The effects of solvents on chemical phenomena is complex because there are various solute-solvent interaction mechanisms. Solvatochromism refers to the effects of solvents on the spectra of probes. The study of this phenomenon sheds light on the relative importance of the solvation mechanisms. Solvation in pure solvents is quantitatively analyzed in terms of a multi-parameter equation. In binary solvent mixtures, solvation is analyzed by considering the organic solvent, S, water, W, and a 1:1 hydrogen bonded species (S-W).

The applications of solvatochromism to understand distinct chemical phenomena, reactivity and swelling of cellulose, is briefly discussed.

Keywords: solvation; solvatochromism; solute-solvent interactions.

Table 1. Correlations between log (observed rate constants, k_{obs}) for the spontaneous decomposition of 6-Nitro-3-carboxyzoxazol in different solvents with their properties.a,b

<table>
<thead>
<tr>
<th>Solvent property</th>
<th>Coefficients of the correlations between log k_{obs} and solvent property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f_{e} = 2(e_{r} - 1) / (2e_{r} + 1)</td>
</tr>
<tr>
<td>E_{c}(30)</td>
<td>0.7864</td>
</tr>
<tr>
<td>E_{c}(30) + f_{e}</td>
<td>0.7791</td>
</tr>
<tr>
<td>E_{c}(30) + E_{b}</td>
<td>0.5167</td>
</tr>
<tr>
<td>E_{c}(30) + f_{e} + E_{b}</td>
<td>0.8928</td>
</tr>
<tr>
<td>E_{c}(30) + f_{e} + E_{b} + E_{r}</td>
<td>0.8916</td>
</tr>
<tr>
<td>E_{c}(30) + f_{e} + E_{b} + E_{r}</td>
<td>0.9485</td>
</tr>
</tbody>
</table>

a- Values of k_{obs} were taken from ref. 1; b- the solvent properties include relative permittivity, e_{r}; empirical polarity, E_{p}; acidity, E_{a}; and basicity, E_{b}; c- the correlation coefficients are (r) and (r^2) for linear, and multiple regression analysis, respectively.

(ii) Can the relative importance of each solute-solvent interaction be identified and quantified? (iii) How can we treat solvation in solvent mixtures? The objective of the following discussion is to offer a simplified, non-mathematical answer to the above-formulated questions. It is intended to help those who are interested in exploiting solvent effects without having to read lengthy, specialized literature. More discussion on the subject can be found in specialized books, and review articles.3,11

The reason for the multi-parameter dependence of chemical phenomena on solvent properties, point (i) above, is that several solute-solvent interactions come into play; their effects should be taken into account. These include both specific and non-specific interactions, e.g., hydrogen-bonding, dipolar-interactions (ion-dipole, dipole-dipole) and dispersion or London interactions.

With regard to (ii), there have been several approaches to quantify the dependence of chemical phenomena on solvent properties, most notably the Taft-Kamlet-Abboud Equation:12

$$SDP = Constant + a \alpha_S + b \beta_S + s (\pi^E_S + d\delta) + h (\delta_S^I)$$  \(1\)

Here a solvent dependent phenomenon, SDP, such as rate cons-

---

*E-mail: elseoud@iq.usp.br

*This paper is dedicated to Prof. Hans Viertler

---

Recebido em 24/5/10; aceito em 28/9/10; publicado na web em 16/11/10
tant, equilibrium constant, spectroscopic shift, is modeled as a linear combination of two hydrogen-bonding terms, in which the solvent acts as a hydrogen-bond donor (α_s), or hydrogen-bond acceptor (β_s), a dipolarity/polarizability term [s (π_s^2 + δ)], and a cavity term (h (δ^2)), related to Hildebrand solubility parameter. The term (δ) is a correction for π_s. A procedure has been given in order to separate solvent dipolarity from its polarizability. The parameters α_s, β_s, and π_s are known as solvatochromic parameters because they are determined by using solvatochromic probes (vide infra). The latter are substances whose spectra, absorption or emission, are particularly sensitive to specific solvent properties (acidity, basicity, etc.). The information about solvation is derived as follows: From the spectra of the probe in a series of solvents, an empirical solvent polarity scale, E_T(probe) is calculated from Equation 2:

\[ E_T(\text{probe}) = \text{Constant} + a \alpha_s + b \beta_s + s (\pi_s^2 + d\delta) + p \log P_s \]  

(3)

Where a new term (p log P_s) has been introduced because the spectroscopic response of merocyanine probes is sensitive to solvent lipophilicity, as measured by the empirical scale log P_s (= partition coefficient of a substance between (mutually saturated) 1-octanol and water: log P = log ([substance]_{octanol}/[substance]_{water})). Figure 2 shows some solvatochromic probes that the author’s group has employed in order to study solvents and their mixtures, along with their pKa in water and log P.

