Influence of apolar aprotic solvents on proton transfer equilibrium between \( m-/o- \)-chlorobenzoic acids and the carbinol base of crystal violet: A chemometric analysis

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A chemometric analysis of equilibrium results for apolar aprotic solvent effects on proton transfer between \( m-/o- \)-chlorobenzoic acids and crystal violet carbinol base using Koppel-Palm’s approach shows that the total solvent effect is contributed mainly by dispersive and dipolar/electrostatic interactions in approximately 7:4 ratio. A parallel study with \( m- \) and \( o- \)-fluorobenzoic acids but under conditions favouring acid-acid anion homoconjugation reflects the role of homoconjugated complexed acids in substantially modifying the detailed pattern of solvent effects.

Apolar aprotic solvents \( (E_T^N = 0.0–0.3) \), as compared to commonly used protic \( (E_T^N = 0.5–1.0) \) and dipolar aprotic \( (E_T^N = 0.3–0.5) \) solvents offer significant advantages for studying proton transfer processes. In these solvents complications due to specific solute–solvent interactions from solvent’s own acidity / basicity are greatly minimized and measured acidities are considerably closer to intrinsic molecular acidities measured in the gas-phase than the acidities of aqueous phase. A number of extensive studies on proton transfer between a variety of donors and acceptors in several apolar aprotic solvents have been reported, and the equilibrium/kinetic parameters are found sensitive to the solvent’s dielectric constant (\( \epsilon \)), refractive index (\( n \)), viscosity coefficient (\( \eta \)), polarity indices (Dimroth-Reichardt’s \( E_T(30) \) and Kamlet-Taft’s \( \pi^* \)) among other variables like temperature, etc. However, studies on detailed pattern of the effects of different solute–solvent interaction parameters on proton transfer processes in apolar aprotic solvents are lacking. Our earlier study on solvent effect analysis for proton transfer equilibria between \( m- \)-fluorobenzoic acid and the carbinol base of crystal violet in a set of eight apolar aprotic solvents by a number of one-, two- and three parameter models based on the parameters for polarity (\( E_T(30) \) and \( \pi^* \)), Koppel-Palm’s polarization \( Y(=\epsilon^{-1/2}\frac{\epsilon}{\epsilon+1}) \) and polarisability \( P(=\frac{n^2 D}{2 D^2}+1, n_D \) for sodium D line) and basicity (Koppel-Palm’s B and Kamlet Taft’s \( \beta \) has shown the two-parameter approach using \( Y \) and \( P \) to be the most appropriate one. The resulting regression explained 95.8% of the variance with \( P \)-term having a slightly higher significance than the \( Y \)-term. However, the strength of \( m- \)-fluorobenzoic acid as reported is not that of only monomeric acid (HA) but of its equilibrium mixture with hyperacidic homoconjugated acid-acid anion complexed acid, \( H^+(A^−…HA) \). The difficulty was averted by arguing that the acid exponent (‘\( n \)’) parameter for the reaction equilibrium, an index for acid-acid anion homoconjugation, did not vary widely among the solvents. Further, two of the solvents, viz., benzene and toluene, have non-zero Koppel-Palm’s acidity/electrophilicity parameter \( (E) \) which was not included for correlation analysis. Thus, the problem needs to be reexamined under conditions where formation of hyperacidic \( H^+(A^−…HA) \) could be reduced to insignificant proportions and in solvents with zero \( E \) value. Proton transfer equilibria for \( m- \) and \( o- \)-chlorobenzoic acids with crystal violet carbinol base were studied conforming to these conditions. Results of chemometric analysis of apolar aprotic solvent effects on the strength of the acids using Koppel-Palm’s model are critically discussed here alongwith parallel results for \( o- \)-fluorobenzoic acid and its \( m- \)-isomer studied under conditions favourable for homoconjugation in solvents including those with non-zero \( E \) parameter.

Experimental

The chemicals used were either of analytical reagent grade or highly purified by standard procedures. The solution of the carbinol base of crystal violet in an apolar aprotic solvent was prepared by basification of a \( 10^{-5} M \) aqueous solution of crystal violet with \( \sim 2 M \) NaOH followed by extraction into the apolar aprotic solvent following a standard procedure.
A set of six apolar aprotic solvents (fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, o-dichlorobenzene and ethoxybenzene) having significant variations in dielectric constant (ε) (4.22-9.93) and refractive index (n_D) (1.4684-1.6200) with Lewis basicity/nucleophilicity (B) in the range (34-77 cm⁻¹) and zero Lewis acidity/electrophilicity (Table 1) was selected.

