

Study of solvent effect on electronic absorption spectra of some chloroanilines. Part II* : Excited state dipole moments and specific solute-solvent interaction energies based on Bakhshiev's expression for solvatochromic frequency shifts

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The excited state dipole moments (μ_e) and specific solute-solvent interaction energies (E_s) of some chloroanilines discussed in a recent paper (Prabhu Mirashi and Varkhede 1989) were estimated by employing McRae's expression (McRae 1957) for solvent induced frequency shift $\Delta\bar{\nu} = \bar{\nu}_{\text{solution}} - \bar{\nu}_{\text{vapour}}$ in electronic absorption spectra. It is wellknown that the derivation of McRae's expression involves several simplifying approximations due to a large number of unevaluated parameters appearing in the perturbation calculation. It is observed that the expression for $\Delta\bar{\nu}$ deduced by Bakhshiev (1961, 1962) by employing a more descriptive and classical electrostatic approach involves much smaller number of approximations and no unevaluated parameters. Bakhshiev himself or any other groups have not applied this particular equation but have always used it in combination with a similar one for the shifts in fluorescence bands. Recently we have illustrated (Prabhu Mirashi and Kunte 1989, 1990) the use of Bakhshiev's expression for $\Delta\bar{\nu}$ in absorption spectra alone for estimation of μ_e s and E_s s of some substituted benzenes. Therefore for the sake of examining general applicability of the latter approach, the μ_e s and E_s s of chloroanilines have been recalculated on the basis of Bakhshiev's expression and compared with the earlier values based on McRae's expression.

Bakhshiev's (1961, 1962) expression for solvatochromic frequency shift $\Delta\bar{\nu}$ of an electronic absorption band is conveniently expressible in the form :

$$\bar{\nu}_s = \bar{\nu}_0 + C_1 f(D, n) + C_2 f(n) + C_3 f'(n) + C_4 f''(n) \text{ cm}^{-1} \quad (1)$$

where the various functions and parameters are defined as

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$$f(n) = (2n^2 + 1)^2(n^2 - 1)/(n^2 + 2)^3, f'(n) = (n^2 - 1)/(2n^2 + 1),$$

$$f''(n) = (n^2 - 1)/(n^2 + 2) \text{ and } f(D, n) = [(2n^2 + 2)/(n^2 + 2)]^2 \times$$

$$[(D - 1)/(D + 2) - (n^2 - 1)/(n^2 + 2)]$$

$$C_3 = 2\mu_g(\mu_g - \mu_e \cos \theta)/hca_0^3 \text{ and } C_4 = (\mu_g^2 - \mu_e^2)/hca_0^3 \quad (2)$$

Here n and D are the refractive index and dielectric constant of a solvent; μ_g and μ_e the ground and excited state dipole moments of a solute molecule with θ being the angle between their directions; C_3 and C_4 are the measures of dynamic and dispersion shifts involving polarizabilities, ionization potentials, etc. of the solute and solvent molecules in their ground and excited states; h the Planck constant, c the speed of light and a_0 the Onsager cavity radius. A systematic and step-wise procedure illustrating the application of eq. (1) has been explained in our recent papers (Prabhu Mirashi and Kunte 1989, 1990). Accordingly, in the case of polar solutes in saturated hydrocarbon (HC) solvents ($D = n^2 \Rightarrow f(D, n) = 0$), eq. (1) can be rewritten in the form

$$\bar{\nu}_g - [C_3 f'(n) + C_4 f''(n)] = \bar{\nu}_0 + [(\mu_g^2 - \mu_e^2)/hca_0^3] f(n) \quad (3)$$

so that the slope of the linear graph of the L.H.S. of eq. (3) as a function of $f(n)$ together with the known values of μ_g (McClellan 1974) and those of a_0 , estimated from molecular dimensions (Sutton *et al* 1958, 1965; Pauling 1960, Parkanyi *et al* 1986, Aaron *et al* 1987, Prabhu Mirashi and Varkhede 1989) lead to the value of μ_e . The values of C_3 and C_4 parameters required in eq. (3) above were used from our previous work (Prabhu Mirashi and Kunte 1989). The specific solute-solvent interaction energiss (E_s) for a solute with different nonhydrocarbon (nonHC) solvents were estimated from the difference between the experimentally measured frequency ($\bar{\nu}_{s(\text{obs})}$) and that calculated ($\bar{\nu}_{s(\text{cal})}$) on the assumption of only universal interactions as implied in eq. (1), by using the expression (Prabhu Mirashi and coworkers 1989, 1990).

$$\dot{E}_s = 0.011(\bar{\nu}_{s(\text{cal})} - \bar{\nu}_{s(\text{obs})}) \text{ kJ mol}^{-1} \quad (4)$$

The experimental method and materials used in the present work were the same as in our previous work (Prabhu Mirashi and Varkhede 1989).

