Correlation analysis of reactivity in the oxidation of substituted benzyl alcohols by quinolinium fluorochromate

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Oxidation of benzyl alcohol and some ortho-, meta- and para-monosubstituted ones by quinolinium fluorochromate (QFC) in dimethyl sulphoxide (DMSO) leads to the formation of corresponding benzaldehydes. The reaction is first order each in both QFC and the alcohol. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{obs} = a + b [H^+]$. Oxidation of $\alpha,\alpha$-dideuteriobenzyl alcohol (PhCD$_2$OH) has exhibited a substantial primary kinetic isotope effect. The reaction has been studied in nineteen organic solvents and the effect of solvent analysed using Taft's and Swain's multi-parametric equations. The rates of oxidation of para- and meta-substituted benzyl alcohols have been correlated in terms of Charton's tri-parametric LDR equation, whereas the oxidation of ortho-substituted benzyl alcohols with tetra-parametric LDRS equation. The oxidation of para-substituted benzyl alcohols is more susceptible to the delocalization effect than that of ortho- and meta-substituted compounds, which display a greater dependence on the field effect. The positive value of $\eta$ suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

Quinolinium fluorochromate (QFC) has been used as a mild and selective oxidizing agent in synthetic organic chemistry. There are, however, not many reports available on the kinetic and mechanistic aspects of oxidation reactions by QFC. We have been interested in kinetics of oxidations by Cr (VI) species and recently a few reports on oxidation by QFC have already been emanated from our laboratory. We report in this paper, the kinetics of oxidation of some monosubstituted benzyl alcohols by QFC in DMSO as solvent. Attempts have been made to correlate rate and structure in this reaction.

Materials and Methods

QFC was prepared by the reported method and its purity checked by an iodometric method. The procedure used for the purification of alcohols has been described earlier. $\alpha,\alpha$-Dideuteriobenzyl alcohol* (PhCD$_2$OH) was prepared by the reported method. Its isotopic purity, as ascertained by its NMR spectra, was 94±5%. Due to non-aqueous nature of the solvent, toluene-$p$-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual methods.

Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, benzyl alcohol (5.4 g, 0.05 mol) and QFC (2.13 g, 0.01 mol) were made up to 50 cm$^3$ in DMSO and kept in the dark for ca. 15 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm$^3$) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm$^{-3}$ HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.46 g (86%) and 2.20 g (77%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. Similar experiments were performed with other alcohols also. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method was 3.92±0.15.

Kinetic measurements

The pseudo-first order conditions were attained by maintaining a large excess ($\times$ 15 or more) of the alcohol over QFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (±0.1 K), by monitoring the decrease in [QFC] spectrophotometrically at 365 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, $k_{obs}$, was evaluated from the linear ($r = 0.990 - 0.999$) plots of log [QFC] against time for up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%.

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The second order rate constant, $k_2$, was obtained from the relation: $k_2 = k_{obs} / [\text{alcohol}]$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

Results
The rates and other experimental data were obtained for all the alcohols. Since the results are similar, only representative data are reproduced here.

Stoichiometry
Oxidation of benzyl alcohols by QFC results in the oxidation of corresponding benzaldehydes. Analysis of products and the stoichiometric determinations indicate the following overall reaction (1).

$$\text{ArCH}_2\text{OH} + \text{CrO}_2\text{FOQH} \rightarrow \text{ArCHO} + \text{(HO)}_2\text{CrFOQH}$$

QFC undergoes a two-electron change. This is in accord with the earlier observations with other halochromes\textsuperscript{1,12} as well as with QFC\textsuperscript{7}.

Rate laws
The reactions were found to be first order with respect to QFC. The individual kinetic runs were strictly first order to QFC. Further, the pseudo-first order rate constant, $k_{obs}$, was independent of initial concentration of QFC. The reaction rate increases linearly with an increase in the concentration of benzyl alcohols (Table 1).

Induced polymerisation of acrylonitrile
The oxidation of benzyl alcohol by QFC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, an addition of a radical scavenger, acrylonitrile, had no effect on the rate (Table 1).

