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Mechanism of Solvation in Solvent Alcohols

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Differential solvation of the different species in reactions are treated in two parts: primary differential solvation involving the functional group of the solvent and secondary differential solvation representing substituent effect on the solvation bond. Aliphatic alcohols of α-series (with changing methyl substitution at α-position), as solvents for a number of solvation-based reactions, are studied.

Quantitative correlation, between reactivity parameters in the solvents and the polar and ponderal substituent parameters of the alkyl substituents in the solvents, has been shown to be leading to the identification of solvation bonds of two modes—one of electrostatic, and the other of orbital, interactions between the solute and the solvent. Such detailed study of the "mechanism of solvation" is shown to lead to a few interesting mechanistic inferences.

Key Words: Mechanism, Solvation, Solvent, Alcohols.

INTRODUCTION

Organic solvents are widely classified[1] as polar-non-polar and protic-non-protic indicating that solute-solvent interactions in organic reactions are electrostatic, involving ion-dipole or dipole-dipole interactions with or without proton transfer. Hydrogen bonding and other interactions generally recognized as covalent in character are not so classified separately. Thus, degree of solvation is correlated to solute-solvent polarity only, irrespective of the exact nature—electrovalent or covalent—of the solvation bond. These are all however known to be positive interactions, *i.e.*, favouring the formation of solvation bond. It has also been shown[2] that solvation can be affected by a negative, ponderal* (or mass) factor which causes hindrance to solvation. Therefore the formation of a solvation bond and its strength must depend on the mutually opposing polar and ponderal characteristics of the solute and solvent.[2, 3]

The effect of solvation on a chemical or physical change is based on the *differential* solvation between the different species present during the process. Thus, for example, differential solvation between initial and transition states can

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*The term "ponderal" stands for mass with size, which is a structural effect, different from isotope effect where change in mass does not create corresponding change in size. Steric effect is not observed on solvation bond, apparently because of its greater length than regular covalent bonds.[2]

change activation energy and consequently rate of the reaction; same between reactants and products can change free energy difference in equilibrium reactions; and that between ground and excited states can change excitation energy. All these become important when solvation forms part of the energetics of a reaction as in the case of solvation-based reactions.

It is therefore imperative, at least in the cases of such solvation-based reactions, to know, as part of the reaction mechanism, the mechanistic details of solvation of the different species (in the reaction) and their effects. This communication is to present a method of determining such details, with theoretical justifications for the method, and some mechanistic inferences obtained by going into such details. Data used are of a number of solvation-based reactions carried out in alcohols of the α-series (MeOH, EtOH, *i*-PrOH and *t*-BuOH).

Determination of 'Solvation Mechanism'

The solvation processs is treated in two parts: primary and secondary solvations.

Primary solvation sets the mode or type of solute-solvent interaction leading to the formation of the solvation bond. The interaction can be either electrovalent in nature, or covalent, or a combination of both. An electrovalent solvation bond implies electrostatic interaction between charges carried by solute and solvent, and increases with increasing magnitude and density of the charges. Covalency of solvation bond implies interaction between molecular orbitals of solute and solvent (usually HOMO-LUMO) which increases with increasing nucleophilicity/electrophilicity of the atoms between which the solvation bond is formed. 'Combination of both' implies that orbital interaction keeps the involved atoms at the optimum distance (solvation bond length), by *partial* electron delocalization between the two, with electrostatic interaction existing between the remaining charge-densities of the two atoms. Of these three possible modes, the energetically most favourable one will of course be chosen by the system.

For a particular pair of atoms held together by 'solute-solvent interaction', the electrostatic interaction is susceptible to *changes in charge densities* at these atoms, whereas the orbital interaction is susceptible to *changes in the molecular mass* at these atoms, caused by the groups attached to the atoms.* Also, while the two atoms have their inherent electronegativity/electropositivity and nucleophilicity/electrophilicity, increasing charge densities at these atoms—consequent to structural features—can favour their mutual interaction (or strengthen the bond) electrovalently or covalently whereas increasing molecular masses attached to these atoms can decrease (or hinder) the interaction (or weaken the bond) and *vice-versa*. Consequently, solutes and solvents of high polarity and large molecular masses are likely to favour electrostatic interaction while those of low polarity and low molecular masses are likely to choose orbital interactions in forming a solvation bond. One or the other mode of interaction may clearly

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*It has been demonstrated[2] that the vibrational frequency and hence the energy of the orbital interaction in a solvation bond depends (as in the case of a regular oscillator) on the masses attached to its ends.

dominate in many reactions, as will be shown, but a combination of the two may be the chosen mode for many others.

