Solvent Effect on the Gibbs Energy of Proton Transfer in the 2,6-Dichlorophenol-Triethylamine Complex

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Using dipole moment measurements, the Gibbs energy ΔG_{PT} of proton transfer in the complex of 2,6-dichlorophenol with triethylamine was determined in different solvents. The effect of solvent on ΔG_{PT} was quantitatively discussed in terms of reaction field models for homogeneous and heterogeneous dielectric media. The specific complex–solvent interactions which, in addition to electrostatic interaction, stabilize the PT polar form of the complex is discussed as a function of the empirical parameters describing the polar and hydrogen-donating (electron-accepting) properties of the solvent.

KEY WORDS: Dipole moment; hydrogen-bonded complex; 2,6-dichlorophenol; triethylamine; proton transfer; solvent effect.

1. INTRODUCTION

When studying the proton transfer process in a particular $AH \cdots B$ hydrogen bond, it is important to consider the influence of the solvent on the protomeric equilibrium

$$\begin{array}{c} AH \cdots B \Leftrightarrow A^{\Theta} \cdots HB^{\oplus} \\ HB \quad PT \text{ form} \end{array}$$
(I)

It has been demonstrated in many papers⁽¹⁻⁴⁾ that proton transfer occurring in the liquid phase is accompanied by a reorganization of the solvation shell. To adequately describe the influence of the solvent, it is necessary to analyze the evolution of the Gibbs energy surface of a given AH–B system as a function of the properties of the solvent. The bulk dielectric permittivity ε has often been

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selected as the single parameter determining the degree of interaction between the complex and the medium. An increase in ε results in a shift of the PT equilibrium to the right, because the dipole moment of the PT form considerably exceeds that of HB. In such a case, the influence of the environment has been discussed on the grounds of a reaction field model for homogeneous dielectric medium.⁽⁵⁻¹¹⁾ In spite of the usefulness of this dielectric model, its direct application to the estimation of the solvation energy of very polar (or ionic) solutes remains limited because of strong local interactions (dielectric saturation).⁽¹²⁻¹⁹⁾ In such cases, the relation between the microstructure of the solvent in the vicinity of a dipolar solute and local dielectric properties must also be considered. Heterogeneous dielectric models have been proposed in mathematically tractable forms.^(20,21) In such models the dipole is surrounded by medium whose dielectric constant is asymptotically increasing with distance or by two concentric shells having local and bulk dielectric permittivities. On the other hand, it has been found, in many cases, that dielectric permittivity could not be considered as the only factor influencing the interaction of a complex with the environment. It is necessary to take into account the specific interactions of the complex with the surrounding molecules of the solvent. Specific environmental effects resulting from hydrogen bond or charge-transfer interactions often facilitate proton transfer $^{(9,22-25)}$ and may contribute considerably to the Gibbs energy of solvation.

Because of the great differences in dipole moments of the HB and PT forms, measurement of the effective dipole moment of the complex is a convenient method for determining the proton transfer constant K_{PT} . In the first part of this paper, we determined the dipole moment of 2,4,6-trichlorophenol–pyridine complex without proton transfer in selected solvents. Then, we determined the Gibbs energy ΔG_{PT} of proton transfer in the 2,6-dichlorophenol–triethylamine system in several solvents with different dielectric permittivities ($2 < \varepsilon < 11$) and chemical properties. The solvent effect on ΔG_{PT} is discussed in terms of simple continuum dielectric models and specific solute–solvent interactions. The contribution of specific interactions is analyzed on the basis of correlations with empirical parameters of the hydrogen-donating (electron-accepting) ability of the solvent.