Effect of acidity
The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence taking the form: $k_{obs} = a + b[H^+]$ (Table 1). The values for $a$ and $b$ for benzyl alcohol are $2.65\pm0.06 \times 10^{-3}$ s\textsuperscript{-1} and $4.66\pm0.10 \times 10^{-3}$ mol\textsuperscript{-1} dm\textsuperscript{3} s\textsuperscript{-1} respectively ($r^2 = 0.9990$).

Effect of substituents
The rates of oxidation of monosubstituted benzyl alcohols by QFC were determined at different temperatures and the activation parameters were calculated (Table 2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$10^4 [\text{QFC}]$ & $[\text{Alcohol}]$ & $[\text{TsOH}]$ & $10^4 k_{obs}$ \\
(mol dm\textsuperscript{-3}) & (mol dm\textsuperscript{-3}) & (mol dm\textsuperscript{-3}) & (s\textsuperscript{-1}) \\
\hline
1.0 & 0.10 & 0.0 & 2.68 \\
1.0 & 0.20 & 0.0 & 5.26 \\
1.0 & 0.40 & 0.0 & 10.6 \\
1.0 & 0.60 & 0.0 & 15.7 \\
1.0 & 0.80 & 0.0 & 21.1 \\
1.0 & 1.00 & 0.0 & 26.4 \\
2.0 & 0.40 & 0.0 & 11.3 \\
4.0 & 0.40 & 0.0 & 10.2 \\
6.0 & 0.40 & 0.0 & 10.8 \\
8.0 & 0.40 & 0.0 & 10.2 \\
1.0 & 1.00 & 0.1 & 31.1 \\
1.0 & 1.00 & 0.2 & 36.2 \\
1.0 & 1.00 & 0.4 & 45.5 \\
1.0 & 1.00 & 0.6 & 53.1 \\
1.0 & 0.00 & 0.8 & 64.4 \\
1.0 & 1.00 & 1.0 & 73.3 \\
1.0 & 0.40 & 0.0 & 10.5* \\
\hline
\end{tabular}
\caption{Rate constants for the oxidation of benzyl alcohol by QFC at 308 K.}
\begin{flushright}
\text{*Contained 0.001 mol dm\textsuperscript{-3} acrylonitrile}
\end{flushright}
\end{table}

Kinetic isotope effect
To ascertain the importance of the cleavage of the $\alpha$--C--H bond in the rate-determining step, oxidation of $\alpha$-$\alpha$-dideuteriobenzyl alcohol was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2).

Effect of solvents
The oxidation of benzyl alcohol was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. Kinetics were similar in all the solvents. The values of $k_2$ are recorded in Table 3.

Discussion
The correlation between activation enthalpies and entropies of oxidation of the thirty three alcohols is not very good ($r^2 = 0.9451$). The value of the isokinetic temperature is $592\pm24$ K. However, according to Exner\textsuperscript{13}, an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log $k_2$ at 288 K and 318 K was linear ($r^2 = 0.9984$). The value of isokinetic temperature evaluated from the Exner's plot is $655\pm28$ K. The linear isokinetic corre-
The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and another acid-dependent. The acid-catalysis may well be attributed to a protonation of QFC as (Eq. 2) to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PFC.

The rate constants, $k_2$, in seventeen solvents (CS$_2$ was not considered as the complete range of solvent parameters was not available) were correlated in terms of linear solvation energy relationship (Eq. 3) of Kamlet et al.\textsuperscript{15}.

$$
\log k_2 = A_0 + \pi^* + b\beta + \alpha\alpha
$$

In Eq. (3) $\pi^*$ represents the solvent polarity, $\beta$ the hydrogen bond acceptor basicities and $\alpha$ is the hydro-
The data on the solvent effect were also analysed in terms of Swain's equation\(^7\) of cation- and anion-solvating concept of the solvents (Eq. 8).

\[
\log k_2 = a A + b B + C \tag{8}
\]

Here A represents the anion-solvating power of the solvent and B the cation-solvating power of the solvent. C is the intercept term. \((A + B)\) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (8), separately with A and B and with \((A + B)\).