Secondary solvation determines the *degree* of solute-solvent interaction, whatever be the mode or type. It represents the effect of structural features on the strength of the solvation bond. The structural changes considered are only the stepwise change in methyl substitution at the α-carbon of the solvent alcohols. This is done by comparing the reactivities, in alcohols of the α-series, of a number of solvation-based reactions. Electronically, methyl groups are known to be electron releasing substituents and the consequent effect on the strength of the bond or its reactivity is measured quantitatively by the (relative) parameter, σ^*, the polar substituent constant due to Hammett and Taft[4]. The ponderal effect, due to the molecular mass on changing alkyl groups has been quantitatively correlated to the reduced molecular mass, μ, of the solute and the solvent.[2]

As for the exact relationships, the linear correlation of polar substituent constants (σ^*-values) of alkyl substituents *in substrates* (*or solutes*) with experimental parameters of reactivity is well-established.[4] As part of the present work such a correlation was attempted for changing alkyl substitution in *solvent alcohols* for those solvation-based reactions, which showed regularity of change-in-reactivity with changing alkyl substitution. The good correlations obtained are shown in Table-1, where the linearity of the polar substituent constant *vs* reactivity parameter is given in terms of correlation coefficients—for different reactions in alcohols of α-series.

The ponderal substituent parameter, log $1/\mu$, has been shown to give very good linear correlation with the energy parameters (experimental parameters corresponding to energy changes*) in a number of solvation-based reactions[2, 3], some of which are listed in Table-2. Here also the degree of linearity of the correlation plots are represented in terms of correlation coefficients.

On the basis of treatment of solvation process as described above at the two levels of primary and secondary solvations and using the quantitative correlations obtained for the polar and ponderal substituent effects on secondary solvation, the mechanism of solvation can be worked out for different reactions as explained below, using selected reactions as examples.

Primary and Secondary Differential Solvations and Reactivity

As mentioned before, reactivity of a (solvation-based) reaction is related to *differential* solvations. The differential solvation has two aspects to it—the functional and the structural. The functional aspect is represented by the *primary differential solvation*—the difference in solvation of the two species (of a pair which determines the energy difference such as, for example, initial state and transition state) through the *functional group* of the solvent. The structural aspect is represented by the secondary *differential solvation*—the difference in solvation of a particular species by two structurally *different* solvents (for example difference in solvation of transition state by methanol and t-butanol). It is a

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*For example, log k (k is rate constant) can be the energy parameter for the change in activation energy.

TABLE-1

QUANTITATIVE CORRELATION OF POLAR SUBSTITUENT EFFECT DUE TO α-METHYL SUBSTITUTION IN ALCOHOLS

Sl. No.	Reactions	Parameters of solvation (experimental)	Values of the parameters in alcohols of α series				Coefficients of correlation with σ* (r)	Ref.
			Methanol	Ethanol	*i*-Propanol	*t*-Butanol		
1.	Transition energies for the intramolecular charge transfer of the pyridinium phenol betaine	Er (30) values (kcal/mole)	55.500	51.900	48.600	43.900	0.999	11
2.	Transition energies associated with the electronic absorption maximum of 1,3,5-triphenyl pyridinium-1,5-diphenyl phenol betaine	Dimroth parameter (E/kJ mol^{-1})	103.000	87.900	74.100	54.400	0.999	12
3.	Energy changes due to solvation of 1-ethyl-4-carbomethoxy pyridinium iodide	Z-value (kcal/mole)	83.600	79.600	76.300	71.300	0.999	11
4.	Solution of the alcohols in water	Differential heats of solution (kcol)	–2.200	–3.200	–4.400	–5.700	0.999	13
5.	Solution of HCl in alcohols at 10°C	Solubilities (x moles/mole of solvent)	0.857	0.950	1.030	—	1.000	14
6.	^{13}C NMR chemical shifts of the *para* carbon atoms of $Ph{\cdot}CF_3$ (solvent polarity/polarisability)	Kamlet-Taft solvent parameter π	0.600	0.540	0.480	0.400	0.999	15
	All above reactions (Nos. 1 to 6)	Polar parameter, σ*, of alkyl groups of the alcohols	0.000	–0.100	–0.190	–0.300	—	15

