Solvent effects on electronic absorption spectra of some chlorophenols: Part I − Excited state dipole moments and specific solute-solvent interaction energies based on McRae's theory

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Received 2 December 1988; revised and accepted 6 February 1989

On the basis of McRae's theory [*J phys Chem*, 58 (1954) 1002] of solvent effect on electronic spectra, a systematic and step-wise procedure for estimating the excited state dipole moments (μ_e) of various chlorophenols and their specific interaction energies (E_s) with different types of solvents is described. The μ_e's estimated by employing only saturated hydrocarbon solvents are found to be more reliable than those estimated using pairs of polar solvents such as acetonitrile and diethyl ether. The E_s values are found to decrease with increase in the number of Cl atoms in the solute molecules. Interaction energies of water are generally the largest and those of carbon tetrachloride and diethyl ether are usually negligibly small. The specific interactions in the present solute-solvent systems are electrostatic in nature.

There is considerable interest in the electronic spectroscopic study of phenols and chlorophenols. The various aspects that have been studied include their dissociation constants in the ground and excited states[1−4]; quantitative estimation from absorbance at isosbestic points[5]; hydrogen bonding (HB) interaction with different kinds of solvents such as triethylamine[6], methanol[7], and dioxane[6−8]; effect of intramolecular HB on fluorescence intensity[9,10]; electron charge densities at various sites in the ground and excited states[11,12]; changes in electronic spectra due to different substituents[13−16]; their behaviour as proton donors[17], etc. These studies reveal many important features of these systems such as their behaviour as proton donors even in proton-donor solvents[7], their quenching action on fluorescence of N-heterocyclics while having no effect on fluorescence of naphthols and naphthylamines[9,10]; increase in acidity with increasing number of Cl atoms in chloro-substituted phenols (e.g. pK values of phenols, monochlorophenols and dichlorophenols being ∼ 10.0, ∼ 9.4 to 8.5 and ∼ 8.6 to 6.8 resp.)[1−4]; increase in acidity on electronic excitation (e.g. phenol: $pK \sim 10.0$, $pK^* \sim 4.0$; p-chlorophenol: $pK \sim 9.4$, $pK^* \sim 3.2$)[3,4], etc. These results clearly demonstrate the changes in electron distribution within phenol molecule due to the presence of one or more Cl atoms and also changes in electronic excitation as shown by the electronic charge density calculations[11,12]. These effects would also be related to other important properties of these molecules such as the excited state dipole moments (μ_e)

and specific solute-solvent interaction energies (E_s) on which no detailed studies have been reported.

In some of our previous studies[18,19] on the effect of solvents on electronic spectra, the μ_e's of a number of substituted benzenes including o-, m-, and p-chlorophenols were estimated with a view to testing the applicability of the concept of 'excited state group moments'[20] and also to see the correspondence, if any, between the electronic absorption bands of mono- and di-substituted benzenes. However, because of somewhat limited scope, the earlier studies were restricted to the use of only hydrocarbon solvents and also involved a number of simplifying approximations (see later under Results and Discussion). Therefore, as a part of our work on solute-solvent interactions, it was considered desirable to carry out a systematic study of o-, m- and p-monochlorophenols, oo'- and mm'-dichlorophenols and opo'-trichlorophenol. Their excited state dipole moments have been estimated with a minimum of simplifying approximations by carrying out spectral measurments in saturated hydrocarbon solvents (pentane, hexane, heptane, iso-octane and cyclohexane) and further their specific interaction energies have been estimated in common nonhydrocarbon solvents of different types such as chloroalkanes (CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$), aliphatic alcohols (methanol, ethanol and iso-propanol), water, diethyl ether and acetonitrile.

Materials and Methods

The solute systems used in the present work,

Table 1 — Physical characteristics of the solvents

Solvent	μ_s/D	n_s	D_s	$f(n_s)$	$f(D_s, n_s)$	$f(D_s, n_s)/f(n_s)$
1. $n\text{-}C_5H_{12}$	0.00	1.360	1.850	0.181	0.000	0.00
2. $n\text{-}C_6H_{14}$	0.00	1.372	1.890	0.185	0.000	0.00
3. $n\text{-}C_7H_{16}$	0.00	1.385	1.924	0.189	0.000	0.00
4. $i\text{-}C_8H_{18}$	0.00	1.388	1.920	0.191	0.000	0.00
5. $c\text{-}C_6H_{12}$	0.00	1.424	2.023	0.203	0.000	0.00
6. H_2O	1.82	1.333	78.54	0.171	0.757	4.45
7. CH_3OH	1.71	1.327	32.63	0.168	0.711	4.23
8. C_2H_5OH	1.73	1.359	24.30	0.180	0.666	3.70
9. $i\text{-}C_3H_7OH$	1.65	1.375	18.30	0.186	0.623	3.35
10. CCl_4	0.00	1.458	2.24	0.214	0.020	0.09
11. $CHCl_3$	1.20	1.446	4.81	0.210	0.293	1.39
12. CH_2Cl_2	1.54	1.424	9.08	0.203	0.474	2.33
13. $(C_2H_5)_2O$	1.17	1.350	4.34	0.177	0.312	1.76
14. CH_3CN	3.80	1.342	37.50	0.174	0.713	4.10