The molecular structures of these probes merits a comment, in order to demonstrate how their judicious choice can be exploited in order to extract information about the relative importance of solute-solvent interactions. Whereas the pKa of merocyanines 2 to 5 (MePBr to OcPMeBr) is the same, their log P vary by 2.86 units (relative to water, OcPMeBr is 724 times more soluble in 1-octanol than MePMeBr). This difference has been employed for evaluation of the relative importance of solute-solvent solvophobic interactions, for binary mixtures of water with both molecular solvents, and ionic liquids, ILs. Although RB is 3467 time more basic than WB, the susceptibility of their solvation toward solvent acidity is almost the same. The reason is that the regression coefficient (a) of Equation 3 for RB is attenuated because the site of hydrogen bonding (the oxygen atom of the phenolate ion) is sterically hindered, due to the two ortho phenyl rings. Indeed, H-bonding ability of RB depends on the acidity and steric hindrance of the proton donor, e.g., it does not form H-bond to 2,6-di-tert-butyl-4-methylphenol. For WB, this severe crowding around the phenolate oxygen is absent. Additionally, its C-Cl bonds are appreciably ionic, so that the chlorine atoms may form additional hydrogen bonds with the solvent, akin to 2,6-dichlorophenol. Figure 3 shows the DFT-optimized geometries of some of the probes depicted in Figure 2.

Figure 2. Molecular structures of zwitterionic solvatochromic indicators, along with the pKa of their conjugate acids in water; and log P. The acronyms of the probes and the corresponding empirical polarity scales are also indicated. Reproduced from ref. 10 with permission of IUPAC.
It is possible that the lower significance of $\beta_b$ is due to inefficient interactions between the solvent (as electron donor) and the heterocyclic quaternary nitrogen of the zwitterionic probe. For example, whereas the (CH$_3$)$_2$N$^+$ ion has no effect on the structure of water, (n-C$_4$H$_9$)$_4$N$^+$ has a net structure-enhancing effect, due to hydrophobic hydration of the alkyl groups. On the other hand, addition of $\beta_b$ to the equation that describes the dependence of Gibbs free energies of solution of tetra-alkylammonium halides on solvent properties did not increase the overall correlation coefficient, so that $\beta_b$ was dropped.

Table 2. Standardized regression coefficients of Equation 3 for some of the probes shown in Figure 2

| probe       | $\beta_{\text{statistical}}^{(a)}$ | $\beta_{\text{statistical}}^{(b)}$ | $\beta_{\text{statistical}}^{(s)}$ | $\beta_{\text{statistical}}^{(p)}$ | $r^2$ | n
|-------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------|-
| MePMBr$_2$  | 0.81                              | 0.02                              | 0.46                              | -0.24                             | 0.9258 | 36
| BuPMBr$_2$  | 0.80                              | -0.01                             | 0.44                              | -0.21                             | 0.9334 | 35
| OcPMBr$_2$  | 0.79                              | -0.01                             | 0.43                              | -0.22                             | 0.9317 | 35
| RB          | 0.80                              | 0.03                              | 0.47                              | -0.06                             | 0.8677 | 57
| WB          | 0.80                              | -0.02                             | 0.37                              | -0.08                             | 0.9412 | 25
| QB          | 0.85                              | 0.01                              | 0.29                              | -0.02                             | 0.9415 | 24

a- Data are taken from ref. 17. The scales of $\alpha_s$, $\beta_s$, etc. are different; use of the standardized values, $\beta_{\text{statistical}}$, makes the regression coefficients of Equation 3 directly comparable; b- number of solvents tested.