2. EXPERIMENTAL

The dielectric permittivity was determined by the superheterodyne beat method at 2 MHz in a Dipolmeter (model DMO1). The capacitance was measured with relative error $\Delta C/C \leq 1 \times 10^{-4}$. The refractive index was measured for the sodium D line with an Abbe refractometer with an accuracy of $\pm 5 \times 10^{-5}$. The density was determined pycnometrically with an accuracy $\pm 1 \times 10^{-4}$ g-cm⁻³. Measurements were carried out at 25°C. Phenols were crystallized from *n*-hexane; amines and solvents were purified and dried by standard methods.⁽²⁶⁾

3. METHODS OF INVESTIGATION AND CALCULATION

The degree of proton transfer in the 2,6-dichlorophenol–triethylamine complex (DCPH-TEA) has been determined by dipole moment measurement. The formation constants K_f of the complex in the studied solvents were of the order 10^2 dm³-mol⁻¹. The formation constants of 2,4,6-trichlorophenol–pyridine complex, which, in this study, has been considered as a standard system without proton transfer, were 29 and 12 dm³-mol⁻¹,⁽²⁷⁾ respectively in CCl₄ and 1,2-dichloroethane. In a large excess of amine, only complexes of 1 : 1 stoichiometry are formed. Under these conditions, the molar dielectric polarization is linearly related to the ratio of complex to amine concentrations:

$$\frac{P - P_{\rm s} x_{\rm s}}{x_{\rm a}} = P_{\rm a} + P_{\rm c} \frac{x_{\rm c}}{x_{\rm a}} \tag{1}$$

where *P* is the molar polarization of the solution, P_s , P_a , and P_c are the molar polarizations of solvent, amine, and complex, and *x* is their molar fraction. A plot of $(P - P_s x_s)/x_a vs. x_c/x_a$ gives a straight line where its slope is the molar dielectric polarization P_c . Moreover, by comparing the value of P_a with independently determined polarization of the amine in a two-component solution, we can verify the complexation degree and the stoichiometry. The molar dielectric polarizations *P* and *P_s* have been calculated from

$$P = \left[\frac{(\varepsilon - 1)}{3g}(1 - \alpha t)^2 - \frac{n^2 - 1}{n^2 + 2}(1 - \alpha t)\right]V$$
(2)

where ε , *n*, and *V* are the dielectric permittivity, refractive index, and molar volume, respectively.

The g and αt parameters depend on the local field model. In our calculations, we employed the Onsager local field model⁽²⁸⁾ and its Block–Walker modification for heterogeneous dielectric medium.⁽²⁰⁾ In the models (hereafter referred as O and B–W), the g and αt parameters are expressed in the following:

$$g^{(0)} = \frac{3\varepsilon}{2\varepsilon + 1}; \quad g^{(B-W)} = \frac{\varepsilon(\ln\varepsilon)^2}{2(\varepsilon\ln\varepsilon - \varepsilon + 1)}$$
 (2.1)

$$(\alpha t)^{(0)} = \frac{2(n^2 - 1)(\varepsilon - 1)}{(n^2 + 2)(2\varepsilon + 1)}; \quad (\alpha t)^{(B-W)} = \frac{n^2 - 1}{n^2 + 1} \left(\frac{3\varepsilon \ln\varepsilon}{\varepsilon \ln\varepsilon - \varepsilon + 1} - \frac{6}{\ln\varepsilon} - 2\right)$$
(2.2)

Both methods were tested on the 2,4,6-trichlorophenol–pyridine complex (TCPH–PYR) in several solvents of different dielectric permittivity. Spectroscopic, thermodynamic, and dipolar data^(27,30–32) confirm that such a relatively weak complex does exist, but only in the normal OH···N form without proton transfer. Moreover, its dipole moment in nonpolar solvents is comparable to the dipole moment of DCPH–TEA. Hence, it seemed to be an ideal system to check the applicability



Fig. 1. Dielectric polarization $(P - P_s x_s)/x_a$ plotted against the x_c/x_a ratio (Eq. 1).

of both approaches and to assess the influence of solvent on the dipole moment of the HB form. The typical results in nonpolar (cyclohexane) and polar (chloroform) solvents are shown in Fig. 1.

The standard deviations of the μ_c and μ_a dipole moments are not higher than 0.06 and 0.03 D, respectively. The dipole moments in all tested solvents are given in Table I.