$$f(n_s) = (n_s^2 - 1)/(2n_s^2 + 1), \quad f(D_s, n_s) = (D_s - 1)/(D_s - 2) - (n_s^2 - 1)/(n_s^2 + 2).$$

viz., phenol and various chlorophenols mentioned above were all GC grade (Fluka) compounds. All the organic solvents (cf. Table 1) were of spectroscopic grade and the water used was triply distilled in an all-glass apparatus. Spectral measurements were performed on a Hitachi 220A double beam UV-Vis spectrophotometer. The absorption maxima for various bands (λ_{max}/nm) were determined by recording the absorption and derivative spectra, and the corresponding frequencies ($\bar{\nu}$/cm^{-1}) in various types of solvents are presented in Table 2. Since the L_a bands were masked under cut-off regions of some solvents like CCl_4 and $CHCl_3$, the studies were restricted to L_b bands which were measurable in all the solvents used.

Results and Discussion

Excited state dipole moments

As in the case of our earlier studies[18,19,21,22], the present work is also based on the well-known theory of Bayliss and McRae[23,24] according to which the absorption frequency ($\bar{\nu}_s$/cm^{-1}) of a solute dissolved in a solvent exhibiting only non-specific interactions towards the former is given by an expression of the form:

$$\bar{\nu}_s = \bar{\nu}_v + (A + B + C)f(n_s) + Ef(D_s, n_s)$$
$$+ F[f(D_s, n_s)]^2 \quad \dots (1)$$

Here $\bar{\nu}_v$ is the vapour phase frequency of the solute, $f(n_s) = (n_s^s) = (n_s^2 - 1)/(2n_s^2 + 1)$ and $f(D_s, n_s) = [(D_s - 1)/(D_s + 2)] - [(n_s^2 - 1)/(n_s^2 + 2)]$ are the functions of the refractive index (n_s) and dielectric constant (D_s) of a solvent (s); (A + B) is the dispersion term; $C = (\mu_g^2 - \mu_e^2)/hca_0^3$, $E = 2\mu_g(\mu_g - \mu_e)/hca_0^3$ and $F = 6\mu_g^2(\alpha_g - \alpha_e)/hca_0^6$ with μ, α and a_0 representing

respectively the dipole moment, polarizability and cavity radius of the solute molecule, the subscripts g and e corresponding to the ground and excited states respectively; h is the Planck's constant and c the speed of light. The contribution of the last term, generally called the solvent Stark effect term, being relatively much smaller ($\sim 10^1$ cm^{-1}) in comparison with all other terms ($\sim 10^4$ cm^{-1}), is generally ignored[23-25], so that Eq. (1) reduces to

$$\bar{\nu}_s = \bar{\nu}_v + (A + B + C)f(n_s) + Ef(D_s, n_s) \quad \dots (2)$$

In the previous work[18,19], the dispersion term (A + B) was also ignored. However, as shown later[21], this can be estimated by carrying out measurements on a nonpolar solute like benzene ($\mu_g = 0$, $\mu_e \simeq 0$) in nonpolar solvents like saturated hydrocarbons [$D_s = n_s^2 \rightarrow f(D_s, n_s) = 0$], so that Eq. (2) reduces to,

$$\bar{\nu}_s = \bar{\nu}_v + (A + B)f(n_s) \quad \dots (3)$$

The term (A + B) was determined from the slope of the linear graph of $\bar{\nu}_s$ vs $f(n_s)$. This view is consistent with that of earlier workers[26,27] who have shown that for a given type of transition, the contribution of the dispersion term (A + B) towards the solvatochromic frequency shift is nearly the same for different kinds of solvents. The present value of the dispersion term for the L_b transition in benzenoid compounds, viz., -3450 cm^{-1} is in close agreement with the range of -2720 to -3330 cm^{-1} reported by the earlier workers[26,27].

