incidence than landslide size. The size of established
landslides seems more closely related to the history and
current condition of the landslide system than to
external stimuli.

Slope aspect and the depth of regolith, rather than
ture soil, rank with a number of more obvious
significant differences between rockfall-like and slump-
like landslide types. ‘Rockfalls’ are found on higher,
cooler, roadcuts with less obvious, apparent rock dip
towards the road-bed. Slumps are found on warmer,
warmer sites with steeper apparent dips, lower roadcuts
and greater depths of beneath-topsoil regolith.

1. Bansal, R. C. and Mathur, H. N., Soil Conservation Digest, 1976,
   4, 36.
2. Valdiya, K. S., Environmental Geology: The Indian Context, Tata
3. Bhandari, R. K. and Gupta, C., in Environmental Regeneration in
   the Himalaya (ed. Singh, J. S.), Central Himalaya Environment
   1989, 9, 25.
6. Valdiya, K. S., Geology of Kumaun Lesser Himalaya, Wadia
7. Haigh, M. J., Rawat, J. S. and Bartarya, S. K., Catena, 1988, 15,
   539.
9. IAEG, International Association of Engineering Geology Bulletin
10. Norcliffe, G. B., Inferential Statistics for Geographers, Hutchinson,
13. Cooke, R. U. and Doornkamp, J. C., Geomorphology in
    Environmental Management (2nd edn), Clarendon Press, Oxford,
    1990, pp. 120–121.
14. Croner, M. J., Landslides: Causes, Consequences and Environment,
15. Sridle, R. C., Pearce, A. J. and O’Loughlin, C. L., Hillslope
    Stability and Landuse, American Geophysical Union: Water Re-
    sources Monograph 11, Washington, DC, 1985, p. 140
16. Zaruba, Q. and Mencel, V., Landslides and their Control (2nd edn),
    Academia, Prague, 1982, p. 324.
    1000.

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RESEARCH COMMUNICATIONS

Estimation of excited state dipole moment of substituted coumarins

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Coumarins are important constituents of natural
products. Many of them exhibit fluorescence. We report
UV-absorption and fluorescence emission spectra of 4-
methy1-5,7-dihydroxycoumarin, 4-methyl-5-ethoxy-7-
methyloxyouarin and 4-methyl-7,8-dihydroxycoumarin in
different polar and nonpolar organic solvents. We
estimated the change in dipole moment upon excitation
using solvatochromic data, and interpret the increase in
excited state dipole moment in terms of the possible
resonance structure. This method cannot be used when
substituent groups are present at two consecutive
positions because of the specific interaction and
hindrance occurring in such cases.

The widespread occurrence of coumarin derivatives in
nature and their variety of applications, viz. as
fluorescent indicators1, 2, fluorescent whiteners in
detergent products3, sunburn preventives4, as laser
dyes5–7, for the estimation of enzymes8, for studying
biological systems9 and also in other interesting areas10, have given impetus to the study of their
fluorescence characteristics.

Coumarin molecule as such in aqueous solution is
non-fluorescent but it becomes moderately/highly
fluorescent on substituting various groups at different
positions in it. In general, fluorescence characteristics of
a fluorophore depend upon the position and the nature
of the substituent as well as the nature of the
surrounding medium11, 12. The magnitude of spectral
changes due to substituents/solvents is linked to the
structural aspects of the molecule and serve as useful
tool for its detail investigations. Up to some extent it is
easy to study the spectral characteristics of single
substituted coumarin, however, when substituents are
present at two or more positions, the study becomes
quite complicated. In the present work we have
investigated the effect of solvent and substituent on
absorption and fluorescence spectra of the coumarin
derivatives, and solvatochromic data so obtained is
used in estimating their excited state dipole moments.