As mentioned earlier (Prabhu Mirashi and Kunte 1989). Bakhshiev's expression for $\Delta\bar{\nu}$ is formally very similar to that of McRae (1957). The sum of the dynamic and dispersion shift parameters viz., $C_3 (= -3050 \text{ cm}^{-1})$ and $C_4 (= -330 \text{ cm}^{-1})$ for the L_b transition of benzene is in close agreement with the value of the similar (A+B) parameter, viz. -3450 cm^{-1} , appearing in McRae's equation (Prabhu Mirashi and Varkhede 1989). Also, the plots of $\bar{\nu}_g - [C_3 f'(n) + C_4 f''(n)]$ vs $f(n)$ corresponding to measurements in HC solvents exhibit good linearity with correlation

coefficient ~ 0.9 . The μ_{θ} s are all larger than the corresponding μ_{θ}^0 s. The μ_{θ} s for the three monochloroanilines are found to vary in the order: $\mu_{\theta}(p) > \mu_{\theta}(m) > \mu_{\theta}(o)$ while those for the di- and trichloroanilines (DCA and TCA) are observed to exhibit the order: $\mu_{\theta}(m, m'DCA) > \mu_{\theta}(o, p, o'TCA) > \mu_{\theta}(o, o'DCA)$. These trends parallel to those exhibit by the respective μ_{θ}^0 s. All these observations and trends are similar to those observed in our previous work (Prabhu Mirashi and Varkhede 1990) based on McRae's equation. The μ_{θ} s obtained on the basis of Bakhshiev's equation are all systematically lower than those based on the application of McRae's equation. Since single electron excitations are not expected to bring about drastic change in electron density distribution within a molecules; and also in view of lesser number of approximations and absence of undetermined parameters in Bakhshiev's expression; the present μ_{θ} s appear more reliable.

While deducing the $\bar{\nu}_{s(\text{cal})}$ values by employing eq. (1), the required vapour phase frequencies ($\bar{\nu}_v$) are frequently not available. Therefore, in view of eq. (4), the intercept of the graph of $\bar{\nu}_v - [C_3 f'(n) + C_4 f''(n)]$ vs $f(n)$ corresponding to spectral measurements in HC solvents (i.e. the value of $\bar{\nu}_0$ corresponding to $f(n) = 0 \Rightarrow \text{vacuum}$) is considered as an approximate measure of $\bar{\nu}_v$. The $\bar{\nu}_0$ values for benzene, chlorobenzene, aniline, *m*-nitroaniline and *p*-nitroaniline so obtained, viz. 38815, 39045, 35860, 30755 and 33930 cm^{-1} respectively are in favourable agreement with the reported $\bar{\nu}_v$ values, viz. 39270, 39260, 36200, 30650 and 34250 cm^{-1} respectively (Kamlet and Ungnade 1960, 1963; Millefiori 1977). Therefore, the present approximation of $\bar{\nu}_v \sim \bar{\nu}_0$ can be considered as reasonable. Further the coefficient of the function $f(D, n)$ in eq. (1), viz. $C_1 = 2\mu_{\theta}(\mu_{\theta} - \mu_{\theta} \cos \theta) / hc\alpha_0^8$ involves the angle θ between the directions of the μ_{θ} and μ_{θ}^0 vectors. However, for majority of aromatic molecules, θ is known to be quite small so that the μ_{θ} and μ_{θ}^0 vectors can be assumed to be collinear (Bakhshiev et al 1969). This assumption is consistent with the results of other workers (Grasso et al 1976, Millefiori et al 1977). The E_s values for various solute-solvent systems estimated by using eq. (4) on the assumption of $\bar{\nu}_v = \bar{\nu}_0$ and $\theta = 0$ while obtaining the required $\bar{\nu}_{s(\text{cal})}$ values are listed in the Table 1. These E_s values are also of the same order of magnitude as those obtained on the basis of McRae's equation in the previous work (Prabhu Mirashi and Varkhede 1989); and, like the μ_{θ} s the present E_s values are also generally smaller than the previous ones. The difference in the two sets of E_s -values can be attributed to those in the estimates of $\bar{\nu}_0$ values based on Bakhshiev's and McRae's equations. However, the general trends exhibited by both the sets of E_s values are quite similar. It is thus observed that the results based on Bakhshiev's expression are essentially similar and quite comparable with

Table I. Excited state dipole moments and specific solute-solvent interaction energies.

Solute (μ_e/D_e , $\sigma_0/\text{\AA}$)	μ_e/D	E_i (kJ/mol) with various types of solvents									
		H ₂ O	C ₂ H ₅ OH	CCl ₄	CHCl ₃	CH ₂ Cl ₂	(C ₂ H ₅) ₂ O	CH ₃ CN			
C ₆ H ₅ NH ₂ (1.49, 2.91)	2.90 (3.76)*	17	11	6	9	8	7	17			
C ₆ H ₅ Cl (1.88, 2.97)	3.13 (3.91)*	16	11	—	5	10	10	17			
o-ClC ₆ H ₄ NH ₂ (1.79, 3.20)	3.32 (5.26)*	12	1	6	0	2	5	1			
m-ClC ₆ H ₄ NH ₂ (2.68, 3.20)	3.64 (6.15)*	11	2	5	1	1	3	1			
p-ClC ₆ H ₄ NH ₂ (3.00, 3.18)	3.90 (8.26)*	8	4	3	3	4	5	2			
o, o'-Cl ₂ C ₆ H ₃ NH ₂ (1.34, 3.37)	3.29 —	15	4	0	6	7	1	4			
m, m'-Cl ₂ C ₆ H ₃ NH ₂ (3.00, 3.37)	5.50 (6.25)*	26	16	5	12	20	11	17			
o, p, o'-Cl ₃ C ₆ H ₂ NH ₂ (1.96, 3.37)	3.55 (4.12)*	13	6	1	7	7	1	4			

*Values based on McRae equation (Prabhu Mirashi and Varkhede 1989).

those based on McRae's expression. These results illustrate general validity of Bakhshiev's expression for studying the solute-solvent interactions from frequency shifts in electronic absorption spectra.

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