When spectral measurements on polar solutes are restricted to saturated hydrocarbon solvents, [$D_s = n_s^2$ so that $f(D_s, n_s) = 0$], Eq. (2) becomes

$$\bar{\nu}_s = \bar{\nu}_v + (A + B + C)f(n_s) \quad \dots (4)$$

Table 2 – Observed and calculated absorption band frequencies ($\bar{\nu}/cm^{-1}$) in different types of solvents

Solute	$\bar{\nu}_0^*$	$\bar{\nu}_s$	Solvents							
			C_6H_{12}	H_2O	C_2H_5OH	CCl_4	$CHCl_3$	CH_2Cl_2	$(C_2H_5)_2O$	CH_3CN
1. C_6H_5OH	39130	Obs	37105	37380	36985	37040	37250	37310	37590	37600
		A		35350	35505	36930	36240	35820	36575	35455
		B		35585	37715	36940	36330	35965	36610	35680
2. $o\text{-}ClC_6H_4OH$	37710	Obs	36455	36640	36130	36430	36540	36550	36190	36360
		A		35655	35720	36345	36040	35840	36210	35705
		B		35760	35810	36350	36070	35900	36250	35800
3. $m\text{-}ClC_6H_4OH$	37590	Obs	36420	36580	36210	36420	36500	36390	36140	36320
		A		35425	35515	36325	36930	35690	36090	35485
		B		35570	35585	36990	35950	35745	36125	35565
4. $p\text{-}ClC_6H_4OH$	36935	Obs	35320	35830	35300	35135	36070	36010	35290	35520
		A		33685	33770	35180	34515	34105	34725	33715
		B		33765	33910	35185	34575	34200	34790	33860
5. $oo'\text{-}Cl_2C_6H_3OH$	36840	Obs	35365	35280	35025	35135	35100	35210	35040	35135
		A		34290	34380	35250	34815	34550	35020	34355
		B		34390	34465	35250	34850	34615	35060	34445
6. $mm'\text{-}Cl_2C_6H_3OH$	36115	Obs	35170	35600	34840	35025	34840	35155	34870	34905
		A		34630	34670	35100	34875	34745	35015	34690
		B		34660	34700	35100	34890	34765	35025	34690
7. $opo'\text{-}Cl_3C_6H_2OH$	34690	Obs	33785	33970	33250	33750	33840	33900	33725	33725
		A		33465	33480	33725	33580	33500	33715	33480
		B'		33480	33490	33725	33585	33510	33720	33485

* $\bar{\nu}_0$: Estimated vapour phase frequency ($\bar{\nu}_v$) from the intercept of the graph $\bar{\nu}_s$ vs $[(n_s^2 - 1)/(2n_s^2 + 1)]$ in hydrocarbon solvents

A = $\bar{\nu}_s$: Calculated by using a_0 value obtained from molecular dimensions.

B = $\bar{\nu}_s$: Calculated by using a_0 value obtained from molar volume.

so that slope of the graph of $\bar{v}_s$ vs $f(n_s)$ yields the value of the term $(A+B+C)$. Combining this with the value of $(A+B)$ already determined, we get the value of $C = (\mu_g^2 - \mu_e^2)/hca_0^3$. From this, the value of μ_e was determined by using the value of μ_g from literature[28] and that of a_0, determined as outlined below.

The concept of 'cavity radius' originally appearing in the reaction field theory by Onsager[29], which is the basis of McRae's theory of solvent effect on electronic spectra[23,24], is somewhat ill-defined. However, it has generally been accepted to identify the size of the cavity with that of the solute molecule contained in it. Therefore, as suggested by earlier workers[30], the a_0-values were estimated from molecular volumes of solutes by using the respective molar volumes. In addition, the molecular volumes required for calculation of a_0-values were also calculated from molecular dimensions by employing the ellipsoidal model[18]. For this purpose, the lengths of the ellipsoid axes (say A',B' and C') corresponding to the nuclear framework of a molecule were first calculated by using the bond lengths and bond angles from the literature[31] and following the procedure as described earlier[18,21]. The space filling effect of the atoms due to their finite sizes was then accounted for by adding the van der Waals radii[32] of the terminal atoms along each direction so as to obtain the lengths of the axes corresponding to molecular ellipsoid (say A,B and C). The ellipsoid volume $V_e = \frac{4}{3}\pi \frac{A}{2}\frac{B}{2}\frac{C}{2}$ was then equated with $\frac{4}{3}\pi a_0^3$

to obtain the required cavity radius a_0. Somewhat similar method of calculating a_0 from molecular dimensions appears to be adopted by Favini and coworkers[33]. The values of cavity radii obtained in these two ways and the corresponding results (μ_e and E_s-values) are presented in Table 3.

