Solvent effect on electronic absorption spectra of some chlorophenols: Part II† − Application of Bakhshiev's theoretical model for elucidating excited state dipole moments and specific solute-solvent interaction energies

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A systematic and simple procedure employing Bakhshiev's expression for solvatochromic frequency shifts in electronic absorption spectra for estimating the excited state dipole moments and specific solute-solvent interaction energies is developed. The results for several chlorophenols based on this method are found to be in close agreement with those obtained by applying the more commonly used McRae's expression for solvent-induced frequency shifts. The method described herein can be employed as an alternative approach for studying solute-solvent interactions.

The excited state dipole moments and specific solute-solvent interaction energies of *o*-, *m*- and *p* chlorophenols, *o,o*- and *m,m*-dichlorophenols and *o,o,p*-trichlorophenol have been discussed in a recent paper[1]. These results were deduced by applying the McRae-Bayliss[2] theory of solvent effect on electronic spectra, which is based on the quantummechanical second order perturbation technique and the Onsager[3] reaction field model. The quantummechanical derivation of McRae's expression for solvent-induced frequency shift of a solute absorption band is known to involve a large number of unevaluated parameters necessitating several simplifying approximations. A simpler and somewhat more descriptive theoretical approach developed by Bakhshiev[4] involves lesser number of approximations and no undetermined parameters in the final expression. However, apart from a large number of papers by Bakhshiev and coworkers[5], this approach is seen to be employed only by a small number of other workers[6] in this area. It was therefore felt desirable to examine Bakhshiev's theoretical expression for elucidation of the solvent effect on electronic absorption spectra of chlorophenols. Further, a stepwise procedure for calculation of μ_e and E_s values from absorption band frequencies by applying Bakhshiev's equation for solvatochromic frequency shifts is developed. The results for various chlorophenols are compared with those based on the application of McRae's equation from the previous studies[1].

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†for Part I, see ref. 1.

Materials and Methods

The experimental methods and the chemicals used were the same as in the previous studies[1].

Bakhshiev's expression for solvatochromic frequency shift

Similar to McRae and Bayliss[2], Bakhshiev[4] also has derived expressions for solvent-induced frequency shifts $\Delta\bar{v}_a$ and $\Delta\bar{v}_f$ in absorption and fluorescence spectra respectively employing the Onsager[3]-Bottcher[7] theory of polarisation of liquid dielectrics but tackling the solute-solvent interaction in classical electrostatic manner. He has divided the intermolecular interactions in solutions into two types: (i) those associated with the collective effect of all the solvent molecules surrounding a solute molecule termed as the 'universal' interactions; and (ii) those involving individual molecules of the solute and solvent resulting in H-bonding (HB), electron donor-acceptor (EDA) complexation etc. The former interactions are nonspecific (i.e. direction independent) while the latter are specific (i.e. direction dependent) in nature. Further, the universal interactions have been subdivided into three parts, viz. (a) orientation and inductive polarisations (arising from the permanent and static induced dipoles in the solute and solvent molecules); (b) dynamic polarisation (resulting from the time-varying field due to the moments induced by light waves in the solute molecules); and (c) dispersive interactions (determined by the polarisabilities (α) and ionisation potentials (I) of the interacting solute and solvent molecules). It may be noted that, though Bakh-

shiev has recognised the possibility of specific interactions among the solute and solvent molecules; he has derived the expressions for $\Delta\bar{v}_a$ and $\Delta\bar{v}_f$ by considering the universal interactions only. The expression for $\Delta\bar{v}_a = (\bar{v}_s - \bar{v}_v)$ (where the subscripts s and v correspond to the solution and vapour phases respectively) can be put in the form:

$$\bar{v}_s = \bar{v}_v + C_1 f(D,n) + C_2 f(n) + C_3 f'(n) + C_4 f''(n) \quad (1)$$

Here

$f(n) = (2n^2+1)^2(n^2-1)/(n^2+2)^3; \; f'(n) = (n^2-1)/(2n^2+1), \; f''(n) = (n^2-1)/(n^2+2),$ and $f(D,n) =$

