Indian Journal of Chemistry
Vol. 61, May 2022, pp. 472-481

Solvation and Solvatochromism: An Overview[#]

Tapati Mallik & Debashis Banerjee*
Department of Chemistry, Chandernagore College, Chandernagore 712 136, West Bengal, India
*E-mail: debashisba@gmail.com

Received 04 September 2021; revised and accepted 11 April 2022

Different examples of solvatochromic shifts are shown and the theory that explain the non-specific general solvent effects are discussed here. The use of solvatochromic shifts for the determination of excited state dipole moment has been presented in detail in connection with a brief overview of different solvent polarity functions. The lack of proper theoretical expressions to explain the specific solvent effect stimulates to introduce the concept of "empirical measures of solvent polarity", based on well known, convenient, solvent sensitive model processes. Various solvent sensitive polarity probes are discussed in this context. So far as quantitative estimation of various parameters responsible for the observed solvatochromic shifts are concerned, introduction of multiparameter approaches, its application in recent years has been carefully analyzed. The review also focuses some of the recent developments on the theoretical calculations of various solute-solvent interaction parameters based on quantum mechanical approaches. This issue solvation interaction by the use of mixed solvents has been discussed in detail, starting from the early development of the theories related to preferential solvation to the recent scenario, with a critical survey on the application of the concept of preferential solvation in the solubilization of drugs, polymers considering the emerging 'green approach' in recent years.

Keywords: Solute-solvent interaction, Solvatochromism, solvent Polarity functions, Polarity probes, Empirical polarity parameters, Multiparameter approach, Preferential solvation

Environmental effect on the physicochemical properties of a molecule (solute) is of key importance in science since most of the chemical and biological processes take place in solution, including pure solvents and their mixtures. The growing interest in recent years in understanding solvation has intensified to a large extent, because the "green" approach in performing chemical reaction is becoming increasingly important. The need for careful selection of green solvents has increased our purpose to understand the nature of solute- solvent interaction at the molecular level[1-2].

The development of solution chemistry essentially governs the study of solvent effects on the structure and spectroscopic behavior of a solute[3-7]. The intensity, frequency as well as the shape of the absorption and/or fluorescence spectra, fluorescence quantum yield as well as the fluorescence life time modifies as the spectrally active molecules pass from the gaseous phase to the liquid phase [8-17]. The change of optical transition energies of the solute is termed solvatochromic shift, which obviously results from the difference in solute-solvent interactions of the solute ground and excited state. The term 'solvatochromism' is used to describe the pronounced change in spectral properties of an electronic absorption or emission characteristics of a solute, accompanying a change in the polarity of the medium[18-21]. One can thus get information about the local electric field acting on the spectrally active molecules[22-24] . In case of polar solvent, the change in charge density of the solute that results due to optical excitation polarizes the solvent and the interaction energy between the reaction field generated due to this mutual polarization effect between the solute and polar solvent with the charge density of the solute is termed as solvation energy[25]. The solvation energy of the excited state is a non equilibrium quantity as a consequence of Franck-Condon principle. On the other hand, in case of non- polar solvent, the polarization is basically inductive, caused by the charge density of the solute. Besides the inductive polarization interaction, the dispersive solute-solvent interaction becomes important in non-polar solvents. Central to the problem of understanding solute-solvent interaction is the question, how the free energy of a solute changes due to the presence of the surrounding interacting solvent molecules.

[#]Dedicated to Prof. Sanjib Bagchi, Ex Retired Professor, Department of Chemistry, Burdwan University, West Bengal

Over the past few decades, both theoretical[3,5,7] and experimental[9-12] studies have been made to understand the nature of solute-solvent interaction, sometimes called ‘’solvation interaction’’ or solvation effect[26]. In earlier studies[27-28] , taking the spectral shift as descriptor of the strength of solvation interaction, some macroscopic solvation model have been developed, using some macroscopic properties of the solvent, such as electric permittivity and refractive indices, which permits the estimation of electrical dipole moments and/or polarizabilities of the indicator solute molecule. In such studies, the macroscopic parameters of the solute (either the van der Waals radius or solute molar volume or ground state dipole moment) are evaluated either by calculations using some approximations or by computation, from which the corresponding values in the excited electronic states can be evaluated. Practically in all such cases, the emphasis has been given on the long range interactions and the presence of possible specific interactions with respect to solvatochromic shifts has not been taken into account.

Different types of intermolecular interactions in solutions were evidenced by solvatochromic studies[29-31] and the separation of the universal and specific interactions remains a challenge for solvation researchers till nowadays. Attempts have been made to correlate the observed solvatochromic shift by empirical polarity parameters[11,32-33] or by linear solvation energy relationships[34-35] . Chemists have tried to understand the environmental effect by introducing the concept of “solvent polarity” which is supposed to represent the overall solvation power of the solvent and includes both specific and nonspecific interactions [18]. In developing a suitable scale of solvent polarity, a “model process” e.g., a chemical reaction or spectral transition is chosen and changes in one of its parameters are recorded when solvent is changed [36-37]. Of the various polarity scale, the Z-value [38] and E_T values[18] have passed the test of time.

In view of the complexity of solute-solvent interaction the representation of polarity by a single parameter is not at all satisfying[39-41] and multiparameter approaches have been proposed[34-35]. The Linear Solvation Energy Relationship (LSER) has been found to be of great importance in the theory of solvent effect and related applications in analytical chemistry[42-43]. Here again the specific interaction plays a crucial role, restricting the above mentioned approaches to act as universal in explaining the solvation behaviour of a particular solute in a particular environment. Solvation interaction studies in recent years involves a, large number of computational studies[29-30,33,44-46] aiming at predicting solvatochromic shifts in different environments based on time-dependent density functional theory (TDDFT), incorporating the effect of specific hydrogen bonding in the process of solvation. Mechanism of solvation interaction and related solvatochromic behavior in biological systems has been the subject of extensive research in recent years[47-49]. The importance of understanding solvation of organic and inorganic species including biologically significant systems, the related solvent effect and resultant solvatochromism, on the basis of experimental, existing theoretical and recently emerging quantum mechanical calculations, is thus understandable by the fact that several books and review articles devoted to these subjects[11,13,18,24,31,39,46].