\[
\log k_2 = 0.75 \pm 0.04 A + 1.66 \pm 0.03 B - 4.60 \quad \ldots (9)
\]

\[
R^2 = 0.9945; \ sd = 0.03; \ n = 19; \ \psi = 0.06
\]

\[
\log k_2 = 0.51 \pm 0.55 A - 3.46 \quad \ldots (10)
\]

\[
\rho^2 = 0.0486; \ sd = 0.44; \ n = 19; \ \psi = 0.91
\]

\[
\log k_2 = 1.60 \pm 0.14 B - 4.36 \quad \ldots (11)
\]

\[
\rho^2 = 0.8918; \ sd = 0.15; \ n = 19; \ \psi = 0.24
\]

\[
\log k_2 = 1.36 \pm 0.12 (A + B) - 4.57 \quad \ldots (12)
\]

\[
\rho^2 = 0.8836; \ sd = 0.15; \ n = 19; \ \psi = 0.25
\]

The rates of oxidation of benzyl alcohol in different solvents show an excellent correlation in Swain's equation (9) with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for ca. 89% of the data. The solvent polarity, represented by \((A + B)\), also accounted for ca. 88% of the data. In view of the fact that the solvent polarity is able to account for ca. 88% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log (rate) against the inverse of the relative permittivity is not linear \((\rho^2 = 0.5388; \ sd = 0.31, \ \psi = 0.53)\).

**Correlation analysis of reactivity**

The effect of structure on reactivity has long been correlated in terms of the Hammett equation\(^6\) or with dual substituent-parameter equations\(^9,20\). In the late 1980s, Charton\(^3\) introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization. This

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### Table 3—Solvent effect on the oxidation of benzyl alcohol by QFC at 308 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(10^4 k_2) (dm(^3) mol(^{-1}) s(^{-1}))</th>
<th>Solvent</th>
<th>(10^4 k_2) (dm(^3) mol(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>10.7</td>
<td>Toluene</td>
<td>2.34</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>9.33</td>
<td>Acetophenone</td>
<td>12.0</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8.71</td>
<td>Tetrahydrofuran</td>
<td>4.07</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>26.4</td>
<td>t-Butyl alcohol</td>
<td>3.80</td>
</tr>
<tr>
<td>Acetone</td>
<td>8.13</td>
<td>1,4-Dioxane</td>
<td>4.35</td>
</tr>
<tr>
<td>DMF</td>
<td>14.8</td>
<td>Dimethoxyethane</td>
<td>2.57</td>
</tr>
<tr>
<td>Butanone</td>
<td>5.89</td>
<td>Ethyl acetate</td>
<td>3.55</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>11.5</td>
<td>Carbon disulfide</td>
<td>1.35</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.95</td>
<td>Acetic acid</td>
<td>1.91</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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The gen bond donor acidity, \(A_0\), is the intercept term. It may be mentioned here that out of the 18 solvents, 13 has a value of zero for \(\alpha\). The results of correlation analyses terms of Eq. (3), a biparametric equation involving \(\pi^*\) and \(\beta\), and separately with \(\pi^*\) and \(\beta\) are given below (Eqs 4-7).

\[
\log k_2 = -4.39 + 1.60 (\pm 0.13) \pi^* + 0.16 (\pm 0.11) \beta + 0.03 (\pm 0.11) \alpha \quad \ldots (4)
\]

\[
R^2 = 0.8397; \ sd = 0.19; \ n = 18; \ \psi = 0.32
\]

\[
\log k_2 = -4.40 + 1.61 (\pm 0.19) \pi^* + 0.15 (\pm 0.16) \beta \quad \ldots (5)
\]

\[
R^2 = 0.8394; \ sd = 0.19; \ n = 18; \ \psi = 0.31
\]

\[
\log k_2 = -4.37 + 1.65 (\pm 0.19) \pi^* \quad \ldots (6)
\]

\[
\rho^2 = 0.8300; \ sd = 0.18; \ n = 18; \ \psi = 0.31
\]

\[
\log k_2 = -3.45 + 0.45 (\pm 0.34) \beta \quad \ldots (7)
\]

\[
\rho^2 = 0.0862; \ sd = 0.43; \ n = 18; \ \psi = 0.86
\]

Here \(n\) is the number of data points and \(\psi\) is Exner's statistical parameter\(^{16}\).