**Procedure**

The equilibrium of chlorobenzene base of crystal violet (10⁻⁵ M) in a dry apolar aprotic solvent producing a coloured ion pair was conveniently measured at 610 nm on a 160A Shimadzu UV-vis spectrophotometer at 28.0 ± 0.1°C. The molar absorptivities (10⁴ dm³ mol⁻¹cm⁻¹) of crystal violet dye cation at 28.0 ± 0.1°C was found to be 3.10 in fluorobenzene, 3.30 in chlorobenzene, 3.76 in bromobenzene, 3.20 in iodobenzene, 3.00 in o-dichlorobenzene and 3.44 in ethoxybenzene.

**Results and discussion**

The acid (HA)- dye carbinol base (Dy) equilibria in an apolar aprotic solvent, (Eq. 1)

\[
\text{HA} + \text{Dye} -\text{OH} \rightleftharpoons \text{Dye}^+ \text{A}^- + \text{H}_2\text{O}
\]  

... (1)

can also be expressed as Eq. (2),

\[
\text{HA} + \text{D} \rightleftharpoons \text{DH}^+ \text{A}^-
\]  

... (2)

where D symbolises the carbinol base and DH⁺A⁻ the colored ion pair, water molecule formed which is hydrogen bonded to one of the species present in the system¹²⁻¹⁷. Both, the carbinol base (10⁻⁵ M) and the acid (10²⁻⁴⁴ M) concentrations being sufficiently low, the activity coefficient terms are assumed to be unity and the corrections to their reaction equilibrium constant due to self association of the reactants and acid-acid anion homo conjugation (H⁺(A⁻→HA)) are found insignificant. The equilibrium data for m-o-chlorobenzoic acid-cystal violet carbinol base reaction in the apolar aprotic solvents chosen fit the expression

\[
K = \frac{[\text{DH}^+ \text{A}^-]}{[\text{D}][\text{HA}]}
\]  

... (3)

The strength of the acids as measured by log K at 28°C in the solvents are given in Table 1 along with various solvent parameters. A glance at the values of log K for both m- and o-chlorobenzoic acids among different monohalogenobenzenes shows that iodobenzene with the lowest polarization (Y) but the highest polarisability (P) parameter gives the largest log K, signifying the important role of dispersion (measured by P)¹ and perhaps other interaction besides dipolar electrostatic interaction (measured by Y)¹. Among the different models¹⁻¹¹⁻¹³ for the analysis of solvent effects, Koppel-Palm's rigorous approach¹, according to which a complete description of all solute-solvent interactions must include both non-specific (polarization and polarisability) and specific (Lewis basicity and acidity) characteristics of the solvent, has been found very successful for various reactions¹¹⁻¹⁴ and is employed here.

\[
\log K = y + pP + bB + eE + h
\]  

... (4)

where Y and P have been defined earlier, B is the Lewis basicity/nucleophilicity solvent parameter measured by the wave number shift (Δν_O-D) of CH₃OD on transfer from gas phase to its solution in the given solvent¹. The Lewis acidity/electrophilicity parameter for a solvent is derived from solvent polarity, E_T (30) scale, corrected for non-specific dielectric effects¹. Further, y, p, b, and e are the

<table>
<thead>
<tr>
<th>Solvents</th>
<th>ε</th>
<th>n_D</th>
<th>Eₜ(30)⁺</th>
<th>Eₜ(30)⁻</th>
<th>Y</th>
<th>P</th>
<th>B (cm⁻¹)</th>
<th>log K (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorobenzene</td>
<td>5.42</td>
<td>1.4684</td>
<td>37.0</td>
<td>0.194</td>
<td>0.373</td>
<td>0.218</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5.62</td>
<td>1.5248</td>
<td>36.8</td>
<td>0.188</td>
<td>0.378</td>
<td>0.235</td>
<td>50</td>
<td>3.99</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>5.40</td>
<td>1.5568</td>
<td>36.6</td>
<td>0.182</td>
<td>0.373</td>
<td>0.244</td>
<td>51</td>
<td>4.12</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>4.49</td>
<td>1.6200</td>
<td>36.2</td>
<td>0.170</td>
<td>0.350</td>
<td>0.260</td>
<td>49</td>
<td>4.42</td>
</tr>
<tr>
<td>Ethoxybenzene</td>
<td>4.22</td>
<td>1.5074</td>
<td>36.6</td>
<td>0.182</td>
<td>0.341</td>
<td>0.229</td>
<td>77</td>
<td>3.46</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>9.93</td>
<td>1.5515</td>
<td>38.0</td>
<td>0.225</td>
<td>0.428</td>
<td>0.242</td>
<td>41</td>
<td>5.18</td>
</tr>
</tbody>
</table>

Notes:

¹Ref. (1).
²Ref. (14).
regression coefficients indicating sensitivity of log $K$ to respective solvent parameters. Since the solvents chosen in the present study has zero $E$, Eq. 4 reduces to

$$\log K = y\ Y + pP + bB + h \quad \ldots (5)$$

Statistically the most significant regressions thus obtained are

$$\log K = 12.821 Y + 20.731 P - 0.0143 B - 5.108 \quad \ldots (6)$$

for $m$-chlorobenzoic acid with $F$-level of significance for $R$ better than 1% and $t$-level significance better than 0.5% for $(y, p)$ and 2.5% for $b$; and

$$\log K = 15.925Y + 29.123P - 8.775 \quad \ldots (7)$$

for $o$-chlorobenzoic acid with $F$-level of significance better than 5% for $R$ and $t$-level significance better than 2.5% for $y$ and 5% for $p$.