Mixed solvents add another dimension to the problem, as it is difficult to make predictions regarding molecular interaction between the solute and solvents based on the properties of pure solvents. Rather complex behaviour is observed as a function of liquid composition owing to the possibility of preferential solvation when the local composition of solvent mixtures in the immediate neighborhood of the solute (in the cybotactic region) differs from that of the bulk composition[50-51]. The preferential solvation phenomenon plays a key role in determining the physicochemical properties of a solute in mixed binary solvents[52].

Pure solvents: Theoretical approach

When a solute is dissolved in a solvent, a solvent specific alteration of its optical properties is resulted. The change of optical transition energies of the solute is termed solvatochromic shift, which results from the variation in solute-solvent interaction in the ground and excites states of the solute. Intermolecular interactions between the solute and the surrounding solvent molecules are, in general, highly complicated and difficult to determine quantitatively. However, the solute-solvent interactions responsible for the spectral changes in a solvent medium are of two types[53-56] . To the first category belong interactions which are due to collective influence of the solvent as a dielectric medium. This includes electrostatic forces arising from Coulomb interaction and polarization forces which are nonspecific in nature and is determined by the static dielectric constant (ϵ) and refractive index (n) of the solvents or functions thereof. Specific solvent effects, on the other hand, refer to the specific chemical interaction between the solvent and the solute and depend solely upon the precise chemical structures of the interacting species.

Numerous equations based on different models of solute-solvent interaction have been proposed to describe the solvent effect on the spectral properties of the solute[57-64]. Practically in all these treatments, described in terms of Onsager theory of dielectrics and the Franck-Condon (FC) principle, the solvent is regarded as a nonstructural continuum in which the solute is contained. For a species capable of exhibiting both absorption and fluorescence spectra, the influence of general solvent effect can be estimated by solvatochromic plots, such as Lippert-Mataga[65], Bakhshiev[23], Kawski-Chama-Viallet[66], McRae[23], Suppan[67] involving macroscopic solvent parameters described by functions containing bulk dielectric constant (ϵ) and refractive index (n). McRae and Suppan equations in this connection are based solely on absorption spectra. Related equations along with the polarity functions are given below:

Lippert-Mataga:

$$\mathrm{E(A) - E(F) = C_1\, F(\in, n) + Constant;\ C_1 = \frac{2(\mu_e - \mu_g)^2}{a^3};\ F(\in, n) = \frac{\in - 1}{2\in + 1} - \frac{n^2 - 1}{2n^2 + 1}} \quad \ldots(1)$$

Bakhshiev:

$$E(A) - E(F) = C_2 F(\in, n) + Constant;\ C_2 = \frac{2(\mu_e - \mu_g)^2}{a^3};\ \mathrm{F}(\in, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\in - 1}{\in + 2} - \frac{n^2 - 1}{n^2 + 2}\right) \quad \ldots(2)$$

Kawski-Chamma-Viallet:

$$\frac{E(A) - E(F)}{2} = -C_3 F(\in, n) + Constant; C_3 = \frac{2(\mu_e - \mu_g)^2}{a^3}; \quad \ldots(3)$$

$$F(\epsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)}\left(\frac{\in - 1}{\in + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2}$$

McRae:

$$E(A) = -C_4 F(\in) + Constant; C_4 = \frac{\mu_g(\mu_e - \mu_g)}{a^3}; F(\epsilon) = \frac{2(\in - 1)}{\in + 2} \quad \ldots(4)$$

Suppan:

$$E(A) = -C_5 F(\in) + Constant;\ C_5 = \frac{\mu_g(\mu_e - \mu_g)}{a^3}; F(\epsilon) = \frac{2(\in - 1)}{2\in + 2} \quad \ldots(5)$$

In all cases, 'a' is the Onsager cavity radius and can be approximated as being equal to $\sqrt[3]{\frac{3V}{4\pi}}$, assuming the solute to be spherical; E(A) and E(F) are the transition energies of absorption and emission maxima, respectively, μ_e and μ_g are the dipole moment of the molecule in the excited and ground state, respectively.

We have also developed a general approach to the solvent effect[12,41] on the spectroscopic transition energies by using the formalism developed by Marcus [57,68] based on the same reasoning but somehow with a different approach. The spectroscopic transition, in general, involves an equilibrium initial state and a nonequilibrium final state. The absorption of a photon by the equilibrated ground state (denoted as '0'), with permanent dipole moment μ_0, occurs within a very short time ($\approx 10^{-15}$ sec). FC principle requires that the nuclear solvent coordinates are 'frozen' during the transition. The time is however enough to allow for a redistribution of electrons, which results in an almost instantaneous change of dipole moment (μ_i). Thus, while the solvent electronic polarization can instantly adjust, the solvent orientation polarization cannot. Therefore, the solvent is out of orientation equilibrium with the excited state (denoted as '1') dipole moment μ_1. This leads to an orientational strain which contributes to a blue shift in the absorption compared to the gas phase. Subsequent to excitation the solvent cage undergoes relaxation and after a sufficiently long-time excited state equilibrium solvation would prevail. The steady state fluorescence brings the molecule from this equilibrated excited state to a FC ground state where again an orientational strain prevails. Assuming that the entropy does not change due to a transition[57,68] we may partition the FC energies E(A) and E(F) as:

$$\mathrm{E(A) = \Delta G\ (Solv.) + E_{RO}^{*}(1)} \quad \ldots(6)$$

$$\mathrm{E(F) = \Delta G\ (Solv.) - E_{RO}^{*}\ (0)} \quad \ldots(7)$$

Where E(A) and E(F) denote the energies corresponding to the maximum absorption and fluorescence, respectively. ΔG(Solv.) denotes the difference in the free energies of the solvated ground and the solvated equilibrium excited states, $\mathrm{E_{RO}^{*}(0)}$ and $\mathrm{E_{RO}^{*}(1)}$ represent the solvent reorganization energy in the ground and excited states, respectively. Under the condition that reorganization energies are equal[56], we obtain

$$E(A) + E(F) = 2\,\Delta G\,(\text{Solv.}) \quad \ldots(8)$$

$$E(A) - E(F) = 2\,E_{RO} \quad \ldots(9)$$

Thus, the Stoke's shift [E(A) – E(F)] is a measure of the nonequilibrium E_{RO} term, while [E(A) + E(F)] terms have only the equilibrium contribution. The ΔG (Solv.) term may be split into two components as shown in Eqn. (10)

$$\Delta G\,(\text{Solv.}) = \Delta G\,(\text{gas}) + [\partial G_1 - \partial G_0] \quad \ldots(10)$$