Kamlet\(^{15}\)'s triparametric equation explains ca. 84% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. Eq. 4). The major contribution is of solvent polarity. It alone accounted for ca. 83% of the data. Both \(\beta\) and \(\alpha\) play relatively minor roles.
difference reflected in a different sensitivity to the electron demand for the phenomenon being studied. It has an advantage of not requiring a choice of parameters as the same three substituents constants are reported to cover the range of electrical effects of the substituents. In this work we have applied the LDR Eq. (13) to the rate constants, $k_2$.

$$\log k_2 = L \sigma_i + D \sigma_d + R \sigma_e + h \quad \cdots \quad (13)$$

Here, $\sigma_i$ is a localized (field and/or inductive) effect parameter, $\sigma_d$ is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and $\sigma_e$ represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by Eq. (14).

$$\sigma_D = \eta \sigma_e + \sigma_d \quad \cdots \quad (14)$$

Here $\eta$ represents the electronic demand of the reaction site and is given by $\eta = R/D$, and $\sigma_D$ represents the delocalized electrical parameter of the diparametric LD equation.

For ortho-substituted compounds, it is necessary to account for the possibility of steric effects and Charton21, therefore, modified the LDR equation to generate the LDRS Eq. (15).

$$\log k_2 = L \sigma_i + D \sigma_d + R \sigma_e + S \psi + h \quad \cdots \quad (15)$$

where $\psi$ is the well known Charton's steric parameter based on Van der Waals radii22.

The rates of oxidation of ortho-, meta- and para-substituted benzyl alcohols show an excellent correlation in terms of the LDR/LDRS equations (Table 4). We have used the standard deviation (sd), the coefficient of multiple determination ($R^2$), and Exner's16 parameter, $\psi$ as the measures of goodness of fit.

The comparison of the L and D values for the substituted benzyl alcohols showed that the oxidation of para-substituted benzyl alcohols is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of ortho- and meta-substituted compounds exhibited a greater dependence on the field effect. In all the cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, $L$, $D$, and $R$, are negative indicating an electron-deficient carbon centre in the activated complex for the rate-determining step. The positive value of $\eta$ adds a negative increment to $\sigma_d$, reflecting the electron-donating power of the substituent and its capacity to stabilise a cationic species. The positive value of $S$ indicates that the reaction is subject to steric acceleration by an ortho-substituent.

To test the significance of localized, delocalized and steric effects in the ortho-substituted benzyl alcohols, multiple regression analyses were carried out with (i) $\sigma_i$, $\sigma_d$ and $\sigma_e$ (ii) $\sigma_D$, $\sigma_e$ and $\psi$ and (iii) $\sigma_i$, $\sigma_e$.
and v. The absence of significant correlations showed that all the four substituent constants are significant.

\[
\log k_2 = -1.42 \pm 0.37 \sigma_1 - 1.51 \pm 0.29 \sigma_2 - 3.09 \\n(\pm 1.68) \sigma_3 - 2.23 \\
\ldots \quad (16)
\]

\[R^2 = 0.8422; \quad \text{sd} = 0.26; \quad n = 12\]

\[
\log k_2 = -1.59 \pm 0.42 \sigma_1 - 1.61 \pm 2.59 \sigma_2 + 0.74 \\
(\pm 0.48) \nu - 3.08 \\
\ldots \quad (17)
\]

\[R^2 = 0.6715; \quad \text{sd} = 0.37; \quad n = 12\]

\[
\log k_2 = -1.85 \pm 0.61 \sigma_1 - 0.34 \pm 2.94 \sigma_2 + 1.13 \\
(\pm 0.55) \nu - 2.30 \\
\ldots \quad (18)
\]

\[R^2 = 0.5778; \quad \text{sd} = 0.42; \quad n = 12\]

Similarly in the cases of oxidation of para- and meta-substituted benzyl alcohols, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituents constants for the three series.