The observed L_b band frequencies of phenol and the six chlorophenols in cyclohexane, as an illustrative hydrocarbon (HC) solvent, are presented in Table 2. The phenol band appears at ~ 37100 cm^{-1} with some vibrational structure, while those of all the chlorophenols are red-shifted with increase in intensity and loss of vibrational structure; the red-shift increases progressively with increasing number of Cl atoms in the molecule. Thus, the order of frequencies among various chlorophenols is found to be: monochlorophenols (MCP)>dichlorophenols (DCP)>trichlorophenol (TCP); o-MCP>m-MCP>p-MCP; o-MCP>oo'-DCP>opo'-

TCP and m-MCP>mm'-DCP (cf Table 2). In DCP and TCP, this band appears as a doublet with separation of ~ 10 nm between the two components. The lower frequency component, being more intense, had been used for further measurements. The band characteristics (i.e. shape, width, intensity, etc.) of the three MCP's bear close resemblance with those of phenol (Ph) and chlorobenzene (CB), which is consistent with the observation[34] that 'the electronic transitions characteristic of the monosubstituted derivatives C_6H_5X and C_6H_5Y persist in the disubstituted compounds C_6H_4XY'. With increasing the number of substituents on the phenyl nucleus, the spectra become more and more complex with loss of structural details due to overlapping bands. Therefore, the solute molecular systems in the present work are restricted to symmetrically substituted phenols, i.e., oo'-and mm'-DCP and opo'-TCP.

In the series of the five HC solvents (cf. Table 1), the L_b band positions of all the phenols studied are progressively red-shifted with increase in refractive index and dielectric constant of the solvents. The μ_e's of all the solute molecules calculated from the $(\mu_g^2 - \mu_e^2)/hca_0^3$ terms are presented in Table 3. The μ_e's deduced using a_0 values derived from molar volumes are larger than the corresponding μ_e's deduced using a_0 values derived from molecular dimensions. This is obvious because of larger magnitudes of former a_0's and dependence of the μ_e on a_0^3. Such an apparent dependence of calculated μ_e's on the choice of the cavity radius is rather strange and is due to the ill-defined nature of the concept of 'cavity radius' in the model of the reaction field theory. The μ_e's so deduced, therefore, can have only a relative significance. In spite of this limitation, the μ_e's are found to be of the correct order of magnitude, similar to those reported in literature[35,36] for other molecules and can, therefore, be considered as reasonable. Some regularities are apparent as outlined below.

All the μ_e's are larger than the corresponding μ_g's. This is consistent with the general theory of polarization red shift[24,37] and is also in agreement with the general observation that, 'when a group such as $-OH$ is substituted onto an aromatic hydrocarbon like benzene, the contribution to the π-dipole moment due to the transfer of a lone pair electron on the substituent to the aromatic ring is much larger in an excited state than that in the ground state'[35]. The μ_e's of the three MCP's vary in the sequence: $\mu_{e(p)} > \mu_{e(m)} > _{e(o)}$, which is parallel to the sequence of the respective μ_g's. The trends in the dipole moments of the DCP's and the TCP

Table 3 – Excited state dipole moments (μ_e) and specific solute-solvent interaction energies (E_s)

solute (μ_g/D)		a_o/Å	μ_e/D			E_s/kJ mole^{-1}						
			I	II	III	H_2O	C_2H_5OH	CCl_4	$CHCl_3$	CH_2Cl_2	$(C_2H_5)_2O$	CH_3CN
1. C_6H_5OH (1.55)	A	2.93	5.92	1.61	1.13	27	16	1	11	16	12	24
	B	3.26	6.90	1.49	0.94	24	14	1	10	15	11	21
2. $o\text{-}ClC_6H_4OH$ (1.34)	A	3.12	4.27	0.39	0.98	11	6	1	6	8	0	7
	B	3.45	4.91	0.05	0.85	10	4	1	5	7	-1	6
3. $m\text{-}ClC_6H_4OH$ (2.19)	A	3.12	4.32	1.57	1.98	13	8	1	6	8	1	9
	B	3.42	4.82	1.37	1.92	12	7	1	6	7	0	8
4. $p\text{-}ClC_6H_4OH$ (2.27)	A	3.10	5.63	1.52	0.43	24	17	-1	17	21	6	20
	B	3.39	6.33	1.29	-0.15	23	15	-1	16	20	6	18
5. $oo'\text{-}Cl_2C_6H_3OH$ (1.57)	A	3.28	5.42	1.04	2.69	11	7	-1	3	7	0	9
	B	3.53	5.99	0.91	2.96	10	6	-1	3	7	0	8
6. $mm'\text{-}Cl_2C_6H_3OH$ (2.18)	A	3.28	3.64	2.04	3.18	11	2	-1	0	5	-2	3
	B	3.53	3.91	2.00	3.43	10	2	-1	0	4	-2	2
7. $opo'\text{-}Cl_3C_6H_2OH$ (1.42)	A	3.47	3.21	1.42	1.12	6	-3	0	3	4	0	3
	B	3.61	3.36	1.42	1.08	5	-3	0	3	4	0	3

A : Using a_o calculated from molecular dimensions.