As shown in Table 1, solvatochromic parameters can be used to explain the effects of solvents on chemical reactions. In fact, solvatochromism of these dyes seems to be a good model for several reactions, as shown in Figure 4 for the pH-independent hydrolysis of two esters, 4-nitrophenyl chloroformate (NPCF) and 4-nitrophenyl heptafluorobutyrate (NPFB), in acetonitrile-water mixtures, over a wide water concentration range. The resemblance between the two plots, i.e., reduced $k_{\text{obs}}$ versus log (water) and reduced $E_0$(probe) versus log (water) is remarkable because the phenomena involved are quite distinct; acyl transfer reactions, and intra-molecular charge transfers, respectively. Note also that the responses to the composition of the binary solvent mixture of the less hydrophobic ester, NPCP, and the less hydrophobic probe, QB, are similar; the same applies to the more hydrophobic ester, NPFB, and probe, WB. This resemblance has also been noted for other acyl-transfer reactions; it can be taken to mean that the phenomenon involved in solvatochromism serves as model for reactions where there is a large difference in dipolarity between the reactants and the corresponding activated complexes.

The use of solvatochromic parameters in order to explain the effects of solvents appears to be of wide applicability. Thus we have studied cellulose swelling by twenty protic and sixteen aprotic solvents, and correlated the extent of swelling with several solvent properties, including solvatochromic parameters, Gutmann’s solvent acceptor and donor numbers, and Hildebrand’s solubility parameters. Swelling of cellulose is an important initial step in several processes including, inter alia, obtaining regenerated fibers (e.g., Rayon and Lyocel); mercerization, and functionalization of cellulose under heterogeneous and homogeneous reaction conditions. Our results have shown that the use of solvatochromic parameters in order to describe the dependence of cellulose swelling on solvent properties resulted in better correlations coefficients, as compared with those based on Gutmann’s, or Hildebrand’s solubility parameters. In fact, we were able to correlate the swelling of twenty eight protic and aprotic solvents simultaneously with the solvent molar volume, $\beta_3$, and $\pi^*$ (for determination of $\beta_4$, was excluded because the dipolar aprotic solvents carry no acidic hydrogens). This is remarkable because previous
work on swelling has either used a very limited number of solvents, or employed solvents of the same nature, either protic or aprotic. This success indicates that the same solute-solvent interactions mechanisms are relevant to probe solvation and cellulose swelling.

Question (iii) above is concerned with solvation by solvent mixtures. I concentrate here on binary mixtures where hydrogen bonding between its components is operative, e.g., those of water (W) and a miscible molecular solvent, or an ionic liquid (S). Ternary solvent mixtures can be treated, in principle, by using a similar approach. Solvation by these media is complex because of a simple fact: The composition of the solvation shell of solvatochromic probes, and presumably other species of interest is seldom, if ever, equal to the composition of the bulk binary mixture. There is “preferential solvation” by one component of the medium. One possible reason for this preferential solvation is the so-called “dielectric enrichment”. This term denotes enrichment of the probe solvation shell in the solvent of higher $\varepsilon_r$, due to probe dipole-solvent dipole interactions. This interaction, if it occurs, implies a positive deviation in the $E_T$ versus $c$ plot ($c$ is concentration on the mole fraction scale), even when the Onsager dielectric function of the mixture is a linear function in $c$. Indeed, $E_T$ were found to be non-linear functions of $c$ for the ideal binary mixtures cyclohexane-THF and cyclohexane-1-butanol. These, after algebraic manipulation, lead to the following solvent exchange equilibria, termed solvent “fractionation factors” $\phi$: $\phi_{WS} = \frac{AX_{\text{Effective}} \cdot X_{\text{Effective}}}{AX_{W} \cdot AX_{S}}$ (8) $\phi_{S-W-S} = \frac{AX_{\text{Effective}} \cdot X_{\text{Effective}}}{AX_{S-W} \cdot AX_{S}}$ (9)

![Figure 4. Plots of the dependence of log ($k_{\text{obs}}$) and of $E_T$ on log (water), at 25°C. Reduced log ($k_{\text{obs}}$) and reduced $E_T$ are employed, so that results of different species (esters, probes) may be directly compared. The esters are 4-nitrophenyl chloroformate (NPCF) and 4-nitrophenyl heptafluorobutyrate (NPFB). Reproduced from ref. 24 with permission of Wiley-Blackwell](image)