As is seen in Table I, the dipole moment determined by the O or B–W method depends slightly on the solvent. The dipole moments, obtained with the Block–Walker method in nonpolar solvents, are higher than those yielded by the Onsager method; their difference decreases with increasing ε of the solvent.

The dielectric polarizations of pyridine and triethylamine were determined independently (see the values in brackets), applying both the local field models and analytical extrapolation to infinite dilution.⁽²⁹⁾

The dielectric polarization of DCPH–TEA complex was determined in the same way and with the same accuracy as for the TCPH–PYR system. Having determined the dipole moment μ_c of the DCPH–TEA complex, the molar fraction of the PT form x_{PT} was derived from

$$\mu_{\rm c}^2 = \mu_{\rm HB}^2 + \left(\mu_{\rm PT}^2 - \mu_{\rm HB}^2\right) x_{\rm PT} \tag{3}$$

Table I. Dielectri	c Polarizatic	n and Dipole M	oment of the	e 2,4,6-Tri	chlorophenol-Py	ridine Com	plex in Va	rious Solvents
				Method ((0)	I	Method (B	(M-
Solvent	ε	$x_{c}x_{a}$	$P_{\rm c}~({\rm cm}^3)$	$\mu_{\rm c}\left({\rm D}\right)$	$P_{\rm a}~({ m cm}^3)^a$	$P_{\rm c}~({\rm cm}^3)$	$\mu_{\rm c} ({\rm D})$	$P_{\rm a}~({ m cm}^3)^a$
Cyclohexane	2.016	0.022-0.138	347.2	4.10	102.3 (102.6)	406.2	4.43	117.3 (117.7)
CC14	2.226	0.040 - 0.071	355.1	4.14	112.1 (116.1)	415.1	4.48	131.3 (135.4)
Benzene	2.274	0.040 - 0.074	356.2	4.15	99.8 (100.0)	430.1	4.56	118.7 (119.0)
Chloroform	4.807	0.024 - 0.148	364.8	4.20	178.6 (181.6)	393.7	4.36	191.8 (196.9)
o-Dichlorobenzene	9.938	0.051 - 0.187	315.9	3.91	112.6 (112.6)	335.4	4.03	120.9 (121.4)
1,2-Dichloroethane	10.342	0.008-0.062	367.5	4.21	125.1 (126.1)	373.1	4.25	128.5 (126.9)
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where μ_{HB} and μ_{PT} are the dipole moments of both protomeric forms. The dipole moments μ_{HB} and μ_{PT} were calculated assuming a linear OH···N bond according to:

$$\mu_{\rm HB} = \vec{\mu}_{\rm o} + \vec{\mu}_{\rm int} \quad ; \quad \mu_{\rm PT} = \vec{\mu}_{\rm o} + \vec{\mu}_{\rm pt} \tag{4}$$

where μ_o is the vector sum of the dipole moments of phenol ($\mu = 2.00$ D) and amine ($\mu = 0.80$ D), and μ_{int} is the interaction dipole moment resulting from induction and charge transfer effects. The interaction dipole moment was taken as $0.8 \text{ D}.^{(33)}$ The dipole moment μ_{pt} equal to 9.3 D⁽³⁴⁾ is the moment resulting from complete proton transfer. The μ_{int} and μ_{pt} moments were assumed to be located along the OH···N bond axis. Thus, the dipole moments $\mu_{HB}^{(O)}$ and $\mu_{PT}^{(O)}$ are 3.0 and 10.9 D, respectively. Dipole moments computed from the Block–Walker method are 1.06 times higher than those given above. It was assumed that μ_{HB} and μ_{PT} did not depend on the solvent. This assumption is justified by the negligible solvent sensitivity of the dipole moment of the TCPH–PYR complex.

The so-called "dielectric" constant of proton transfer K_{PT} results simply from the ratio $x_{\text{PT}}/x_{\text{HB}}$. If the K_{PT} constants is known, the standard molar Gibbs energy ΔG_{PT}^{o} of proton transfer can be calculated and the influence of solvent on ΔG_{PT} discussed.