B : Using a_o calculated from molar volume.

I : μ_e estimated from band frequencies in hydrocarbon solvents using eq. (4).

II : μ_e estimated from band frequencies in ether and acetonitrile using eq. (5).

III : μ_e estimated from band frequencies in cyclohexane and chloroform using eq. (5).

are not so straightforward. Thus, the μ_e of oo'-DCP is larger than that of mm'-DCP while their μ_g's exhibit an opposite order and the μ_e as well as μ_g of opo'-TCP are both smaller than the respective μ_g's of the DCP's. These trends naturally reflect the changes in intramolecular charge distributions and the consequent changes in acidities of the chlorophenols on electronic excitation.

Estimation of μ_e as described above requires spectral measurements to be carried out in a series of HC solvents, which is somewhat tedius and time-consuming. Ito and coworkers[38] have proposed a quicker and short-cut method based on the arguments that if spectral measurements are carried out in two solvents (designated as 1 and 2) having nearly the same refractive indices but widely different dielectric constants, then the McRae Eq. (1){or (2)} can be shown to reduce to:

$$\Delta \bar{v}_{1,2} = [2\mu_g(\mu_g - \mu_e)/hca_0^3]\Delta f(D)_{1,2} \qquad \dots (5)$$

Here $\Delta \bar{v}_{1,2} = (\bar{v}_1 - \bar{v}_2)$ is the difference between the frequencies of a solute absorption band in the two solvents and $\Delta f(D)_{1,2} = f(D_1) - f(D_2)$ is the corresponding difference between the dielectric constant functions $f(D) = (D-1)/(D+2)$ of the two solvents. The solvents acetonitrile ($n = 1.344$, $D = 37.50$) and diethyl ether ($n = 1.356$, $D = 4.34$) are frequently considered to form such a desired pair of solvents and several workers[38-41] have reported μ_e's of a number of molecules based on the above approach using either absorption or a combination of absorption and emission spectral measurements in these solvents. Occasionally, use of other pairs of solvents, e.g., cyclohexane ($n = 1.420$, $D = 2.02$) and chloroform ($n = 1.448$ and $D = 11.90$), has also been suggested[42] though there are few reports of determination of μ_e's by employing such latter pairs of solvents.

In order to make a comparative study, the μ_e's of all the solutes used in the present work were estimated by carrying out spectral measurements in both the pairs of solvents mentioned above. The results are incorporated in Table 2 alongwith the μ_e's estimated from measurements in HC-solvents.

The μ_e's obtained in this latter manner are, however, found to be considerably different and frequently much smaller than those deduced from measurements in the HC solvents. Majority of the μ_e's obtained from the pairs of solvents' method are even smaller than the respective μ_g's and they do not exhibit any regularities or general trends within a group of similar molecules as exhibited by the μ_e values obtained by spectral measurements in the series of HC solvents. It may be re-

called that McRae's expression for frequency shift [Eq. (1)/(2)] is based on the assumption of only nonspecific interactions between the solute and solvent molecules and, therefore, the same applies to Eq. (5) which is deduced from the former. Therefore, though Eq. (5) appears to be quite satisfactory in principle, the solvents used in such measurements such as chloroform, ether and acetonitrile are appreciably polar and known to exhibit specific interactions such as H-bonding, electron donor-acceptor complex formation, etc. Such specific interactions are bound to alter the electron charge distribution in the solute molecules leading to different μ_e values which could be responsible for the above-referred discrepancies in the two sets of μ_e-values. Thus, though the use of Eq. (5) appears quite attractive due to its simplicity, it is rather difficult to get the desired pairs of solvents having comparable refractive indices and widely different dielectric constants and at the same time being nonpolar so as to exhibit no specific interactions towards the solute molecules. It can, therefore, be concluded that, to obtain reliable and consistent μ_e's from solvatochromic frequency shifts, it is essential to restrict the spectral measurements to saturated hydrocarbon sovlents only.