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

are the functions of the refractive index (n) and dielectric constant (D) of a solvent; the parameters

$$C_1 = 2\mu_g(\mu_g - \mu_e\cos\theta)/hca_0^3 \text{ and}$$
$$C_2 = (\mu_g^2 - \mu_e^2)/hca_0^3 \quad (2B)$$

are the functions of the ground and excited state dipole moments of a solute molecule (μ_g and μ_e), θ the angle between the directions of μ_g and μ_e, a_0 the cavity radius, h the Plank constant and c the speed of light; the parameter $C_3 = -e^2 f 8\pi^2 cm\bar{v}_v a_0^3$ (where e and m are charge and mass of an electron, and f the oscillator strength) is a measure of the dynamic shift; and the parameter C_4 (which is a complicated and lengthy function of the ground and excited state polarisabilities and ionisation potentials of the solute and solvent molecules) is a measure of the dispersion shift. The expression for $\Delta\bar{v}_f$ is quite similar with a slight difference in the definition of the parameter C_1, viz. $C_1 = 2\mu_g(\mu_g\cos\theta - \mu_e)/hca_0^3$.

As these expressions are quite lengthy and inconvenient for practical application, Bakhshiev has proposed combinations (i.e. sum/difference, ratio etc.) of the expressions for $\Delta\bar{v}_a$ and $\Delta\bar{v}_f$ for a solute in solvents of comparable refractive indices which, because of cancellation of certain terms, result in simplified expressions. The use of such combined expressions obviously necessitates the measurement of fluorescence spectra in addition to the absorption spectra. The fact that fluorescence is not quite a general phenomenon observable for all the solutes in variety of solvents severely restricts applicability of Bakhshiev's approach. This appears to be the main reason for Bakhshiev's expressions being applied less frequently by other workers in this area. It is shown in the subsequent discussion that Bakhshiev's expression for $\Delta\bar{v}_a$ alone can be applied for evaluation of excited state dipole moments (μ_e) and specific solute-solvent interaction energies (E_s) in a systematic and stepwise manner so as to get rid of the necessity of measurement of fluorescence spectra.

Estimation of μ_e and E_s by applying Bakhshiev's expression for $\Delta\bar{v}_a$

Step 1: Determination of parameters C_3 and C_4: When spectral measurements on a nonpolar solute (e.g. benzene for which $\mu_e = \mu_g = 0 \Rightarrow C_1 = C_2 = 0$) are carried out in an alkane solvent [e.g. cyclohexane for which $D = n^2 \rightarrow f(D,n) = 0$], Eq. (1) reduces to

$$\Delta\bar{v}_s = \Delta\bar{v}_v + C_3 f'(n) + C_4 f''(n) \quad (3)$$

Measurement of frequencies of a solute absorption transition in three alkane solvents (designated below by k, l, m) and taking pairwise differences lead to simultaneous equations of the form (4),

$$\bar{v}_k - \bar{v}_l = C_3[f'(n_k) - f'(n_l)] + C_4[f''(n_k) - f''(n_l)] \quad (4)$$

the solution of which leads to the values of C_3 and C_4. (If the vapour phase frequency $\bar{v}_v$ of the solute absorption band is known, there are only two unknowns in Eq. (3) and measurements in two solvents are adequate to evaluate C_3 and C_4).

Step 2: Estimation of μ_e: In case of spectral measurements on a polar solute in hydrocarbon (HC) solvents [again $f(D,n) = 0$], Eq. (1) can be put in the form (5)

$$\bar{v} - [C_3 f'(n) + C_4 f''(n)] = \bar{v}_v + [(\mu_g^2 - \mu_e^2)/hca_0^3]f(n) \quad (5)$$

The slope of the linear plot of the LHS of Eq. (5) versus $f(n)$ corresponding to measurements of $\bar{v}_s$ in a series of HC solvents leads to the value of μ_e with the use of μ_g from literature[8] and a_0 determined from molecular dimensions (i.e. bond lengths, bond angles and van der Waals radii)[9,10] as explained in our previous work[1].

Step 3: Estimation of E_s: As already mentioned, Bakhshiev's expression (Eq. 1) is based on the consideration of only nonspecific interactions. Therefore, as in the case of our earlier studies

based on McRae's equation, the frequency of a solute absorption band in nonhydrocarbon (nonHC) solvent is calculated [$\bar{v}_{s(calc)}$] by substituting various predetermined parameters in Eq. (1). The difference ($\Delta \bar{v}_s$) between the observed frequency [$\bar{v}_{s(obs)}$] and [$\bar{v}_{s(calc)}$] in a particular solvent will then be a measure of the specific interaction energy E_s for the particular pair of solute-solvent system (Eq. 6).

$$E_s = \Delta \bar{v}_s \, cm^{-1} = 0.011 \, \Delta \bar{v}_s \, kJ \, mol^{-1} \qquad \ldots (6)$$

The number 0.011 in Eq. (6) is the conversion factor corresponding to the product of the Avogadro number (N), Plank's constant (h) and speed of light (c).