4. RESULTS AND DISCUSSION

The dipole moments of the DCPH–TEA complex in eleven pure solvents and a mixture of $C_2Cl_4 + 1$, 1-dichloroethane (3 : 1 volume fraction) are presented in Table II. In contrast to the TCPH–PYR system, there is a strong effect of the solvent on the dipole moment.

The ΔG_{PT}^{o} values of proton transfer are listed in Table III. The maximal error in the estimation of ΔG_{PT}^{o} is of the order of 0.3 kJ. The data in Table III indicates that the PT equilibrium is shifted to the right with increasing polarity of the environment.

The standard molar Gibbs energy ΔG_{PT}^{o} can be split into two parts: $\Delta G_{PT}^{(i)}$ and $\Delta G_{PT}^{(solv)}$. The intrinsic $\Delta G^{(i)}$ is related to the PT process in the isolated hydrogen bond system. The $\Delta G_{PT}^{(solv)}$ term represents the contribution of total solvation effects to ΔG_{PT}^{o} . The solvation effect can be discussed in terms of non-specific (electrostatic) and specific interaction. Other effects, arising from dispersion interaction and creation of solvent cavity, do not give the dominant contribution to the PT process. They can be assumed slightly dependent on the solvent and are included in the $\Delta G_{PT}^{(sp)}$ term. Thus, the standard molar Gibbs energy may be given by the following equation:

$$\Delta G_{\rm PT}^{\rm o} = \Delta G_{\rm PT}^{\rm (i)} + \Delta G_{\rm PT}^{\rm (sp)} + \Delta G_{\rm PT}^{\rm (el)} \tag{5}$$

Solvent Effect on Proton Transfer

		I	Method ((0)	M	ethod (B	–W)
Solvent	$x_{\rm c}/x_{\rm a}$	$P_{\rm c}~({\rm cm}^3)$	$\mu_{\rm c}$ (D)	$P_{\rm a}({\rm cm}^3)^a$	$P_{\rm c}~({\rm cm}^3)$	$\mu_{\rm c}$ (D)	$P_{\rm a}({\rm cm}^3)^a$
Cyclohexane	0.045-0.137	198.9	3.10	10.0 (10.6)	228.9	3.33	12.6(13.2)
Benzene	0.072-0.251	487.9	4.85	13.1 (13.2)	577.5	5.28	16.3 (16.6)
Mesitylene	0.060-0.094	354.4	4.14	11.8 (11.9)	419.7	4.50	14.9 (15.0)
Tetrachloroethylene	0.044-0.076	221.1	3.27	15.1 (15.1)	261.2	3.55	19.0 (18.9)
Trichloroethylene	0.045-0.159	485.3	4.84	33.0 (34.1)	558.6	5.20	38.6 (39.8)
$C_2Cl_4 +$	0.113-0.233	413.7	4.47	17.5 (18.3)	476.0	4.80	20.6 (21.4)
1,1-Dichloroethane							
1,2-Dibromoethane	0.078-0.259	411.4	4.46	54.7 (54.2)	476.7	4.80	60.9 (60.2)
Chloroform	0.045-0.174	1070.4	7.19	80.2 (78.7)	1132.5	7.40	88.8 (87.0)
Chlorobenzene	0.060-0.159	571.4	5.26	24.8 (24.5)	623.5	5.49	28.1 (27.8)
n-Bromobutane	0.084-0.231	475.8	4.80	19.9 (20.2)	498.5	5.00	28.5 (28.7)
n-Chlorobutane	0.078-0.290	523.5	5.03	16.5 (18.3)	547.8	5.15	21.1 (22.4)
1,2-Dichloroethane	0.028-0.061	1058.3	7.15	47.2 (46.3)	970.3	6.85	47.8 (47.1)

 Table II.
 Dielectric Polarization and Dipole Moment of the 2,6-Dichlorophenol–Triethylamine Complex in Various Solvents

^a See footnote Table I.

where $\Delta G_{\text{PT}}^{(\text{el})}$ and $\Delta G_{\text{PT}}^{(\text{sp})}$ represent the energies of electrostatic and specific complex–solvent interaction.