Specific solute-solvent interaction energies (E_s)

When spectral measurements are performed in non-hydrocarbon (non-HC) solvents, for which $D_s \neq n_s^2$, none of the terms in Eq. (2) becomes zero. Therefore, as illustrated earlier[22], the expected frequency of a solute absorption band in a particular solvent, assuming only nonspecific interactions, was calculated ($\bar{v}_{s(cal)}$ by employing Eq. (2) and the previously known values of all the terms therein. The difference between the experimentally measured frequency ($\bar{v}_{s(obs)}$ and the $\bar{v}_{s(cal)}$ so deduced will then be a measure of the specific solute-solvent interaction energy (E_s)[39,43,44]. Thus,

$$E_s = Nhc \quad (\bar{v}_{s(obs)} - \bar{v}_{s(cal)}) = 0.011\Delta \bar{v}_s \quad kJ \quad mol^{-1} \qquad \dots (6)$$

wherein N, h and c are the Avogadro number, Planck's constant and speed of light, respectively. Frequently, the experimentally measured vapour phase frequency $\bar{v}_V$ of a solute absorption band, which is required for obtaining the $\bar{v}_{s(cal)}$ value from Eq. (2), is not available. Under these circumstances, in view of Eq. (4), the intercept of the linear graph of $\bar{v}_s$ vs $f(n_s)$ corresponding to measurements in HC solvents is used as an approximate measure of $\bar{v}_V$. This approximation is supported by the observations and conclusions of several other

workers[26,27,36,45]. Further, the parameter $E = [2\vec{\mu}_g \cdot (\vec{\mu}_g - \vec{\mu}_e)/hca_0^3]$ in Eq. (2) involves the dot product of two vector quantities. However, in view of single electron excitations responsible for the bands under study, the change in dipole moment upon electronic excitation $(\vec{\mu}_e - \vec{\mu}_g)$ is approximately collinear[24,26] with $\vec{u}_g$ so that the above mentioned dot product can be replaced by simple numerical product. With these approximations, the $\bar{\nu}_{s(cal)}$ values for all the solutes in various non-HC solvents estimated using the two a_0-values as in the case of m_e's are presented in Table 2 together with $\bar{\nu}_{s(obs)}$ values. The corresponding E_s values calculated using Eq. (6) are presented in Table 3.

The absorption bands of unsubstituted phenol (Ph) and all the chlorophenols (CP) in water exhibit blue shifts with respect to those in HC solvents. In all other non-HC solvents, Ph-bands are blue-shifted while those of CPs experience red shifts with respect to those in the HC solvents. The actual magnitude of the red or blue shift is found to depend on the number and relative positions of Cl atoms in a CP molecule. The $\bar{\nu}_{s(cal)}$ values generally differ to varying extents from the $\bar{\nu}_{s(obs)}$ values. These observations are indicative of the dependence of the type and magnitude of the specific interaction on a particular solute-solvent pair. Unlike the μ_es, the E_s values calculated using two different a_0s are found to be comparable in magnitude. Because of the approximations involved in calculating the E_s values, there will be some uncertainty ($\sim \pm 2\text{-}3$ kJ mol^{-1}) in their magnitudes. However, the various systems studied show certain regularities and general trends as noted below.

The specific interactions of water and alcohols with any solute are obviously of hydrogen bonding (HB) type due to their amphiprotic nature. The E_s of water with any solute is generally the largest among all the solvents. This is attributable to the stronger HB ability of a water molecule due to its very small size, relatively large dipole moment and very high dielectric constant. As the E_s values of the three alcohols (MeOH, EtOH and i-PrOH) are very nearly the same, only those of EtOH are illustrated in Table 3. The specific interactions of CCl$_4$, Et$_2$O and CH$_3$CN can be of electron donating (ED) or proton accepting (HA) type due to the presence of atoms with lone pair of electrons in them (Cl, O, N), while those of CHCl$_3$ and CH$_2$Cl$_2$ can be of HB and/or ED type due to the presence of dissociable protons and Cl atoms in them. Within the group of the three chloroalkanes, the E_ss increase in the order: CCl$_4 \rightarrow$ CHCl$_3 \rightarrow$ CH$_2$Cl$_2$ which is the order of increasing dipole moments

and dielectric constants of these solvents. The E_s of CCl$_4$ with any solute is negligibly small. This is ascribable to its large molecular size and spherically symmetric and diffuse electronic charge distribution resulting in effectively zero dipole moment. Its dielectric constant is also very small and $D \simeq n^2$, as in the case of the HC's so that its interaction is almost non-specific as that of the latter. The E_s of ether with all the solutes is also very small which again is ascribable to its rather large molecular size and relatively small values of its dipole moment and dielectric constant. Steric hindrance of the two CH$_3$ groups in an Et$_2$O molecule would also affect the approach of any solute molecule towards the O-atom of the former. The E_s values of CH$_3$CN, except with mm'-DCP and opo'-TCP, are moderately large (comparable with those of water and CH$_2$Cl$_2$) which would also be due to rather high values of its dipole moment and dielectric constant. Such a parallelism of E_s with dipole moments and dielectric constants of solvents implies that the specific interactions in the present solute-solvent systems are electrostatic in nature.