The coumarins used were prepared by standard
methods\textsuperscript{1,3} and checked for purity by m.p. and TLC according to the literature values. The absorption spectra were recorded using a UV-vis recording spectrophotometer (Shimadzu-260) and the fluorescence spectra using a spectrophotofluorometer (Aminco-Bowman). In order to avoid aggregation and to minimize inner filter effect, the concentration of the solute was kept quite low ~ \(10^{-6}\) M. The recorded absorption wavelengths are accurate within ± 1 nm and fluorescence wavelengths within ± 2 nm.

Solvants are found useful to determine the values of quantum yield, polarization, radiative lifetime, excited state dipole moment and solute-solvent interactions\textsuperscript{14,15}. In the present study we have estimated the change in dipole moment of 4-methyl-5,7-dioxoxygenarain (I), 4-methyl-5-ethoxy-7-methoxycoumarin (II) and 4-methyl-7,8-dioxyxygenarin (III) upon excitation, using solvatochromic data. To calculate the excited state dipole moment, the following mathematical equations were used\textsuperscript{14}.

\[
(\tilde{\nu}_a - \tilde{\nu}_f) = S_1 F_1(D,n) + C_1 \quad (1)
\]

according to Bakshi, and

\[
1/2(\tilde{\nu}_a + \tilde{\nu}_f) = S_2 F_2(D,n) + C_2 \quad (2)
\]

Table 1. Solvatochromic shift data of 4-methyl-5,7-dioxoxygenarin (I), 4-methyl-5-ethoxy-7-methoxycoumarin (II) and of 4-methyl-7,8-dioxoxygenarin (III) along with the calculated values of \(F_1(D,n)\) and \(F_2(D,n)\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\tilde{\nu}_a) (\times 10^2) cm(^{-1})</th>
<th>(\tilde{\nu}_f) (\times 10^2) cm(^{-1})</th>
<th>(\tilde{\nu}_a - \tilde{\nu}_f) (\times 10^2) cm(^{-1})</th>
<th>(1/2(\tilde{\nu}_a + \tilde{\nu}_f)) (\times 10^2) cm(^{-1})</th>
<th>(F_1(D,n))</th>
<th>(F_2(D,n))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>313</td>
<td>256</td>
<td>57</td>
<td>285</td>
<td>0.005</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>314</td>
<td>260</td>
<td>54</td>
<td>287</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>313</td>
<td>240</td>
<td>72</td>
<td>277</td>
<td>0.65</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>314</td>
<td>244</td>
<td>70</td>
<td>279</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma)-Butanol</td>
<td>312</td>
<td>245</td>
<td>67</td>
<td>279</td>
<td>0.74</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>312</td>
<td>245</td>
<td>67</td>
<td>279</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\pi)-Propanol</td>
<td>315</td>
<td>220</td>
<td>95</td>
<td>208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>313</td>
<td>220</td>
<td>93</td>
<td>267</td>
<td>0.81</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>244</td>
<td>66</td>
<td>277</td>
<td>0.81</td>
<td>0.65</td>
</tr>
<tr>
<td>Water</td>
<td>310</td>
<td>229</td>
<td>87</td>
<td>270</td>
<td>0.91</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>312</td>
<td>228</td>
<td>84</td>
<td>270</td>
<td>0.91</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>198</td>
<td>116</td>
<td>256</td>
<td>0.91</td>
<td>0.68</td>
</tr>
<tr>
<td>Formamide</td>
<td>313</td>
<td>239</td>
<td>72</td>
<td>275</td>
<td>0.89</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>251</td>
<td>64</td>
<td>263</td>
<td>0.89</td>
<td>0.75</td>
</tr>
<tr>
<td>Dioxane</td>
<td>312</td>
<td>251</td>
<td>64</td>
<td>263</td>
<td>0.89</td>
<td>0.75</td>
</tr>
<tr>
<td>Chloroform</td>
<td>314</td>
<td>256</td>
<td>58</td>
<td>285</td>
<td>0.37</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>229</td>
<td>84</td>
<td>271</td>
<td>0.37</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Data given in the first line are for 4-methyl-5,7-dioxoxygenarin, in the second line for 4-methyl-5-ethoxy-7-methoxycoumarin and in the third line for 4-methyl-7,8-dioxoxygenarin.
From equations (3) and (4) it follows that the ratio of the excited state and ground state dipole moments is given by

$$\frac{\mu^*}{\mu} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \tag{5}$$