The correlations explain 99.6% and 96.6% of the variance for $m$- and $o$-chlorobenzoic acids respectively. The relative order of significance of the terms in log $K$ as found by stepwise regression is $Y > P > B$ explaining 69.9%, 22.6% and 7.1% of the variance for $m$-chlorobenzoic acid, and $Y > P$ explaining 69.1% and 27.5% of the variance for $o$-chlorobenzoic acid. The percent character of solvent polarization ($\%y$) and polarisability ($\%p$) are respectively 38.20% and 61.76% for the $m$-isomer (besides 0.04% for $\%b$), and 35.40% and 64.60% for the $o$-isomer. Further, calculated values log $K$ according to Eq. 5 follow the same order as that for observed log $K$ among the solvents $c.f.$

$m$-isomer: $log K (obs.) = 0.982 log K (calc.) + 0.0935 \quad \ldots (8)$

$$\quad (n = 6, r^2 = 0.995)$$

$o$-isomer: $log K (obs.) = 0.978 log K (calc.) + 0.0978 \quad \ldots (9)$

$$\quad (n = 5, r^2 = 0.960)$$

There does not appear to be any need for inclusion of any other parameter for quantifying the solvent’s ‘special effects’ to log $K$ correlation of $m$-/o-chlorobenzoic acids. Thus, the pattern of apolar aprotic solvent effects on proton transfer from $m$- and $o$-chlorobenzoic acids are quite similar except that the solvent’s Lewis basicity/nucleophilicity ($B$) effect is found significant for the $m$-isomer only. The bulk of $o$-chloro group seems to be an impediment to nucleophilic solvation of the carboxylic hydrogen in the $o$-isomer. Another impediment to solvation could be occurrence of chelation to some degree in the undissociated acid. Interestingly, the sign of the basicity term in Eq. 5 for $m$-chlorobenzoic acid is negative, indicating decreasing reaction yield with increasing basicity of the solvent. Thus, more basic the solvent, greater is the nucleophilic stabilization of the carboxylic acid and more hindered would be the attack by crystal violet carbinol base.

Results of a previous study with $m$-fluorobenzoic acid and a parallel one with $o$-fluorobenzoic acid at higher concentrations (up to $5 \times 10^{-3}$ $M$) enough for significant acid-anion homoconjugation, $H^+ (A \rightleftharpoons HA)$ in a set of apolar aprotic solvents including those with non-zero Lewis acidity/electrophilicity ($E$) parameter in otherwise same conditions as described under ‘Experimental’, fit the expression as given in Eq. 10.

### Table 2—Solvent parameters ($\varepsilon$, $n_D$, $E_T^{(30)}$, $E_T^{(\infty)}$, $Y$, $P$, $B$, and $E$) and (log $K$ and $n$) of $m$- and $o$-fluorobenzoic acids for different solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\varepsilon$</th>
<th>$n_D$</th>
<th>$E_T^{(30)}$ (kcal.mol$^{-1}$)</th>
<th>$E_T^{(\infty)}$</th>
<th>$Y$</th>
<th>$P$</th>
<th>$B$  (cm$^{-1}$)</th>
<th>$E$</th>
<th>log $K$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.275</td>
<td>1.5011</td>
<td>34.3</td>
<td>0.111</td>
<td>0.230</td>
<td>0.228</td>
<td>52</td>
<td>2.0</td>
<td>1.91</td>
<td>0.76</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.380</td>
<td>1.4969</td>
<td>33.9</td>
<td>0.099</td>
<td>0.240</td>
<td>0.226</td>
<td>54</td>
<td>1.3</td>
<td>2.36</td>
<td>0.94</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>2.270</td>
<td>1.4958</td>
<td>33.1</td>
<td>0.074</td>
<td>0.229</td>
<td>0.226</td>
<td>58</td>
<td>0</td>
<td>1.82</td>
<td>0.80</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>5.420</td>
<td>1.4684</td>
<td>37.0</td>
<td>0.194</td>
<td>0.373</td>
<td>0.218</td>
<td>34</td>
<td>0</td>
<td>2.40</td>
<td>0.72</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5.620</td>
<td>1.5248</td>
<td>36.8</td>
<td>0.188</td>
<td>0.378</td>
<td>0.235</td>
<td>50</td>
<td>0</td>
<td>4.06</td>
<td>1.08</td>
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<tr>
<td>Bromobenzene</td>
<td>5.400</td>
<td>1.5568</td>
<td>36.6</td>
<td>0.182</td>
<td>0.373</td>
<td>0.244</td>
<td>51</td>
<td>0</td>
<td>3.76</td>
<td>1.10</td>
</tr>
<tr>
<td>$o$-Dichlorobenzene</td>
<td>9.930</td>
<td>1.5515</td>
<td>38.0</td>
<td>0.225</td>
<td>0.428</td>
<td>0.242</td>
<td>41</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>2.238</td>
<td>1.4602</td>
<td>32.4</td>
<td>0.052</td>
<td>0.226</td>
<td>0.215</td>
<td>31</td>
<td>0</td>
<td>1.43</td>
<td>0.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvents</th>
<th>log $K$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$-Fluorobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$o$-Fluorobenzene</td>
<td></td>
<td></td>
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</tbody>
</table>