The first term in the right hand side represents the value of ΔG in the gas phase and the second term represents the differential contribution towards free energy due to solute-solvent interaction in the ground and excited state. The solvent dependent ∂G terms contain optical, orientational contributions and a specific contribution part[59]. The optical and orientational depend on certain solvent response functions B_{OP} and B_{OR}. Thus,

$$\partial G_X = -(1/2)\,(B_{OP} + B_{OR})\,\mu_X^2 + \Delta\,(Sp)_X : X = 0,1 \ldots(11)$$

The nonequilibrium term may be written as

$$E_{RO} = B_{OR}\,[\mu_1 - \mu_0]^2/2 \quad \ldots(12)$$

Using Onsager reaction field model[60] for B_{OP} and B_{OR} and neglecting the polarization of the solute, one may write Eqns. 8 and 9 as,

$$E(A) - E(F) = [(\mu_1 - \mu_0)^2/a^3]\,[2\,(\epsilon - 1)\,(2\epsilon + 1) - 2(n^2 - 1)/\,(2n^2 + 1)] \quad \ldots(13)$$

$$E(A) + E(F) = [(\mu_0^2 - \mu_1^2)/a^3]\,[2\,(\epsilon-1)/\,(2\epsilon + 1)] + 2\,\Delta G(\text{gas}) + \Delta(\text{sp}) \quad \ldots(14)$$

Where ϵ and n represent the dielectric constant and the refractive index of the solvent, respectively, 'a' is the radius of the solvent cavity in which the solute is placed and Δ(sp) denote the contribution towards the free energy change due to specific solute-solvent interaction. Eqn (8) is the well-known Lippert-Mataga equation.

The expression of the solvent Stoke's shift depends only on the absolute magnitude of the change in the dipole moment due to the transition. The expression also provides a means for the determination of the dipole moment of the excited state (μ_1), when μ_0 is known. In the deduction of the expression, it was assumed that the specific interaction does not contribute towards E_{RO}. Thus, the solvents to be chosen for the determination of μ_1 by studying Stoke's shift should not have specific interaction (e.g., hydrogen bonding or donor-acceptor). This method of determination of μ_1 requires a correct estimate of 'a', the cavity radius.

From Eqns. (13) and (14) we find that the ratio of the slopes of the plots of [E(A) – E(F)] and [E(A) + E(F)] versus the appropriate dielectric function for the case where specific interactions are absent provides an estimate of (μ_1/μ_0) from which μ_1 may be calculated. This procedure also does not require a prior knowledge of cavity radius. Besides the plot of 'Stoke's shift or absorption maxima with the appropriate polarity functions so far discussed, we have presented in an early communication that an analysis of the band-width parameter (70) of the charge-transfer (CT) absorption band can provide information about the change in dipole moment (Δμ) upon excitation and thereby the excited state dipole moment, with a prior knowledge of ground state dipole moment taking the experimentally determined band-width of the CT absorption band of N-ethyl-4-cyano pyridinium iodide and Reichardt's betaine. Here it has been assumed that reorganization energy of a solute in a particular solvent, capable of exhibiting CT band is made up of two parts: one is the solvent independent part that arises due to structural difference between the equilibrium configuration of the solute and another is related to solvent reorganization energy. This method is particularly useful for non-fluorescent compounds.

It may be stated that all the methods for the estimation of excited state dipole moment have the following assumptions[67,71-72] :

(1) The dipole moment in the FC and relaxed state must be the same: i.e., $\mu_1(\text{rel}) = \mu_1(\text{FC})$ and $\mu_0(\text{rel}) = \mu_0\,(\text{FC})$.

(2) The cavity radius 'a' must remain unchanged in the ground and excited states. The conditions require that the solute molecule does not undergo a major geometrical reorganization in the excited state as encountered in the twisted intramolecular charge transfer (TICT) of some flexible molecules [73].

All these models can explain the general solvent effects rather quantitatively[74-75] . Within such theoretical framework, the specific solvent effects are easily recognized as deviations from the predictions of the theory.

A procedure has been developed[76] by Samanta et al. using the empirical solvent polarity parameter E_T^N of Reichardt, instead of using solvent bulk macroscopic parameters such as relative permittivity and refractive index. The mathematical argument minimizes the error in estimating Onsager cavity radius 'a'. This method considers hydrogen bond donating/accepting characteristics of the solvent and often results in better correlation of solvatochromic shifts with the microscopic solvent polarity parameters E_T^N, rather than traditionally used polarity functions, as discussed earlier.

The solvatochromism of the absorption and fluorescence band would, according to the theory depend on the ground and excited state dipole moment. For the molecule where $\mu_0 > \mu_1$, a large shift in the absorption spectra with solvent polarity is observed. On the other hand, when the emitted photon will have much less energy than the absorbed photon with increasing solute-solvent interaction, there will consequently be a large red shift of the fluorescence band. Moreover, the fluorescence bands are found to be much more sensitive towards solvent polarity. Many examples of such type of fluorophore are found in the literature[67-68]. Besides, consideration of the change of dipole moment in the ground and excited states, the finite relaxation time τ_R for the rearrangement of the solvent molecules surrounding the solute in the FC excited state and the finite lifetime τ_e of the molecule in the relaxed excited state have also to be taken into account in order to explain the solvent dependence of the position of emission bands[77]. Hynes et al.[78] have introduced the concept of dielectric friction which is a measure of the dynamic interaction of a charged or dipolar solute with the surrounding polar solvent molecules in order to account for the solvent and time dependent fluorescence shifts. If solvent molecules are strongly coupled to the charge distribution in ground and excited states, the relatively slow solvent reorientation leads to an observable time-evolution of the fluorescence spectrum in the nano to picosecond range. This time dependent fluorescence (TDF) shift has been shown to be proportional to the time dependent dielectric friction of the absorbing dipolar molecules. That is, the relaxation rate of the fluorescence spectrum directly reflects a dynamic solvent polarity, namely, the reorientation rate of the surrounding polar solvent molecules closest to the fluorescent solute molecules.