Table 1 summarizes the band shift data for I, II and III coumarins respectively, along with the calculated values of various solvents. For coumarins I and II, graphs for \((\bar{\nu}_a - \bar{\nu}_e)\) versus \(F_1(D,n)\) and \(1/2(\bar{\nu}_e + \bar{\nu}_g)\) versus \(F_2(D,n)\) give good linear plots within the limit of experimental errors (Figures 1 and 2). But for coumarin III graphs are not linear (Figure 3). Taking the slopes of the graphs given in Figures 1 and 2 along with the equation (5) it is obtained that: For 4-methyl-5, 7-diethoxy-coumarin (I) \(\mu^* = 4.3 \mu\) and for 4-methyl-5-ethoxy-7-methoxycoumarin (II) \(\mu^* = 5.0 \mu\).

Small scattering in the points (Figures 1 and 2) occurs due to approximations made in the present solvatochromic theories. The increase in the values of dipole moment for I and II coumarins upon excitation may happen due to their possible resonance structures (Figures 4 and 5), which suggests higher polarity in the excited state. Further, replacing a ethoxy group at position 7 of 4-methyl-5, 7-diethoxy-coumarin by a methoxy group, an increase in the \(\mu^*\) value is obtained. It suggests that the excited state of 4-methyl-5-ethoxy-7-methoxycoumarin in more polar than 4-methyl-5,7-diethoxy-coumarin. It is also seen that the calculated value of \(\mu^*\) for 4-methyl-5-ethoxy-7-methoxycoumarin.
xycoumarin is more than the value of 4-methyl-7-methoxy-xycoumarin\textsuperscript{15}.

Let us consider the data and graphs of coumarin III, it is clear that the wavelength shift plots are not straight lines (Figure 3). Therefore we could not calculate the change in dipole moment of 4-methyl-7, 8-diehtoxy-xycoumarin with the help of present solvatochromic methods. It appears as solute–solvent interaction and steric hindrance effects take place due to the substituents present at two adjacent positions. We had also observed the same problem in determining the excited state dipole moment of 4-methyl-6, 7-dimethoxy-xycoumarin in an earlier work\textsuperscript{15}.

Further, solvatochromic data can be used to identify the spectra, viz. $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc. It is noticed from the Table 1 that, with increase in the polarity of the solvent, the fluorescence emission peak undergoes a bathochromic shift, confirming a $\pi \rightarrow \pi^*$ transition. The shift of the fluorescence wavelengths towards longer wavelengths could be caused if the excited state charge distribution in the solute is markedly different from the ground state charge distribution and is such as to give rise to a stronger interaction with polar solvents in the excited state.

\textsuperscript{1} Chern., R. E., \textit{Anal. Lett.}, 1968, \textbf{1}, 423.

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Monsoon effect on isotopic composition of atmospheric carbon dioxide

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The Indian subcontinent and the adjoining seas (the Arabian Sea and the Bay of Bengal) experience seasonal reversal of wind systems and associated weather changes resulting from summer and winter monsoons. The monsoons are associated with significant changes in the oceanic and continental biosphere and are therefore expected to have considerable effect on the content and isotopic composition of atmospheric carbon dioxide. We have attempted to measure this effect in ground-level carbon dioxide samples collected in the city of Ahmedabad during 1990. The CO\textsubscript{2} content is in general agreement with values obtained elsewhere. The $\delta^{13}$C value of air CO\textsubscript{2} shows a minor effect due to the increase of productivity on land during the southwest monsoon season. The $\delta^{18}$O value of CO\textsubscript{2} is slightly enriched compared to northern high-latitude values owing to the equilibration of CO\textsubscript{2} with enriched leaf water expected in a tropical country like India.

The southwest monsoon brings a dramatic change in the climatic regime operating on the Indian subcontinent.