Many theories have been proposed to evaluate the electrostatic component of the solvation energy. A classical example is the Onsager reaction field theory,^(28,35) which considers a dipole in a spherical cavity immersed in a continuous dielectric medium of bulk ε . This dielectric model has been commonly applied to describe the solvent effect on the proton transfer equilibrium.^(5–11) However, at least one objection concerns the use of a bulk dielectric permittivity arises in this approach. Therefore, the modification proposed by Block–Walker⁽²⁰⁾ seems to be attractive. In their model, dielectric saturation in the area closest to the polar solute is allowed. The dielectric permittivity does not reach the bulk ε value after crossing the boundary of the cavity, but approaches it asymptotically according to

$$\varepsilon(r) = \varepsilon e^{-k/r}$$

where *r* is the distance from the center of the cavity and *k* is equal to $a \ln \varepsilon$, *a* being the radius of the spherical solvent cavity. In this sense, the solvent may be treated as a heterogeneous dielectric medium. According to both reaction field models, expression (5) can now be written as:

$$\Delta G_{\rm PT}^{\rm o} = \Delta G_{\rm PT}^{\rm (i)} + \Delta G_{\rm PT}^{\rm (sp)} - N_{\rm A} \frac{\left(\mu_{\rm PT}^2 - \mu_{\rm HB}^2\right)}{a^3} f(\varepsilon)$$
(6)

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Solvent	E_{T}	π^*	α	A	$f(\varepsilon)^{(O)}$	$f(\varepsilon)^{(\mathrm{B}-\mathrm{W})}$	$\Delta G_{\rm PT}^{\circ}$ (0)	$\substack{(kJ-mol^{-1})\\(B-W)}$	$-\Delta G_{\rm PT}^{\rm (el)}$ (0)	(kJ-mol ⁻¹) (B-W)
Cyclohexane	30.9	0.00	0.00	0.02	0.202	0.056	13.1	12.1 (5)	13.2	4.1
Benzene	34.3	0.59	0.00	0.15	0.229	0.064	4.7	4.4 (5)	14.9 (5)	4.7
Mesitylene	32.9	0.41	0.00	0.06	0.230	0.064	6.3	6.0	15.0	4.7
Tetrachloroethylene	31.9	0.28	0.00	0.10	0.230	0.065	10.4	9.7	15.0	4.8
Trichloroethylene	35.9	0.53	0.00	0.16	0.308	0.093	4.7	4.6	20.1	6.8
$C_2Cl_4 + 1, 1$ -Dichloroethane	I	I	I	I	0.323	0.099	5.5	5.3 (5)	21.1	7.3
1,2-Dibromoethane	38.3	0.75	0.00	I	0.359	0.116	5.4 (5)	5.3	23.4	8.5
Chloroform	39.1	0.58	0.20	0.42	0.359	0.116	1.1 (5)	1.4	23.4	8.5
Chlorobenzene	36.8	0.71	0.00	0.20	0.377	0.126	3.9 (5)	4.1	24.6	9.2 (5)
<i>n</i> -Bromobutane	36.6	0.50	0.00	I	0.400	0.139	4.7	4.9 (5)	26.1	10.2
<i>n</i> -Chlorobutane	36.9	0.39	0.00	I	0.403	0.141	4.3 (5)	4.7	26.3	10.3(5)
1,2-Dichloroethane	41.3	0.81	0.00	0.30	0.431	0.161	1.20	2.1 (5)	28.1	11.8

Table III. Gibbs Energies of Proton Transfer (ΔG_{PT}) and Electrostatic Interaction ($\Delta G_{PT}^{(el)}$) in Various Solvents