Results and Discussion

The physical properties of the solvents used together with the values of the various polarity functions as appearing in Bakhshiev's expression (Eq. 1) as defined in Eq (2A) for all the solvents used are incorporated in Table 1 for ready reference.

It may be noted that inspite of a different method adopted by Bakhshiev, his expression for $\Delta \bar{v}_a$ is formally very similar to that of McRae. The sum of the values of the dynamic and dispersion shift parameters, viz. $C_3 = -3050 \, cm^{-1}$ and $C_4 = -330 \, cm^{-1}$ for the L_b transition is in close agreement with the value of the (A+B) parameter in McRae's equation, viz. $-3450 \, cm^{-1}$ estimated in our earlier work[11]. The plots of

$\bar{v}_s - [C_3 f'(n) + C_4 f''(n)]$ versus f(n) corresponding to measurements in HC solvents (cf. Eq. 4) exhibit good linearity (correlation coefficient = 0.9).

Excited state dipole moments (μ_e)

The μ_e values in the L_b state of the six chlorophenols studied together with those for chlorobenzene and phenol estimated on the basis of Bakhshiev's expression are presented in Table 2. Corresponding values obtained on the basis of McRae's expression as reported in our earlier work[1] are also presented in Table 2 for comparison. Numerically, the two sets of μ_e are in close agreement, with the earlier values being somewhat higher. The trends exhibited by the present μ_es are similar to those by the earlier[1] ones. e.g., all the μ_es are larger than the respective μ_gs, which is consistent with the general theory[2] of polarisation red shift, and also in agreement with the general observation, that, the contribution to the π-dipole moment due to the transfer of a lone pair electron from an OH substituent to the benzene ring is considerably larger in an excited state than that in the ground state[12]. Similarly, the μ_es for the three monochlorophenols are found to be in the order: $\mu_e(p) > \mu_e(m) > \mu_e(o)$ which parallels the sequence of the respective μ_gs. The μ_es for the di- and tri-chlorophenols, however, do not exhibit such regularities.

Specific solute-solvent interaction energies (E_s)

For calculation of E_s in terms of $\bar{v}_{s(obs)}$ and $\bar{v}_{s(calc)}$, it is essential to know the vapour phase

Table 1 – Physical properties of solvents and values of their polarizability functions appearing in Bakhshiev's expression

Solvent	μ	n	D	f(n)	f'(n)	f''(n)	f(D, n)
C_5H_{12}	0.00	1.360	1.85	0.329	0.181	0.221	0.000
C_6H_{14}	0.00	1.372	1.89	0.342	0.185	0.227	0.000
C_7H_{16}	0.00	1.385	1.92	0.358	0.189	0.234	0.000
i-C_8H_{18}	0.00	1.388	1.92	0.360	0.191	0.236	0.000
c-C_6H_{12}	0.00	1.424	2.02	0.401	0.203	0.255	0.000
H_2O	1.82	1.333	78.54	0.299	0.171	0.206	1.101
CH_3OH	1.71	1.327	32.63	0.294	0.169	0.202	1.028
C_2H_5OH	1.73	1.359	24.30	0.331	0.180	0.220	0.992
i-C_3H_7OH	1.65	1.375	18.30	0.346	0.186	0.229	0.941
CCl_4	0.00	1.458	2.24	0.441	0.214	0.273	0.032
$CHCl_3$	1.20	1.446	4.81	0.429	0.210	0.267	0.467
CH_2Cl_2	1.54	1.424	9.08	0.402	0.203	0.255	0.747
$(C_2H_5)_2O$	1.17	1.350	4.34	0.317	0.177	0.215	0.461
CH_3CN	3.80	1.342	37.50	0.308	0.174	0.211	1.046

$f(n) = (2n^2 + 1)^2 \quad (n^2 - 1)/(n^2 + 2)^3$; $\quad f'(n) = (n^2 - 1)/(2n^2 + 1)$; $\quad f''(n) = (n^2 - 1)/(n^2 + 2)$; $\quad f(D, \quad n) = (2n^2 + 1)(n^2 + 2)^2 [(D-1)/ (D+2) - (n^2 - 1)(n^2 + 2)]$; $i =$ iso-, $c =$ cyclo-, $\mu =$ dipole moment; $n =$ refractive index; $D =$ dielectric constant.