The percent contribution\textsuperscript{22} of the delocalized effect, \(P_D\), is given by Eq. (19).

\[
P_D = \left( \frac{|D| \times 100}{|L| + |D|} \right) \\
\ldots \quad (19)
\]

Similarly, the percent contribution of the steric parameter\textsuperscript{22} to the total effect of the substituent, \(P_S\), was determined by using Eq. (20).

\[
P_S = \left( \frac{|S| \times 100}{|L| + |D| + |S|} \right) \\
\ldots \quad (20)
\]

The values of \(P_D\) and \(P_S\) are also recorded in Table 4. The value of \(P_D\) for the oxidation of para-substituted benzyl alcohols is ca. 52%, whereas the corresponding values for the meta- and ortho-substituted alcohols are ca. 41 and 46% respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzyl alcohols. The less pronounced resonance effect from the ortho-position than from the para-position may be due to the twisting away of the alcoholic group from the plane of the benzene ring. The magnitude of the \(P_S\) value shows that the steric effect is significant in this reaction.

The positive value of \(S\) showed a steric acceleration of the reaction. This may be explained on the basis of high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore results.

**Mechanism**

A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate. The presence of a substantial kinetic isotope effect confirms the cleavage of an \(\alpha\)-C-H bond in the rate-determining step. The negative values of the localization and delocalization electrical effects i.e. of \(L\), \(D\) and \(R\) points to an electron-deficient reaction centre in the rate-determining step. It is further supported by the positive value of \(\beta\), which indicates that the substituent is better able to stabilise a cationic or electron-deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents. The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickle\textsuperscript{23} have shown that a dependence of kinetic isotope effect on temperature can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one. The data for protio- and deuterio-benzyl alcohols, fitted to the familiar expression: \(k_H/k_D = \frac{A_H}{A_D} (\Delta H^*/RT)\)\textsuperscript{24,25} show a direct correspondence with the properties of a symmetrical transition state in which activation energy difference for protio and deuterio compounds is equal to the difference in the zero-point energy for the respective \(C\)-H and \(C\)-D bonds (\(\approx 4.5\) kJ mol\(^{-1}\)) and the entropies of activation of the respective reactions are almost equal. Similar phenomena were observed earlier in the oxidation of benzhydrol by PCC\textsuperscript{21} and of alcohols by QFC\textsuperscript{22}. Bordwell\textsuperscript{26} has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic bimolecular process. It is well-established that intrinsically concerted sigmatropic reactions, characterised by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer\textsuperscript{27}. Littler\textsuperscript{28} has also shown that a cyclic
hydride transfer, in the oxidation of alcohols by 
Cr(VI), involves six electrons and, being a 
Huckel-type system, is an allowed process. Thus, a 
transition state having a planar, cyclic and symmetrical 
structure can be envisaged for the decomposition 
of the ester intermediate. Hence, the overall mech­ 
anism is proposed to involve the formation of a chro­
mate ester in a fast pre-equilibrium step and then a 
decomposition of the ester in a subsequent slow step 
via a cyclic concerted symmetrical transition state 
leading to the product (Schemes 1 and 2).

The observed negative value of entropy of activa­
tion also supports the proposed mechanism. As the 
charge separation takes place in the transition state, 
the charged ends become highly solvated. This results 
in an immobilization of a large number of solvent 
molecules, reflected in the loss of entropy$^{29}$. 

It is of interest to compare the mode of oxidation of 
benzyl alcohols by pyridinium halochromates (PCC$^{30}$, 
PFC$^{3}$ and PBC$^{31}$) and QFC. The oxidation by PFC$^{3}$ 
exhibited Michaelis-Menten type of kinetics with re­
spect to the alcohols. However, the oxidation by other 
halochromates and QFC exhibited a first order de­
pendence on the alcohol. The hydrogen-ion depend­
dence, kinetic isotope effect and effect of solvents are 
similar in all the cases. In the oxidation by PFC, PBC 
and QFC excellent correlations were obtained in 
terms of Swain’s equation with the cation-solvating 
power of the solvents playing the major role.

Acknowledgement

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