![Figure 5. Solvent polarity/temperature/solvent composition contours for MePMBr$_2$, BuPMBr$_2$ and OcPMBr$_2$ in MeOH / W. Reproduced from ref. 14 with permission of ACS](image)
where (m) represents the number of solvent molecules whose exchange in the probe solvation shell affects $E_T^\text{(probe)}$; usually $m \leq 2$. Bk refers to bulk solvent, and the concentrations of the solvent species are "effective" not analytical ones. Note that (m) should not be confused with the total number of solvent molecules that solvate the probe. This model enabled us to calculate the effective compositions in the solvation shells of these probes for a large number of mixtures of water with molecular solvents and ILs. Examples of the results of these calculations for the above-mentioned ILs are shown in Figure 7.

The information about preferential solvation is extracted from the values of the different $j$ of Equation 8-10. For example, for $j_{W/S} > 1$, the solvation shell is richer in (W) than the bulk mixture; the converse holds for $j_{W/S} < 1$, i.e., the probe is preferentially solvated by (S). Finally, a solvent fractionation factor of unity indicates an ideal behavior, i.e., solvation shell and bulk mixture have equal compositions. The same line of reasoning applies to $j_{S-W/S}$ (complex solvent substituting S) and $j_{S-W/W}$ (complex solvent substituting W), Equations 9 and 10, respectively.

Examples of this type of analysis for W-S are shown in Table 3 for mixtures of water with alcohols and the above-mentioned ILs, respectively. As shown, the values of (m) indicate that a small number of solvent molecules (1 to 2) affect the energy of intra-molecular CT.

I finish this account on solvation by a brief discussion of thermo-solvatochromism, i.e., effect of increasing temperature on solvation, see Figures 5 and 6. We have studied solvatochromism in the temperature range, where feasible, from 10 to 60 °C. In all cases, the values of $E_T^\text{(probe)}$ were found to decrease as a function of increasing the temperature. Raising the latter decreases the structure of the pure solvent, and the hydrogen-bonding between its components, affecting solvation. This change makes it possible to calculate the energy of desolvation of the probe. Although the desolvation of reactants and activated complexes is known to contribute to temperature effects on reaction rates, there is no obvious way to calculate its contribution to $\Delta H'$ from the Arrhenius plot. This desolvation energy is readily calculated from thermo-solvatochromism. Our results have shown that the magnitude of this energy is sizeable (e.g., range from 2.1 to 3.7 kcal mol$^{-1}$ over a 50 °C range for WB in aqueous alcohols) relative to the activation enthalpies of many organic reactions.

**CONCLUSIONS**

A simplified, non-mathematical description of solvation is provided. Effects of solvents and solvent mixtures on distinct chemical phenomena can be rationalized by a common reasoning, namely, analysis of the solvent effects in terms of a linear combination of properties such as solvent acidity, basicity, dipolarity/polarizability, and lipophilicity. Evaluation of the relative importance of these interactions requires studying solvatochromism of probes of adequate molecular structures. Solvatochromism in binary solvent mixtures can be described by a general mechanism, based on the presence in solution of hydrogen bonded species between the two
precursor solvents. All probes studied are preferentially solvated by the organic solvent, or IL and, much more efficiently, by the (S-W) hydrogen-bonded species. Values of $E_a$(probe) decrease as a function of increasing the temperature because of effects of the latter on the structures of water and the organic component, and on their mutual interactions. The dependence of $E_a$(probe) on the composition of the binary mixture, the properties of the probe, and the temperature can be fruitfully employed in order to better explain reactivity data, e.g., the (complex) dependence on medium composition of rate constants and activation parameters. Studies of solvatochromism and thermosolvatochromism are becoming increasingly important because of the current interest in the use of green solvents, e.g., super-critical CO$_2$, ILs, and super-critical water.

ACKNOWLEDGEMENTS

I would like to thank FAPESP (State of São Paulo Research Foundation) for financial support; CNPq (National Council for Scientific and Technological Research) for a research productivity fellowship; my research co-workers L. P. Novaki, E. B. Tada, P. L. Silva, M. Antonious, C. T. Martins, M. S. Lima, L. C. Fidale, E. L. Bastos, B. M. Sato, and P. A. R. Pires for doing the work reported here.

REFERENCES