TABLE-2

QUANTITATIVE CORRELATION OF PONDERAL SUBSTITUENT EFFECT DUE TO α-METHYL SUBSTITUTION IN ALCOHOL SOLVENTS

Reactions	Parameters of solvation experimental	Values of the parameters in alcohols of α series				Coefficients of correlation with log $1/\mu$	Ref.
		Mathanol	Ethanol	*n*-propanol	*t*-Butanol		
1. Solvolysis of *tert*-butyl chloride*	Y-values $\log(1/\mu) + 2$	−1.09 0.6234	−2.03 0.5120	−2.73 0.4385	−3.26 0.3855	0.999	5
2. Solvolysis of *tert*-butyl chloride* in *aq*. alcohols (in constant molar ratio)	$(\log k) + 7$ $\log(1/\mu) + 2$	4.0611 0.6234	3.1796 0.5120	2.5298 0.4385	2.1950 0.3855	0.999	1
3. Solvolysis of *tert*-butyl bromide*	$(\log k) + 7$ $\log(1/\mu) + 2$	2.54 0.5855	1.65 0.4624	1.00 0.3790	0.50 0.3179	1.000	7
4. Solvolysis of *tert*-butyl iodide*	$(\log k) + 6$ $\log(1/\mu) + 2$	2.10 0.5640	1.24 0.4336	0.64 0.3438	0.16 0.2769	0.999	7
5. Solvolysis of benzhydryl* chloride	$(\log k) + 6$ $\log(1/\mu) + 2$	2.9206 0.5922	1.7332 0.4714	0.7559 0.3897	—	0.998	7
6. Reaction of pyridine and ethyl iodide	$(\log k)_{rel} + 1$ $\log(1/\mu) + 2$	1.3979 0.5499	1.1461 0.4142	1.0294 0.3200	0.9685 0.2492	0.988	8
7. Solution of *m*-fluoro-nitrobenzene in the alcohols	NMR signal shift $\log(1/\mu) + 2$	−3.38 0.6061	−3.53 0.4896	— —	−3.73 0.3552	0.999	9
8. Enolization of methyl acetoacetate*	$\log k$ $\log(1/\mu) + 2$	1.1776 0.6007	1.0345 0.4823	0.9157 0.4029	0.8179 0.3451	0.997	10
9. Enolization of ethyl acetoacetate*	$\log k$ $\log(1/\mu) + 2$	1.0923 0.5904	0.9167 0.4688	0.7957 0.3867	0.7003 0.3265	0.999	10
10. Solvation No. 'N' for solution of HCl in alcohol (x moles of alcohol/mole of HCl)	$\log N + 1$ $\log(1/\mu) + 2$	1.0670 0.7682	1.0223 0.6914	0.9872 0.6441	—	0.987	14
11. Solvation No. (N) for solution of benzoic acid in alcohols	$\log N + 1$ $\log(1/\mu) + 2$	0.6531 0.5960	0.5908 0.4760	0.5417 0.3950	0.5097 0.3360	1.000	18
12. Absorbance by sat. soln. of $Co[(NH_3)_5Cl]Cl_2$ in aq. alcohols at $\lambda = 534$ (Å)	$\log A + 1$ $\log(1/\mu) + 2$	0.7202 0.5467	0.4502 0.4101	0.2810 0.3147	0.1461 0.2428	0.998	3

*From Ref. 2 listed here for convenience.

combination of the two that determines the differential solvations in the two solvents and hence the reactivity in the two solvents.