Ref. (1).
Ref. (14).
Ref. (4).
where ‘n’, the acid exponent, differs significantly from unity and has been argued\(^2\)\(^-\)\(^7\) to be an index for acid-acid anion homoconjugation. Values of log \(K\) and ‘n’ along with those for solvent parameters are given in Table 2. Chemometric analysis of the effects of \(Y, P, B\) and \(E\) parameters on log \(K\) of \(m\)- and \(o\)-fluorobenzoic acids using Eq. 4 leads to the following regressions as statistically the most significant

\[
\log K = 5.614 Y + 60.190 P - 12.078 \quad \text{(11)} \\
(n = 8, R = 0.978)
\]

for \(m\)-fluorobenzoic acid with F-level of significance for \(R\) better than 1% and \(t\)-level of significance better that 1% for \(y\) and 0.5% for \(p\). Also,

\[
\log K = 7.564 Y + 53.967 P - 11.954 \quad \text{(12)} \\
(n = 7, R = 0.957)
\]

for \(o\)-fluorobenzoic acid with F-level of significance for \(R\) better than 1% and \(t\)-level significance better than 2.5% for \(y\) and 5% for \(p\) respectively.

Interestingly, in apolar aprotic solvents, \(o\)-fluorobenzoic acid is found weaker than the \(m\)-isomer (Table 2). This was also reported in a study on determining acid strengths in benzene using 1,3-diphenylguanidine as the reference base and bromophthalein magenta E as the indicator acid\(^{15}\) and may be ascribed to fluoro group’s considerable +\(R\) effect and insufficient bulk to cause steric inhibition of resonance and substantial chelation with carboxylic hydrogen in \(o\)-fluorobenzoic acid. Further, values of ‘n’ an index for acid-acid homoconjugation, are consistently lower for the \textit{ortho} isomer as compared to the \textit{meta} isomer (Table 2). This appears to be a result of hinderance to homoconjugation by chelation in the \textit{ortho} isomer.

A comparison on solvent effect results of \(m\)-/\(o\)-fluorobenzoic acids under conditions of significant acid-acid anion homoconjugation with those of \(m\)-/\(o\)-chlorobenzoic acids under conditions of insignificant homoconjugation clearly shows two differences: One is the absence of basicity term (B) as a significant one in log \(K\) correlation for \(m\/-\)\(o\)- fluorobenzoic acids reflecting preference of acid-anion homoconjugation over nucleophilic solvent stabilization for carboxylic proton. The second difference is the considerably larger correlation coefficients in one parameter, log \(K\) versus \(P\) regression for the fluorobenzoic acids (\(r_{K,P} = 0.904\) for \(m\)-isomer and = 0.810 for \(o\)-isomer) as compared to the chlorobenzoic acids (\(r_{K,P} = 0.460\) for \(m\)-isomer, and = 0.489 for \(o\)-isomer) although \(r_{K,Y}\) values for log \(K\) versus \(Y\) regression are virtually same for all the four acids (\(r_{K,Y} = 0.850\) for \(m\)-\(F\); 0.836 for \(o\)-\(F\); 0.836 for \(m\)-\(Cl\) and 0.831 for \(o\)-\(Cl\) benzoic acids).

This too is a reflection of acid-acid anion homoconjugation for fluorobenzoic acids. It may be noticed that the acid exponent (‘n’) values, an index for homoconjugation, show an upward trend with increasing \(P\) (Table 2).

The present study shows that apolar aprotic solvents influence acid strengths mainly through dispersion and dipolar/electrostatic interaction at approximately 7:4 ratio. However, at acid concentrations sufficient for acid-acid anion homoconjugation, there occurs a marked change in the above ratio to around 9:1.

References