Table 2 — Excited state dipole moments (μ_e) and specific solute-solvent interaction energies (E_s) based on Bakhshiev's and McRae's equations*

Solute $(\mu_g/D, a_0/\text{Å})$	μ_e/D	E_s (kJ mol^{-1}) in various 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
1. C$_6$H$_5$Cl (1.88, 2.97)	3.13(3.91)	16(17)	11(12)	−(−)	5(4)	10(10)	10(11)	17(19)
2. C$_6$H$_5$OH (1.55, 2.93)	4.51(5.42)	21(27)	16(16)	3(1)	14(11)	19(16)	11(12)	23(24)
3. o-ClC$_6$H$_4$OH (1.34, 3.12)	3.25(4.27)	10(11)	4(6)	1(1)	6(6)	8(8)	−1(0)	7(7)
4. m-ClC$_6$H$_4$OH (2.19, 3.12)	3.48(4.32)	11(13)	6(8)	2(1)	7(6)	8(8)	0(1)	8(9)
5. p-ClC$_6$H$_4$OH (2.27, 3.10)	4.39(5.63)	22(24)	15(17)	1(−1)	18(17)	22(21)	5(6)	18(20)
6. o,o'-Cl$_2$C$_6$H$_3$OH (1.57, 3.28)	4.09(5.42)	10(11)	6(7)	0(−1)	4(3)	8(7)	0(0)	8(9)
7. m,m'-Cl$_2$C$_6$H$_3$OH (2.18, 3.28)	3.04(3.64)	9(11)	1(2)	−1(−1)	0(0)	4(5)	−2(−2)	2(3)
8. o,p,o'-Cl$_3$C$_6$H$_2$OH (1.42, 3.47)	2.53(3.21)	5(6)	−3(−3)	1(0)	3(3)	4(4)	0(0)	2(3)

*The μ_e and E_s values based on McRae's equation are given in parentheses.

frequency for obtaining $\bar{v}_{s(calc)}$ using Eq. (1); which is, however, frequently not available. Under these circumstances, in view of Eq. (4), the intercept of the linear plot of $\bar{v}_s - [C_3 f'(n) + C_4 f''(n)]$ versus $f(n)$ corresponding to the spectral measurements in alkane solvents, (i.e. the value of $\bar{v}_0$ corresponding to $f(n) = 0 \rightarrow$ vacuum) can be considered as an approximate measure of $\bar{v}_v$. This is reasonable in view of such extrapolated frequencies being found in close agreement with the reported vapour phase frequencies for some molecules, e.g. the $\bar{v}_0$ values obtained for benzene, chlorobenzene and aniline are 38815, 39045 and 35860 cm^{-1} respectively, the corresponding $\bar{v}_v$ values reported in literature[13] being 39270, 39260 and 36200 cm^{-1}. Similarly the $\bar{v}_0$ values for m- and p-nitroanilines, viz. 30755 and 33930 cm^{-1}, respectively are found in favourable agreement with the respective $\bar{v}_v$ values[14], viz. 30650 and 34250 cm^{-1}. The coefficient of the function $f(D, n)$ in Eq. (1), viz. the parameter $C_1 = 2\mu_g(\mu_g - \mu_e)\cos\theta$ involves the angle θ between the directions of the μ_g and μ_e vectors. However, for majority of aromatic molecules, Bakhshiev[4,5] has shown that the angle θ is frequently quite small so that μ_g and μ_e vectors can be taken to be collinear $(\theta = 0^0)$. this

is also consistent with the findings of other workers[2,14,15]. The E_s values for various types of solvents calculated as described in step (3) with the assumptions $\bar{v}_v = \bar{v}_0$ and $\theta = 0^0$ are presented in Table 2. The present E_s values are in good agreement with those estimated on the basis of McRae's equation in our earlier work[1]. Consequently the trends exhibited by the present E_s values are also essentially similar to those described in the earlier work[1].

It is thus observed that Bakhshiev's expression for frequency shift in absorption spectra alone can be employed for estimating μ_e and E_s values in the same way as that of McRae. The close agreement between the results based on the two approaches justifies the general correctness of Bakhshiev's expression. The application of Bakhshiev's expression as exemplified herein, therefore, offers an alternative method for estimating μ_e and E_s values for the study of solvent effect on electronic absorption spectra.

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