The direction and magnitude of differential solvations are determined on the basis of solute-solvent polarity (favouring solvation) and solute-solvent molecular mass (not bulk) (hindering solvation). For many reactions, one effect or the other can be distinctly dominating separately in the primary and in the secondary differential solvations. It is such reactions which show a steady trend of change-in-reactivity, at least qualitatively, corresponding to steady change in alkyl substitution in the solvent alcohols, as in α-series.

The question now arising is how to distinguish between the polarity dependence and molecular mass dependence of the differential solvations. Regarding the primary differential solvation, in many reactions it is easy to decide this by simple inspection. But wherever this is not possible one has to consider both possibilities and move on to secondary differential solvation to make the decision. Secondary differential solvation can be decided to be polarity-dependent if the reactivity parameter gives good linear correlation with the polarity substituent constant, σ^*, on changing the (alkyl) substitution in the solvent (alcohols); on the other hand if there is good linear correlation between the energy parameter of the reaction and ponderal substituent parameter, log $1/\mu$, the secondary differential solvation can be decided to be molecular-mass dependent. In the former case the primary solvation bonds (from which primary differential solvation is determined) are indicated to be electrostatic in character. In the latter case they must be made of orbital interaction. If neither correlation is obtained for the secondary differential solvation, it means that one or both of the primary solvation bonds is/are formed of a combination of electrostatic interaction and orbital interaction—not distinctly one or the other. These explanations will be clarified by the following examples.

Example I: *Reaction of tert-butyl chloride solvolysis in alcohols of* α-series (Reaction 1, Table 1) [$(CH_3)_3CCl + ROH \rightarrow (CH_3)_3COR + HCl$]: The reactivity or rate-determining step is

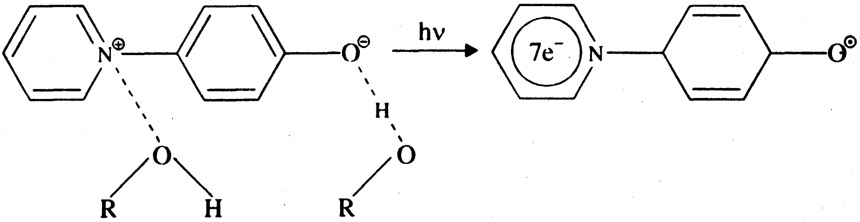
$$(CH_3)_3CCl \xrightarrow[\text{(Slow) Solvent ROH}]{[(CH_3)_3C^{\delta+}\ldots Cl^{\delta-}]} (CH_3)_3C^+ \ldots OH + Cl^-$$

$$\xrightarrow[\text{(fast)}]{} \text{products}$$

From inspection it can be seen that there is little difference in molecular mass of the initial state and transition state of the rate-determining step; only the distribution of mass has slightly changed at the central carbon due to the extension of the bond in transition state On the other hand there is a large difference in the charge density at the central carbon in the initial and transition states. Therefore, combining the fact that alcohols are strongly polar solvents, it can be easily concluded that primary differential solvation (difference between I.S. solvation and T.S. solvation) must be on the basis of solute-solvent polarity and not on the basis of solute-solvent molecular mass, and also that it must be in favour of more polar transition state.

On changing alkyl substitution in the solvent alcohol, the secondary differential solvation is such that qualitatively the degree of solvation of transition state decreases with increased alkyl substitution (rate constant, k, decreases); and quantitatively there is very good linear correlation between the activation energy parameter, log k, and the ponderal parameter, log $(1/\mu)$. Both indicate that the secondary differential solvation is based on solute-solvent molecular mass which, in turn, leads one to conclude *that the primary solvation bonds are covalent, made of orbital interaction and not electrostatic in character.*

Example 2: *Transition energies of intramolecular charge transfer of pyridinium phenol betaine in alcohols of* α*-series* (Reaction 1, Table 2): The excitation process is represented below structurally:



In this change also, it can be seen by inspection that molecular masses of the ground and excited states are the same so that the primary differential solvation cannot be on ponderal basis. On the other hand, the excited state is very considerably less polar than the ground state so that in the very polar, alcohol solvents, the primary differential solvation must be on polar basis and in favour of ground state. On changing alkyl substitution in solvent alcohol, the secondary differential solvation of ground state is such that qualitatively the degree of solvation decreases with increased alkyl substitution (excitation energy E decreases) and quantitatively there is very good linear correlation between the reactivity parameter, E, and the polar substituent parameter, σ^*. The correlation indicates that the secondary solvation is based on solute-solvent electrostatic interaction; and the direction of the change in solvation indicates that the strong, quantitatively significant solvation is at the oxygen of the betaine through the protic hydrogen of the alcohol, whose protic character gets reduced by increased electron release due to increased alkyl substitution [Note that the same electron releasing substituent effect would increase solvation at the pyridinium ion and if this solvation bond were distinctly stronger, E would have increased with increasing alkyl substitution].

RESULTS AND DISCUSSION

Some of the mechanistically interesting inferences which are arrived at by following the detailed "mechanism of solvation" as above in some of the chemical and physical changes which are energetically dependent on solvation are discussed below.

1. Parameters of Solvent "Polarity"

The two sample reactions cited earlier—t-BuCl alchoholysis and charge transfer of a betaine in alcohol—are actually two recognized standard reactions used for quantitative parameters of solvent "polarity" in the names of 'γ-value' and '$E_T(30)$ value'* respectively. Even though in both reactions the solvation bonds responsible for primary differential solvation could be predicted to be formed on the basis of solute-solvent polarity (*i.e.*, the more polar species being more solvated in all the alcohols), the secondary differential solvations are not so similar. They *appear to be similar qualitatively*, in that, in both cases the secondary differential solvation decreases in going from MeOH to t-BuOH, along the α-series. But *quantitatively*, the correlations obtained are different: in the case of *t*-BuCl alcoholysis the linear correlation is between energy parameter, log k, and *ponderal* substituent parameter, log $(1/\mu)$; whereas in the case of charge-transfer reaction linear correlation is between the excitation parameter, E (excitation energy obtained from absorption frequency), and *polar* substituent parameter, σ^*. Following the explanations given earlier, it is suggested that *this difference is due to the solvation bond being distinctly covalent in the former (solvolysis reaction) and distinctly electrovalent in the latter (charge transfer reaction). Conversely it is also suggested that the ponderal dependence of reactivity on secondary differential solvation can be used as a criterion for covalency, and polar dependence (dependence on polar substituent constant) of the same as criterion for electrovalency of a solvation bond.* The justifications for the suggestions are:

1. Only a covalent bond formed by overlap of orbitals is capable of vibrational motion (between the bonded atoms) and only such a motion (as in the case of a regular oscillator) can show dependence on mass and therefore be subjected to ponderal substituent effect in particular, quantitatively as per the correlation cited, which has been derived by treating solvation bond as a regular oscillator[2] Electrostatic interactions are in no way related to mass.
2. Electrostatic interaction in an electrovalent bond is solely dependent on the magnitude and density of the charges at the two bonded atoms; it is this charge density that is affected by the *polar* substituent effect and makes the reactivity correlate with the polar substituent constant.

Thus while both Y-value and $E_T(30)$ value are recognized as "polarity parameters", the reality seems to be that in one instance (Y-value) it represents the solvating capacity of the alcohol by orbital overlap (nucleophilicity) which is being compared, while in the other [ET(30) value], it represents the relative capacity of the alcohol to solvate a dipole through electrostatic interaction, by itself acting as a dipole.

2. Self-solvation of alcohols

It has been shown[6] that energy parameters of different physical changes due to chain-lengthening alkyl substitution in alcohols (*i.e.*, the parameters of alcohols along the normal series) show very good linear correlation with the ponderal parameter, log $(1/\mu)$, (these energy parameters include logarithms of boiling points, of viscosity coefficients, of surface tension, of diamagnetic susceptibility and polarizability) clearly indicating that in these alcohols EtOH, *i*-PrOH,

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*Z-value and Dimroth parameter of solvent polarity are based on similar reactions.

i-BuOH, . . . , *n*-DecOH—the (self) solvation bonds are covalent in character. Since the only possible solvation bonds in the self-solvation of alcohols are hydrogen bonds, the correlation shows that these hydrogen-bonds are *distinctly* covalent, supporting the idea of orbital interaction between the non-bonded *p*-orbital of oxygen (HOMO) of one molecule and the antibonding O-H orbital, σ^*_{OH} (LUMO) of another molecule, of alcohol.