The E_s-values for unsubstituted phenol(Ph) with water and acetonitrile are the largest and decrease with increase in the number of Cl-atoms in the CP molecule. Thus, $E_s(\text{Ph}) > E_s(\text{MCP}) > E_s(\text{DCP}) > E_s(\text{TCP})$. In fact, the E_s-values of mm'-DCP and opo' TCP with all solvents (except water) are negligibly small. This implies that the proton donating ability of DCP and TCP is offset by their increased electron donating ability so that in electron donor solvents, the net specific interaction is averaged to a very small value. This might be the reason for the observed decrease in E_s-values with increase in the number of Cl-atoms inspite of increase in acidity of the corresponding CP's. In the group of Ph and the three MCP's, the E_s values are found to vary as $E_s(\text{Ph}) \simeq E_s(p\text{-MCP}) > E_s(o\text{-MCP}) \simeq E_s(m\text{-MCP})$. The comparable magnitude of E_s for p-MCP with that of Ph could be due to increased contribution of dipolar structure such as

$$^-Cl \overset{+}{\longleftrightarrow} \overset{+}{O}H$$
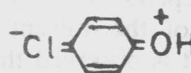
in the former similar to that in the case of p-chloroaniline[47]. The E_s-values of o-MCP and oo'-DCP are comparable and are both smaller than that for p-MCP which can be attributed to intramolecular HB in the former molecules. The difference between the E_s-values of p-and o-chlorophenols with any solvent is attributable to the strength of intramolecular HB in o-chlorophenol and the present value of ~ 12 kJ mol^{-1} (excepting CCl$_4$

and Et_2O) is comparable with the literature value[6] of ~ 10.5 kJ mol^{-1} deduced from the differences between similar interaction energies of o-and p-chlorophenols with triethylamine and dioxan. Similarly, the specific interaction energy of phenol with ethanol, dichloromethane and diethyl ether ranging over 12 to 16 kJ mol^{-1} is in good agreement with the reported[48] value of ~ 16 kJ mol^{-1} for the HB energy of phenol with dioxan.

The theoretical expression for frequency shifts [Eq. (1)] does not contain the dipole moment of a solvent molecule (μ_s) in any of its terms. An attempt to see the dependence of the specific interaction energy (E_s) on μ_s revealed that the graphs of E_s versus μ_s exhibit considerable scatter if all the solvents are included in a single plot. However, if the E_s values are plotted as a function of μ_s of the protic solvents (H_2O, MeOH, EtOH and PrOH) and similarly those of aprotic solvents (CCl_4, $CHCl_3$, CH_2Cl_2, Et_2O and CH_3CN) separately, the resulting graphs show much better linearity with clearly distinct slopes. Within such groups, the E_s values for a particular solute are found to increase approximately linearly with the solvent dipole moments μ_s. This observation is similar to the earlier[22] one and is consistent with the observation of different linear plots of frequency shifts in different families of solvents[27]. Thus, the solute-solvent interaction energies depend not only on the polarity or nonpolarity of a solvent but also on its chemical nature.

The present paper thus describes a general approach for the study of solvent effect on electronic absorption spectra with a systematic and step-wise procedure for estimating the excited state dipole moments of solute molecules and their specific interaction energies with different kinds of solvents from the measured absorption band frequencies. It shows that reasonably good and reliable excited state dipole moments can be obtained by restricting the spectral measurements to saturated hydrocarbon solvents, and further that the specific interaction energies depend not only on the polar or nonpolar nature of the solvent but also on its chemical nature. It is observed that the μ_e's of o-, m- and p-chlorophenols vary in the same order as their ground state dipole moments while the dipole moments of di- and tri-chlorophenols do not exhibit any regular trends. The specific interaction energies are found to decrease with increasing number of Cl-atoms in the molecules. Specific interaction energies of water are generally the largest while those of alcohols, acetonitrile and dichloromethane are of comparable magnitude and those of CCl_4 and diethyl ether are frequently neg-

ligibly small. The dependence of the E_s-values of a solute on the dipole moments and dielectric constants of the solvents in a particular class indicates that the specific solute-solvent interactions in the present systems are electrostatic in nature.

