity. Both of these effects are functions of the size and shape of the solvent molecule.

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