However, physical constants of alcohols of α-series do not seem to correlate in either way—neither with the ponderal, nor with the polar parameters. This indicates that, as methyl substitution increases the electrostatic character also increases so that, in alcohols of this series, the solvation bond consists of a combination of the two modes of interaction [perhaps more covalent in the less massive lower aocohols and more electrovalent along the more polar and more massive *i*-PrOH and *t*-BuOH], even though these are also "hydrogen bonds"!

3. Solvation of alcohol by water

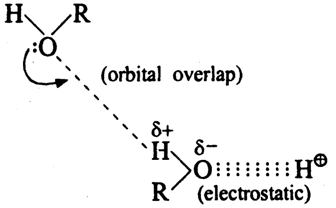
In solution of alcohols of α-series in water (No. 4 in Table-2), the reactivity (ease of solution) parameter, namely the heat of solution, gives good linear correlation with the polarity substituent constant, σ*, of the corresponding alkyl groups. This can be taken as indication of purely electrostatic character of the alcohol-water solvation bonds (unlike the alcohol-alcohol bonds) and these are also "Hydrogen bonds"!! [Note that both interactions justify the linearity of H-bond, which favours maximum overlap in one case and minimum repulsion in the other].

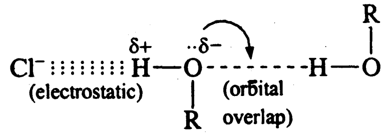
4. The energy parameters of different physical processes (such as mentioned in 2 above for alcohols) have been found to give very good linear correlations with the ponderal parameter (log 1/μ) for liquid alkanes of the normal series.[16] By the same argument as for alcohols these observations must indicate that the intermolecular forces in these liquids are fully covalent in nature and created by orbital overlaps. Though it is not very apparent as to which orbitals are involved in the mutual interactions of these non-polar molecules, the interactions could be of the type of London forces, which were explained (for liquid inert gases) by Fritz London,[17] using wave mechanics. The observation is, however, against the idea of temporary dipoles being created due to non-symmetrical electron motions and then being subjected to temporary dipole-dipole interactions. The impressive ponderal dependence shown by these homologous series of alkanes [ranging from hexane to hexacosane for boiling points, from 1-propane to 1-docosane for polarizability, etc.] cannot, as mentioned before, be explained by any electrostatic interactions.

5. Solvation of HCl in solvent alcohols

It can be noted from Table 1 (No. 5) and Table 2 (No. 10) that the *solubilities* of HCl (moles of HCl per mole of solvent), as reactivity parameter of the process gives good linear correlation, with the polar substituent constants, σ*, of the alkyl groups, in alcohols of the α-series, whereas, in the same alcohol series, the logarithm of *solvation number* for HCl (moles of alcohol per mole of HCl), as energy parameter for the process of *solvation*, give good linear correlation with the ponderal parameter, log $(1/\mu)$(!) (as does the solvation number for benzoic acid (No. 11).

This leads to the interesting inference (suggested) that while the process of solution of HCl depends on solute-solvent (HCl-alcohol) dipole-dipole interaction, the process of further solvation of the separated ions is carried out by orbital interactions. One may imagine the approximate picture for HCl and the alcohol molecules (of the α-series)* in the solutions as given below. The solubility of an inorganic complex, however, seems to be by covalent solvation bonding (No. 12).





Conclusion

Available data suggests that for solvation-based reactions the details of solvation mechanism needs to be taken into account as part of reaction mechanism. The possibility that electrostatic and orbital interactions in solvation bonds are distinguishable from each other opens up a new path for greater understanding of solvation, with more corroborating data.

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*The drawback here is that out of the four points possible for the linear correlation (by theoretical limitation), data is available only for 3 points in this case.