Differential solvent interactions with ground and excited state molecules may also lead to perturbation of the relative intensities of the vibrational fine structure of emission bands[79]. Besides this, other fluorescence parameters, e.g. the fluorescence quantum yield [80] and life time of the excited state [15] also show solvent sensitivity.

Solvent polarity – Empirical measures

Chemists have tried to understand solvent effect in terms of solvent polarity. The term 'polarity' reflects the complex interplay of all types of solute-solvent interactions i.e., non-specific and specific intermolecular interactions[11]. It is believed that the dielectric approach provides an isomorphic model for describing nonspecific interactions. Thus, the use of physical constants e.g., dielectric constant or refractive index of the medium is not adequate for describing the total solvating ability of the medium as they do not take into account the specific interactions. In such a situation, other indices of solvent polarity are sought. The lack of theoretical expressions for calculating solvent effects as well as the complexity that involves in theoretical calculations and the inadequacy of defining 'solvent polarity' in terms of physical constants have stimulated attempts to introduce empirical scale of solvent polarity, based on convenient, well known, solvent sensitive reference processes or model processes[11,18] . If one carefully selects an appropriate, sufficiently solvent-sensitive reference process, one may assume that this process would reflect faithfully all possible solute-solvent interactions which are also present in related solvent-influenced processes. It should, therefore, give an empirical measure of the solvation capability of a particular solvent for the given reference process. This reference process can be considered as a probe in the solvation shell of the standard solute – a probe that sums up a wide variety of possible intermolecular interactions.

A study of absorption/emission characteristics of a suitable probe in various pure solvent or solvent mixtures lead to an overall estimate of solvent polarity. Spectroscopic parameters of solvent polarity have been derived from Solvent sensitive standard compound (reporter) absorbing light in the spectral region corresponding to UV-visible, IR-, ESR- and NMR spectra. The solvent dependence of the $n \rightarrow \Pi^*$ transition energies of two meropolymethine dyes (I) was used by Brooker et al.[81-82] to establish the solvent polarity parameters χ_R and χ_B . Kosower[38] a comprehensive scale by introducing the polarity parameter Z, as the transition energy, E_T, expressed in kcal mol^{-1} for the longest wavelength charge transfer (CT) absorption band of 1-ethyl-4-methoxy carbonyl pyridinium iodide (IIa). The position of the band shifts to the blue as the solvating ability of the solvent (in the chemical sense) increases. The use of 1-ethyl 4-cyano pyridinium iodide (IIb) has also been advocated [83]. Dimorth and Reichardt[11] have proposed a solvent polarity parameter, $E_T(30)$, based on the transition energy in kcal mol^{-1} for the longest wavelength solvatochromic absorption band of the pyridinium betaine dye (III). Owing to exceptionally large displacement of the solvatochromic absorption band, the $E_T(30)$ values provide an excellent and very sensitive characterization of the polarity of the solvents [18].

Besides these solvatochromic compounds, a large number of compounds capable of acting as solvent polarity probes have been reported in the literature[13,18,20,27-29,33,74-75]. Compared with many traditional tools, fluorescent probes remain the most commonly employed mean for detecting polarity in vitro and in biological systems, on account of operational simplicity, high selectivity and sensitivity in addition to real time monitoring, non-invasion[84]. Kessler and Wolfbeis have reported a group of fluorescence solvatochromic ketocyanine dyes (IV a, IV b)[85]. Parasassi et al. have reported the use of Laurdan (VI) and Prodan (VII) as polarity-sensitive fluorescent membrane probes[86] . Use of Laurdan and Prodan as polarity-sensitive fluorescent probes in lipid bilayers to bridge spectroscopic behavior with microenvironmental properties have also been reported in recent years[87].

Structure of some solvent sensitive polarity probes are shown in Fig. 1. Although a large number of polarity probes have been reported to be sensitive to polarity or microenvironmental property as discussed above, none of them satisfies the criteria to establish a universal scale of solvent (medium) polarity based on a single empirical parameter, because in establishing such a scale, it is assumed that the combination of solute-solvent interactions between the indicator solute and the solvent (medium) is the same as the particular solute under consideration. In many cases, this becomes an oversimplification. To overcome this problem, multiparameter correlation equations have been introduced.

Multiparameter approach

In general, any solvent dependent property (A) of a solute 'S' in a solvent 'i' may be represented as