Solvent Effect on Proton Transfer

The reaction field factors $f(\varepsilon)$ of the homogeneous (Onsager) and the heterogeneous (Block–Walker) dielectric models are defined as follows:

$$f^{(0)}(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1}$$
(7.1)

$$f^{(\mathrm{B-W})}(\varepsilon) = \frac{3\varepsilon \ln \varepsilon}{2\varepsilon \ln \varepsilon - 2\varepsilon + 2} - \frac{3}{1n\varepsilon} - 1$$
(7.2)

In the absence of specific interactions, $\Delta G_{\text{PT}}^{\text{o}}$ is a linear function of $f(\varepsilon)$. The dependences of $\Delta G_{\text{PT}}^{\text{o}}$ on $f(\varepsilon)$ are shown in Fig. 2.

First we can compare the experimental and calculated slopes (S) of the straight lines ΔG_{PT}^{o} vs. $f(\varepsilon)$. The experimental values of $S^{(O)}$ and $S^{(B-W)}$ are equal to 44 ± 5 and 82 ± 12 kJ-mol⁻¹, respectively, if the points in mesitylene, benzene, trichloroethylene, and chloroform are omitted (see further discussion). The radius of the spherical cavity, estimated from the apparent molar volumes of DCPH and TEA is 4.67 Å. Close values of the radius a of 4.47 to 4.7 Å are obtained from Böttcher's relation: $a^3 = \alpha (n^2 + 2)/(n^2 - 1)$, when the refractive index of the complex varies within the reasonable limits of 1.55 to 1.45. Thus, a radius of cavity equal to 4.67 Å, together with the estimated $\mu_{\rm HB}$ and $\mu_{\rm PT}$ values give $S^{(O)}$ and $S^{(B-W)}$ of 65 and 76 kJ-mol⁻¹, respectively. As can be seen, the homogeneous model overestimates the electrostatic contribution to ΔG_{PT}^{0} giving values of $\Delta G^{(el)}$ considerably higher than those observed. The electrostatic contribution to the solvent effect may be simply discussed by comparison of pairs of systems. For example, the experimental $\Delta G_{PT}^{o}(S_1 \rightarrow S_2)$ values on going from tetrachloroetylene to n-chlorobutane determined from the (O) and (B-W) procedures, are -6.0 and -5.0 kJ-mol⁻¹, respectively. The Gibbs energies of electrostatic interaction calculated according to the two models are shown in Table III. It may be seen that for the above pair of solvents, the calculated $\delta \Delta G_{\text{PT}}^{(\text{tr},\text{O})}$ and $\delta \Delta G_{\rm PT}^{(\rm ir,B-W)}$ are -11.3 and -5.5 kJ-mol⁻¹. For the remaining pairs of solvents that do not interact specifically, the experimental $\Delta G_{PT}^{(tr)}$ appear lower than those calculated from the Onsager model and higher than those predicted by the Block-Walker model. Nevertheless, the heterogeneous model better assesses the energy of electrostatic interaction. It is due to the expected (at least partial) loss of freedom of solvent molecules orientation in the nearest neighborhood of the polar complex.

The effect of specific solute–solvent interactions is evidenced by a negative deviation from the linear correlation $\Delta G_{PT}^{o} vs. f(\varepsilon)$. As indicated in Table III, the position of the PT equilibrium in chloroform, trichloroethylene, benzene, and mesitylene is affected not only by electrostatic interactions, but also by specific effects. In chloroform, it is due to hydrogen-bond interaction of the CH group of chloroform and the lone pairs of hydroxyl oxygen. In the PT structure, the specific interaction is much stronger, because of the stronger basic character of the oxygen atom.