References

1 Biggs A J & Robinson R A, J chem Soc, (1961) 388.
2 Robinson R A, J Res Nat Bur Std, 68A (1964) 159.
3 Bartok W, Lucchesi P J & Snider N S, J Am chem Soc, 84 (1962) 1842.
4 Wehry E L & Rogers L B, J Am chem Soc, 87 (1965) 4234.
5 Kashima T & Kondo T, Chem Abstr, 61 (1964) 12638d; Chem Abstr, 65 (1966) 11556b.
6 Chiorboli P, Fortunato B & Rastelli A, Chem Abstr, 64 (1966) 15192f.
7 Namethy G & Ray A, J phys Chem, 77 (1973) 64.
8 Baba H & Suzuki S, J chem Phys, 35 (1961) 1118.
9 Mataga N & Tsuno S, Bull chem Soc Japan, 30 (1957) 711.
10 Mataga N, Bull chem Soc Japan, 31 (1958) 487.
11 Sandorfy C, Can J Chem, 31 (1953) 439.
12 Zimmerman H E & Sandel V R, J Am chem Soc, 85 (1963) 915.
13 Fedorov V P, Korets A Y, Kind V V & Yudin A L, Optics &Spectrosc, 30 (1971) 554.
14 Ansari B J & Srivastava S L, Indian J pure appl Phys, 9 (1971) 820.
15 Pandey S M & Singh S J, Curr Sci, 43 (1974) 713.
16 Varadarajan T S & Kalkar A K, Indian J pure appl Phys, 13 (1975).125.
17 Gerrard D L, Maddams W F & Tucker P J, Spectrochim Acta, 34A (1978) 1225.
18 Prabhumirashi L S & Satpute R S, Spectrochim Acta, 40A (1984) 953.
19 Prabhumirashi L S, Satpute R S & Kshirasagar R J, Indian J Phys, 58B (1984) 239.
20 Prabhumirashi L S, Speculations Sci Technol, 6 (1983) 503.
21 Prabhumirashi L S & Kunte S S, Spectrochim Acta, 42A (1986) 435.
22 Prabhumirashi L S & Kunte S S, Spectrochim Acta, 44A (1988) 213.
23 Bayliss N S & McRae E G, J phys Chem, 58 (1954) 1002.
24 McRae E G, J phys Chem, 61 (1957) 562.
25 Brealy G J & Kasha M, J Am chem Soc, 77 (1955) 4462.
26 Baur M E & Nicol M, J chem Phys, 44 (1966) 3337.
27 Nicol M, Swain J, Shun Y Y, Merin R & Chen R H H, J chem Phys, 48 (1968) 3587.
28 McClellan A L, Tables of experimental dipole moments, Vol. 2, (Rahara Enterprises, California) 1974.
29 Onsager L, J Am chem Soc, 58 (1936) 1486.
30 Rosenberg J J & Brinu I M, J chem Soc Faraday Trans 1, 72 (1976) 448; Suppan P, Spectrochim Acta, 41A (1985) 1353.
31 Sutton L E, Donahaue J & Bowen H J M, Tables of interatomic distances and configurations in molecules and ions [The Chemical Society, London; Special Publications, No. 11 (1958) & 18 (1965)].
32 Pauling L, The nature of the chemical bond, 3rd edition, (Cornell University, Ithaca, New York) 1960, Ch 7.
33 Favini G, Gamba A, Grasso D & Millefiori S, Trans Faraday Soc, 67 (1971) 3139.

34 Lutskii A E, *Russian J Chem*, 40 (1966) 695.

35 Mataga N & Kubota T, *Molecular interactions and electronic spectra* (Marcel Dekker, New York) 1970, Ch. 8.

36 Bakhshiev N G, Knyazhanskii M I, Osipov O A, Minkin V I & Saidov G V, *Russian chem Rev*, 38 (1969) 740.

37 Bayliss N S, *J chem Phys*, 18 (1950) 292.

38 Ito M, Inuzuka K & Imanishi S, *J Am chem Soc*, 82 (1960) 1317.

39 Balasubramaniyan A & Rao C N R, *Spectrochim Acta*, 18 (1962) 1337.

40 Baba H, Goodman L & Valenti P C, *J Am chem Soc*, 88 (1966) 5410.

41 Suppan P, *Chem Phys Lett*, 94 (1983) 272.

42 Moxon R H & Slifkin M A, *Spectrochim Acta*, 28A (1972) 2919.

43 Kamlet M J, Kayser E G, Eastes J W & Gilligan W H, *J Am chem Soc*, 95 (1973) 5210.

44 Tokoyama T, Taft R W & Kamlet M J, *J Am chem Soc*, 98 (1976) 3233.

45 Bhoumik B B & Chattopadhyaya S, *Spectrochim Acta*, 37A (1981) 445.

46 Millefiori S, Favini G, Millefiori A & Grasso D, *Spectrochim Acta*, 33A (1977) 21; Grasso D, Fasone S, Gandolfo C & Buemi G, *Tetrahedron*, 32 (1976) 2105.

47 Forbes W F & Leckie I R, *Can J Chem*, 36 (1958) 1371.

48 Nagakura S & Baba H, *J Am chem Soc*, 74 (1952) 5693.