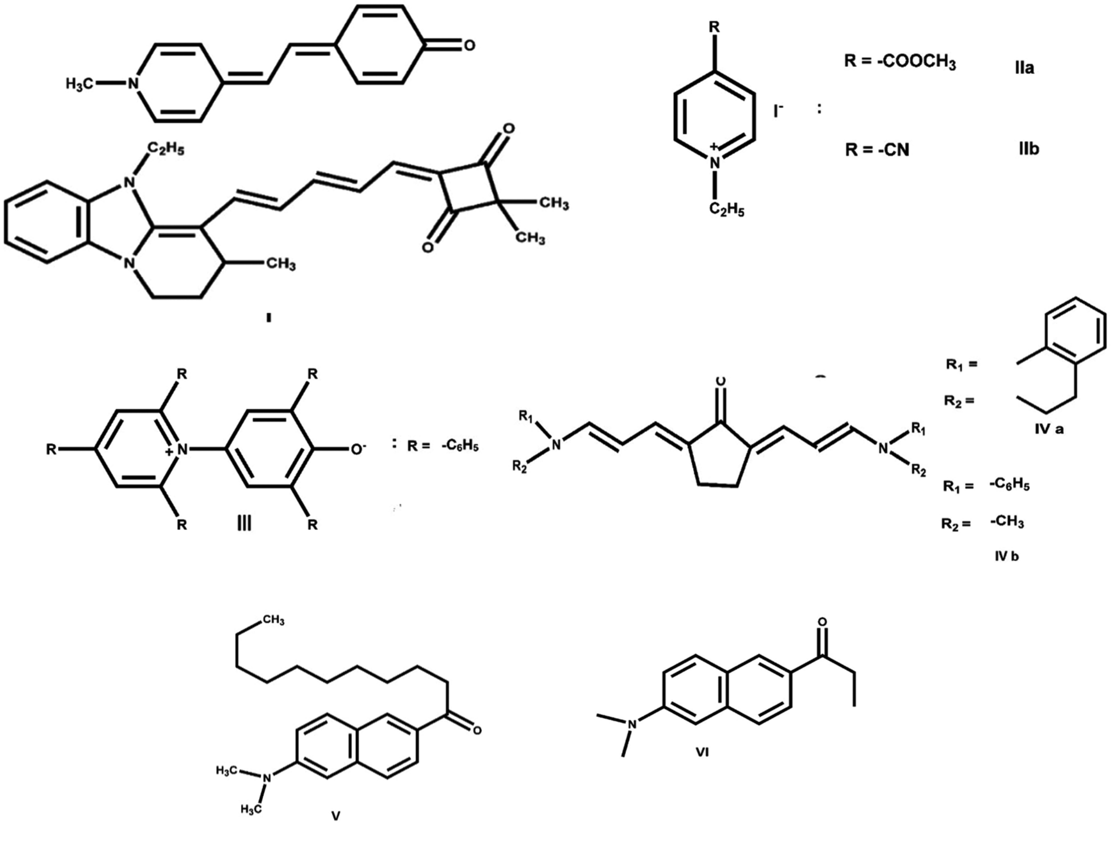

Fig. 1 — Some Solvent sensitive polarity probes

$$A_S(i) = A(S) + B(S, i) \quad \text{...(15)}$$

Where A(S) is the solvent independent part. The term B (S, i) is in general a complex function of both solvent and solute involving several modes of solute-solvent interactions. Thus, a much- longed-for 'universal polarity scale' seems to be a remote possibility. In essence there are three types of interactions[88] : (i) non-specific, long range solute-solvent interactions (ii) specific short-range solvent-solute interactions and (iii) solvent-solvent interactions from the cavity effect. The most important non-specific interactions are considered to be determined by macroscopic physical parameters of the solvent, i.e., the relative permittivity or dielectric constant (ϵ) and refractive index (n). The specific solvation is mainly determined by the acidity and basicity of the solvent, in terms of Lewis concept, which are measures of the solvent hydrogen bond ability to donate (HBD) and to accept (HBA) a proton respectively. Disruption and reorganization of solvent-solvent interaction are measured by the work necessary to separate solvent molecules to create a suitable cavity, large enough to accommodate a solute.

It has been shown that under certain simplifying assumptions the solute-solvent interaction term B (S, i) may be factorized as [89]:

$$B(S, i) = \sum a_\alpha(S) P_\alpha(i) \quad \text{...(16)}$$

Where suffix α represents various modes of interaction, the parameters $a_\alpha(S)$ and P_α (i) depending on the solute and solvent respectively. This expression, often called Linear Solvation Energy Relationship (LSER), has been found to be of great significance in the theory of solvent effect [34-35,89] and extensive applications in recent years [43,90] . Thus, it is customary to express a solvent sensitive property of a solute as a multiparameter equation:

$$A = A_\alpha + \sum a_\alpha P_\alpha \quad \text{...(17)}$$

Where the parameters P_α's is linearly independent and represent physically meaningful properties. Two main approaches in the field of multiple linear regression analysis (MLRA) may be distinguished, viz., the approach suggested by Koppel and Palm (KP) [91] and that by Abraham, Kamlet and Taft (AKT)[35]. In the KP approach functions of dielectric constant (ϵ) and refractive index (n) were used to describe the nonspecific interaction. Thus Onsager reaction field parameter $(\epsilon -1)/(2\epsilon +1)$ was used to describe the nonspecific dipolar interaction, while $(n^2 - 1)/(n^2 + 2)$ described the polarizability term. In the AKT approach the dipolarity and polarizability were described by experimentally determined parameter Π^{*}[58] . The specific interaction was described by the parameter 'E' (electrophilic solvation ability) and 'B' (nucleophilic solvation ability) in the KP procedure[83]. But AKT have preferred the use of hydrogen bond donating (HBD) or hydrogen bond accepting (HBA) ability of the solvent by the empirical Kamlet-Taft parameter α and β, respectively [92]. The endothermic cavity formation term was taken in the AKT approach as equal to solute molar volume times the Hildebrand cohesive energy density (∂_H^2) defined as enthalpy of vaporization per unit volume. The original KP approach did not take this factor into account.

Thus, the KP equation is

$$A = A_0 + yY + pP + eE + bB \quad \text{...(18)}$$

$$Y = 2(\epsilon -1)/(2\epsilon + 1);\ P = (n^2 - 1)/(n^2 + 2)$$

While the AKT equation is

$$A = A_0 + S\,\Pi^{*} + a\,\alpha + b\,\beta + C\,\partial_H^2 \quad \text{...(19)}$$

$$\partial_H^2 = (\Delta H - RT)/V$$

Where ΔH is the molar enthalpy of vaporization of the solvent whose molar volume is V. It has been found that the various empirical polarity parameters e.g., $E_T(30)$, Z etc. depend linearly on α, β, Π^{*} values [83,93]. In recent times, the Kamlet-Taft parameters have been used extensively to explain the solvatochromic behavior of various solvent sensitive compounds in different environments and also in analytical chemistry[94-95]. The major drawbacks of Kamlet-Taft parameters (α, β and Π^{*}) is that, they are not based on a well-known reference process, rather they are derived from an average of measurements using numerous examples: also, the dipolarity and polarizability of the solvent are included in only one parameter Π^{*}.

Catalan and co-workers [96-97] in this connection have introduced three alternative empirical polarity scales: SA, SB and SPP. In this approach, each solvatochromic parameters is based on a pair of well-defined homomorphous solvatochromic probes and these parameters (SP) measure gradual differences in the surrounding's polarizability by the solvatochromic method (ref). The multiparameter equation proposed by Catalan comprises two parameters for specific :the solvent acidity (SA), the solvent basicity (SB)and two parameters for non-specific : Solute polarity (SP) and polarizability (SdP). It may be mentioned that Kamlet-Taft α and β parameters corresponds to SA and SB respectively, wheras the non specific term Π^* corresponds to SP and SdP terms in Catalan's scale. It is difficult to predict that the Kamlet-Taft model is universally better than the Catalan because the regression quality of the two models will vary from compound to compound.