Large proton transfer constants in hydrogen-donating media had already been explained (9, 22-25) by such a mechanism of specific complex-solvent interaction. Most probably this interaction is also responsible for relatively high negative deviation of ΔG_{PT}^{o} in trichloroethylene. An additional indication of specific HB interactions in chloroform and trichloroethylene is the high dipole moment of triethylamine in these solvents (see Table II). The aromatic nonpolar solvents very often behave like solvents of higher effective polarity than that expected from their bulk dielectric permittivity. For example, the value $\varepsilon = 7.5$ is proposed to explain the influence of benzene on the conformational equilibria.^(36,37) This value adopted to the Block–Walker model gives $\delta \Delta G_{PT}^{(tr)} = -5.7 \text{ kJ-mol}^{-1}$ on going from tetrachloroethylene to benzene, when the experimental value is -5.2(5) kJ-mol⁻¹. The somewhat abnormal behavior of aromatic solvents, particularly benzene, is due to the local complex-solvent interaction, in which inductive and charge transfer forces play a decisive role. Departure from the relation ΔG_{PT}^{o} vs. $f(\varepsilon)$ is less pronounced in mesitylene, because of the anisotropy of its polarizability and the steric hindrances prevented optimal orientation.

To describe more quantitatively the influence of the solvents on the PT equilibrium, we looked toward the solvent parameter scales,⁽³⁸⁾ such as Dimroth–Reichardt's $E_{\rm T}$,⁽³⁹⁾ Kamlet-Taft's π^* , and $\alpha^{(40)}$ and Swain *et al*'s "acity" $A^{(41)}$ parameters. The $E_{\rm T}$ scale is based on transition energy of aryl-substituted *p*-phenoxypyridinium dyes. Polar ground state of the dye is stabilized not only by electrostatic, but also by HB interaction. The quantities π^* and α indicate the solvatochromic properties of the solvent, i.e., they are determined from the solvent influence on the energies of $\pi \to \pi^*$ transitions in a probe solutes. The π^* parameter is the polarity/polarizability term and α is a quantitative measure of the solvent properties involved in local interaction with negatively charged centers in the solute. The above parameters have been collected in Table III. To predict the solvent effect on $\Delta G_{\rm PT}^{\circ}$, we used the linear free energy relationships (LFER) in the form:

$$\Delta G_{\rm PT}^{\rm o} = \Delta G_{\rm PT}^{\rm (i)} + xX + yY + \cdots \tag{8}$$

where *X* and *Y* are the solvent parameters, whereas the *x* and *y* coefficients are characterististic of the considered systems. The correlations between ΔG_{PT}^{O} and one (E_T) or two ($\pi^* - \alpha$) and ($\pi^* - A$) independent variables can be written as:

$$\Delta G_{\rm PT}^{\rm o} = 39.3 - 0.947 E_{\rm T} \qquad (R = 0.90) \qquad (8.1)$$

$$(\pm 5.57) \quad (\pm 0.115)$$

$$\Delta G_{\rm PT}^{\rm o} = 11.15 - 10.73\pi^* - 17.62\alpha \quad (R = 0.93) \tag{8.2}$$

$$(\pm 1.0) \quad (\pm 1.83) \quad (\pm 7.03)$$

$$\Delta G_{\rm PT}^{\rm o} = 12.6 - 10.16\pi^* - 11.30A \qquad (R = 0.97) \tag{8.3}$$

$$(\pm 0.96) \quad (\pm 2.47) \quad (\pm 4.84)$$

As can be seen, ΔG_{PT}^{o} may be satisfactory correlated with the π^* parameter connected with the electrostatic interaction and with the α or A parameters dealing with the specific HB interaction of the negatively charged oxygen (Scheme II).

It may be concluded that the heterogeneous model of dielectric medium describes the contribution of electrostatic interactions to the Gibbs energy of PT processes better than the Onsager model. However, in solvents with weak CH acidic properties (chloroform, trichloroethylene) and in nonpolar aromatic solvents, the specific interactions promote proton transfer in hydrogen bond, decreasing ΔG_{PT}^{o} as compared with the value anticipated from the electrostatic model. The influence of electrostatic and specific effects on the PT equilibrium may be rationalized on the grounds of correlation with the empirical parameters of the solvent, characterizing as well its polar as well as its hydrogen-donating (electron-accepting) properties.

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