Mixed Binary Solvents: Preferential Solvation

The use of binary solvent mixture adds a new dimension to the problem of solvation. Here due to a difference in the interaction of the solute with the component solvent, the composition of the solvents in the immediate vicinity of the solute may be different from that in the bulk. This phenomenon, known as preferential solvation (PS), has been found to be important for explaining spectroscopic, equilibrium and kinetic data in mixed binary solvents[98-101]. The spectral parameters usually vary nonlinearly with the solvent composition (expressed in terms of mole fraction or volume fraction). A nonlinear variation of the parameter has often been explained as due to the preferential solvation of the indicator solute[102-103]. Obviously, due to the existence of PS, an unambiguous measure of solvent polarity may not be possible. A very careful analysis by Marcus[104] has shown that several chemically dissimilar probes produce convergent values of the respective solvent parameters (at a given composition). Thus, in most cases the solute acts as stand-ins and report the property of the mixed binaries.

The spectral response (R_{12}) in a mixed binary solvent is usually written as a weighted mole fraction average of the responses R_1 and R_2 of the solute in two pure solvents [105] .

$$R_{12} = X_1^L R_1 + (1 - X_1^L) R_2 \qquad \ldots(20)$$

Where X_1^L is the local mole fraction of the solvent component 1. Several spectral parameters have been used for monitoring the preferential solvation characteristics. These include shifts in the absorption/ emission wavelength[12-13,67,79,106] , quantum yield of fluorescence [78,80,107] and luminescence lifetime [16,78,108]. The local mole fraction X_1^L may be calculated using the equation as:

$$X_1^L = (R_{12} - R_2)/(R_1 - R_2) \qquad \ldots(21)$$

The local excess or deficiency of the 1st solvent component in a binary mixture over the bulk composition is described by the parameter ∂_{S1} as, $\partial_{s1} = X_1^L - X_1$; where X_1^L and X_1 are the local and bulk mole fraction of the solvent component 1, in the binary mixture. The descriptor of PS, K_{PS} is defined as $K_{PS} = [(X_1^L X_2)/(X_1 X_2^L)]$. The parameter K_{PS} is related to ∂_{s1} , following the Bagchi-Chatterjee model of PS [109], as

$$\partial_{s1} = - \partial_{s2} = X_1(1 - X_1)\,(K_{PS} - 1)/\,[1 + X_1\,(K_{PS} - 1) \qquad \ldots(22)$$

$$\text{Or, } K_{PS} = 1 + \partial_{s1}/\,[X_1(1 - X_1 - \partial_{s1})]$$

Several theoretical approaches to the problem of PS of a solute in a mixed binary solvent can be found in the literature. In the thermodynamic treatment of PS, first published by Grunwald et al. [110] and later elaborated by Covington et al.[111], the phenomenon is described in terms of a chemical model involving stepwise solvent-exchange (SSE) equilibria. Langford and coworkers described a two-phase model for solvation and described PS as becoming similar to preferential adsorption phenomena[112]. The quasi-lattice quasi-chemical (QLQC) statistical mechanical model of Marcus[113] uses a lattice theory of solution and attempts to calculate the extent of PS in terms of nearest-neighbor interactions. Ben-Naim developed a theory[114] for calculating the extent of PS in terms of Kirkwood-Buff (KB) parameters[115] . It needs to be mentioned here, that, whether the dielectric enrichment model of Suppan[102], preferential solvation model of Bosch and Roses[99] and the Bagchi-Chatterjee model[109] uses spectrochemical data in order to provide quantitative predictions of the local solvent composition, the model of Marcus[113] is one of the prominent model based on thermodynamic studies. All the theories so far presented describe the PS characteristics of a solute in a mixed binary solvent in terms of solute-solvent and solvent-solvent interaction that results in the variation in number of a particular solvent component in local and bulk phase. Despite several theoretical approaches to the problem, the role of various factors in determining the PS characteristics is not yet fully understood. In order to relate the various formulations of PS, we have developed a model in terms of solute-solvent and solvent-solvent interaction parameter as a function of composition and temperature[103] . In recent years, the question of understanding the nature and extent of PS in mixed binary solvents is not only restricted in developing theoretical models, but extensive computational studies based on TDDFT [44-45] is going on, aiming to evaluate the various component of solvation interaction in different environments. The problem of understanding the nature of solvation is now not only restricted in developing various models, but extensive studies are going on in recent years[116-117] based on these models, in the field of solubilization of various drugs, particularly, in mixed aqueous solvent systems, which seems to be of great importance in the field of medicinal chemistry, so far as green approach is considered.

Conclusions

Stereoselective catalysis for drug synthesis, solubilization of drugs, folding up of protein chain, solubilization of polymer in green environments and many more aspects: all are chemical problems and all these are concerned in one way or another with the question of interaction of solvent molecules or surface with the particular solute under investigation. Mastering the problem of solvation in general sense is hampered due to an inadequate understanding of the issue of solvation. One thing is clear following the preceding discussion: the details of solvation, solvatochromism and related phenomena cannot be understood in a universal manner on the basis of either a simple principle or a suitable unique model developed on the basis of reasonable arguments or computational calculations in quantum mechanical or statistical framework or empirical approaches; as the essence of solvation lies with the mode of interaction of the particular environment with the local environment of the particular solute. Therefore, experimental researcher will always be in search of the much longed-for “the universal scale of solvent polarity”, the theoretical chemists will be in search of a universal model process and quantum chemists extend the calculation of various modes of solvation to large molecules. All these will be of immense help to solidify the basics of green approach to all branches of experimental chemistry. Let’s hope the phenomenon of “solvation” will be acknowledged as a distinct branch of molecular science and identified as the interface between chemistry, physics and biology.

References

1 Jessop P G, Jessop D A, Fu D & Phan L, *Green Chem*, 14 (2012) 1245.
2 Anastas P T & Warner J C, *Green Chemistry: Theory and Practice*, (Oxford University Press, New York) 1998, p 30.
3 de Almeida K J, Ramalho T C, Rinkevicius Z, O Vahtras, Argen H & Cesar A, *J Phys Chem A*, 115 (2011) 1331.
4 Sidir Y G, Sidir I, Taşal E & Ermiş E, *Spectrochim Acta A*, 78 (2011) 640.
5 Adegoke O A & Idowu O S, *Spectrochim Acta A*, 75 (2010) 719.
6 Baughman B M, Stennett E, Lipner R E, Rudawsky A C & Schmidtke S J, *J Phys Chem A*, 113 (2009) 8011.
7 Kosenkov D & Slipchenko L V, *J Phys Chem A,* 115 (2011) 392.
8 Zheng D, Yuan X-A, Ma H, Li X, Wang X, Liu Z & Ma J, *R Soc Open Sci*, 5 (2018) Article ID 171928.
9 Sancho M I, Almandoz M C, Blanco S E & Castro E A, *Int J Mol Sci,* 12 (2011) 8895.
10 Banerjee D & Bagchi S, *Spectrochim Acta*, 51(A) (1995) 1079.
11 Reichardt C, *Chem Rev*, 94 (1994) 2319.
12 Banerjee D, Laha A K & Bagch S, *J Photochem Photobiol A: Chem*, 85 (1995) 153
13 El Seoud O A, *Pure Appl Chem*, 79 (2007) 1135.
14 Kulinich A V, Mikitenko E K & Ishchenko A A, *Phys Chem Chem Phys*, 18 (2016) 3444.
15 Hilaire M R, Mukherjee D, Troxler T & Gai F, *Chem Phys Lett*, 685 (2017) 133.
16 Pramanik R, Das P K, Banerjee D & Bagchi S, *Chem Phys Lett*, 341 (2001) 507.
17 Pramanik R, Das P K & Bagchi S, *J Photochem Photobiol A: Chem*, 124 (1999) 135.
18 Reichardt C, *Solvents and solvent effect in Organic Chemistry,* 3rd Edition, (Wiley-VCH, Weinheim) 2003.
19 Buncel E & Rajagopal S, *Acc Chem Res*, 23 (1990) 226.
20 Nigam S & Rutan S, *Appl Spectrosc*, 55 (2001) 362A.
21 El Seoud O A, *Quim Nova*, 33 (2010) 2187.
22 McRae E G, *J Phys Chem*, 61 (1957) 562.
23 Bakhshiev N G, *Opt Spectrosc*, 13 (1962) 24.
24 Dogonadze R R, Kalman E, Kornyshev E & Ulstrup J, *The Chemical Physics of Solvation*, (Elsevier, Amsterdam) 1985.
25 Renger T, Grundkotter B, El-Amine Madjet M & Muh F, *Proc Natl Acad Sci USA*, 105 (2008) 13235.
26 Han W G, Liu T, Himo F, Toutchkine A, Bashford D, Hahn K M & Noodleman L, *ChemPhysChem*, 4 (2003) 1084.
27 Airinei A, Rusu E & Dorohoi D O, *Spectrosc Lett*, 34 (2001) 65
28 Suganya K & Kabilan S, *Spectrochim Acta* A, 60 (2004) 1225
29 Zuehisdorff T J, Haynes P D, Payne M C & Hine N D M, *J Chem Phys*, 146 (2017) Article 124504.
30 Marini A, Munoz-Losa A, Biancardi A & Mennucci B, *J Phys Chem B*, 114 (2010) 17128.
31 Suppan P & Ghoneim N, *Solvatochromism,* (The Royal Society of Chemistry, Cambridge) 1997.
32 Dorohoi D, *J Mol Struct*, 704 (2004) 31.
33 Santosh K, Grandhi G K, Ghosh S & Samanta A, *Pure Appl Chem*, 85 (2013) 1451.
34 Taft R W, Abboud J L M, Kamlet M J & Abraham M H, *J Solution Chem*, 14 (1985) 153.
35 Abraham M H, Grellier P L, Abboud J L M, Doherty R M & Taft R W, *Can J Chem*, 66 (1988) 2673.
36 Nunes R, Nunes N, Elvas-Leitao R & Martins F, *J Mol Liq*, 266 (2018) 259.
37 Blasiak B, Lee H & Cho M, *J Chem Phys*, 139 (2013) 044111.
38 Kosower E M, *An Introduction to Physical Organic Chemistry*, (Wiley, New York) 1968.
39 Katrizky A R, Fara D C, Yang H, Tamm K, Tamm T & Karelson M, *Chem Rev*, 104 (2004) 175.
40 Laurence C, Mansour S, Vuluga D & Legros J, *J Phys Org Chem*, 33 (2020) e4067.
41 Banerjee D, Laha A K & Bagchi S, *Indian J Chem*, 34A (1995) 94.

42 Studzinska S & Buszewski B, *Chromatographia*, 75 (2012) 1235.
43 Apul O G, Perreault F, Ersan G & Karanfil T, *Environ Sci: Water Res Technol*, 6 (2020) 2949.
44 Wada T, Nakano H & Sato H, *J Chem Theory Comput*, 10 (2014) 4535.
45 Mennucci B, *Int J Quantum Chem*, 115 (2015) 1202.
46 Karmakar N K, Pandey S, Pandey R K & Shukla S S, *Appl Spectrosc Rev*, 56 (2021) 513.
47 Borisover M, Reddy M & Graber E R, *Environ Sci Technol*, 35 (2001) 2518.
48 Klymchenko A S, *Acc Chem Res*, 50 (2017) 366.
49 Madeira P P, Loureiro J A, Freire M G & Coutinho J A P, *J Mol Liq*, 274 (2019) 740.
50 Marcus Y, *Ion Solvation*, (Wiley, Chichester) 1985.
51 Roses M, Buhvestov U, Rafols C, Rived F & Bosch E, *J Chem Soc Perkin Trans 2*, (1997) 1341.
52 Marcus Y, *J Chem Soc Perkin Trans 2*, (1994) 1751.
53 Sidir I, Sidir Y G, Berber H & Turkoglu G, *J Mol Liq*, 215 (2016) 691.
54 Mabesoone M F J, Palmans A R A & Meijer E W, *J Am Chem Soc*, 142 (2020) 19781.
55 Brady J E & Carr P W, *J Phys Chem*, 89 (1985) 5759.
56 Brunschwig B S, Ehrenson S & Sutin S, *J Phys Chem*, 91 (1987) 4714.
57 Marcus R A, *J Chem Phys*, 43 (1965) 679.
58 Luzhkov V & Warshel V, *J Am Chem Soc*, 113 (1991) 4491.
59 Bader J S, Cortis C M & Berne B J, *J Chem Phys*, 106 (1997) 2372.
60 Lozzi M F, Cossi M, Improta R, Rega N & Barone V, *J Chem Phys*, 124 (2006) Article ID 184103.
61 Skyner R E, McDonagh J L, Groom C R, van Mourik T & Mitchell J B O, *Phys Chem Chem Phys*, 17 (2015) 6174.
62 Alibakhshi A & Hartke B, *Nat Commun*, 12 (2021) 3584.
63 Marcus R A, *J ChemPhys*, 38 (1963) 1858.
64 Chol H, Kang H & Park H, *J Cheminform*, 5(8) (2013) 1-13.
65 Mataga N, Kaifu Y & Koizumi M, *Bull Chem Soc Japan*, 29 (1956) 465.
66 Kawski A, *Acta phys Pol*, 25 (1964) 285.
67 Suppan P, *J Photochem Photobiol A: Chem*, 50 (1990) 293.
68 Marcus R A, *J Chem Phys*, 38 (1963) 1858. (Same as ref 63)
69 Onsager L, *J Am Chem Soc*, 58 (1936) 1486.
70 Das P K, Pramanik R, Banerjee D & Bagchi S, *J Chem Soc Faraday Trans*, 94 (1998) 3573.
71 Suppan P, *Chem Phys Lett*, 128 (1986) 160.
72 Valeur B in S.G.Schulman (EO.) Molucular Luminescence Spectroscopy, *Chemical analysis series, vol. 77*, Wiley New –York (1993) Part 3.
73 Bhattacharyya K, Chowdhury M, *Chem Rev*, 93 (1993) 507.
74 Patil S K, Wari M N, Panicker C Y & Inamdar S R, *Spectrochimica Acta A*, 123 (2014) 117.
75 Divac V M, Sakic D, Weitner T & Gabricevic M, *Spectrochimica Acta A*, 212 (2019) 356.
76 Ravi M, Samanta A & Radhakrishnan T P, *J Phys Chem*, 98 (1994) 9133.
77 Lakowicz J R, *Principles of fluorescence spectroscopy*, 3rd edn, (Springer, Boston) 2006.
78 Van der Zwan G & Hynes J T, *J Phys Chem*, 89 (1985) 4181.
79 Acree W E, Tucker S A & Wilkins D C, *J Phys Chem*, 97 (1993) 11199.
80 Banerjee D, Bagchi S, Mondal S & Ghosh S, *J Photochem Photobiol A: Chem*, 90 (1995) 171.
81 Brooker L G S, Keyes G H & Heseltine DW, *J Am Chem Soc*, 73 (1951) 5350.
82 Brooker L G S, Craig A C, Heseltine D W, Jenkins P W & Lincoln L L, *J Am Chem Soc*, 87 (1965) 2443.
83 Medda K, Chatterjee P, Chandra A K & Bagchi S, *J Chem Soc Perkin Trans 2*, (1992) 343.
84 Pushkarova Y & Kholin Y, *Cent Eur J Chem*, 10 (2012) 1318.
85 Kessler M A & Wolfbeis O S, *Spectrochim Acta Part A*, 47 (1991) 187.
86 Parasassi T, Krasnowska E K, Bagatolli L & Gratton E, *J Fluoresc*, 8 (1998) 365.
87 Krasnowska E K, Gratton E & Parasass T, *Biophys J*, 74 (1998) 1984.
88 Goncalves R M C, Simoes A M N & Albuquarque L M P C, *J Chem Soc Perkin Trans 2*, (1990) 1379.
89 Abboud J L M & Taft R W, *J Phys Chem*, 83 (1979) 412.
90 Vitha M & Carr P W, *J Chromatogr A*, 1126 (2006) 143.
91 Koppel I A & Palm V A, *Advance in linear free energy Relationships*, Ed. N B Chapman & J Shorter, (Plenum Press, New York) 1972.
92 Kamlet M J, Aboud J L M, Abraham M H & Taft R W, *J Org Chem*, 148 (1983) 2877.
93 Marcus Y, *J Solution Chem*, 20 (1991) 929.
94 Islam T, Sarker Md Z I, Uddin A B M H, Yunus K B, D M R Prasad, Mia Md A R & Ferdosh S, *Anal Chem Lett*, 10 (2020) 550
95 Black J J, Dolan A, Harper J B, Aldous L, *Phys Chem Chem Phys*, 20 (2018) 16558.
96 Catalan J & Hopf H, *Eur J Org Chem*, (2004) 4694.
97 Catalan J, *J Phys Chem B*, 113 (2009) 5951.
98 Langford C H & Tong J P K, *Pure Appl Chem*, 49 (1977) 93.
99 Roses M, Rived F & Bosch E, *J Chem Soc, Faraday Trans*, 89 (1993) 1723.
100 Nunes N, Ventura C, Martins F, Leitao R E, *J Phys Chem B*, 113 (2009) 3071.
101 Papadakis R, *J Phys Chem B*, 120 (2016) 9422.
102 Suppan P, *J Chem Soc, Faraday Trans 1*, 83 (1987) 495.
103 Banerjee D, Laha A K, Bagchi S, *J Chem Soc, Faraday Trans*, 91 (1995) 631.
104 Marcus Y, *J Chem Soc Perkin Trans 2*, (1994) 1015.
105 Chatterjee P & Bagchi S, *J Chem Soc Faraday Trans*, 86 (1990) 1785.
106 Sasirekha V & Ramakrishnan V, *Spectrochim Acta: A*, 70 (2008) 626.
107 Koppal V V, Patil P G, Melavanki R, Kusanur R, Patil N R, *Macromolecular Symposia*, 387 (1) (2019)1800210.
108 Ito O, Ito E, Yoshikawa Y, Watanabe A, Kokubun H, *J Chem Soc Faraday Trans*, 92 (1996) 227.
109 Chatterjee P & Bagchi S, *J Phys Chem*, 95 (1991) 3311.
110 Grunwald E, Baugman G, Kohnstam G, *J Am Chem Soc*, 82 (1960) 5801.
111 Covington A K & Newman K E, *Pure Appl Chem*, 51 (1979) 2041.
112 Frankel L S, Langford C H, Stengle T R, *J Phys Chem*, 74 (1970) 1376.
113 Marcus Y, *Aust J Chem*, 36 (1983) 1719.
114 Ben-Naim A, *J Phys Chem*, 93 (1989) 3809.
115 Ben-Naim A, *Cell Biophys*, 12 (1988) 255.
116 Martinez F, Jouyban A & William E Acree Jr, *Phys Chem Liq*, 55 (2017) 291.
117 Marcus Y, *Pharm Anal Acta*, 8 (2017) 1.