

DIELECTRIC RESPONSE OF MOLECULAR INTERACTIONS IN LIQUIDS

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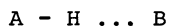
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Abstract - A survey was carried out concerning chosen problems of dielectric behaviour of the solute-solute-solvent interaction. Special attention was paid to the dipole moments of molecular complexes and to the solvent effect upon them. Problems of the proton density distribution in hydrogen bonded systems and the so-called superpolarizability of hydrogen bridges was discussed in the light of contemporary views. The phenomenon of the non-linear dielectric effect and "anomalous" positive effect in hydrogen bonded systems seemed to be of particular interest. Attention was paid to the existing conceptions dealing with this problem, namely the equilibrium model, the significant structures model, and the proton-jumping conception. Finally, an attempt was made to present a general outlook on the problem of the dynamics in solution from the point of view of dielectric relaxation in the case of forming simple molecular complexes.

DIPOLE MOMENTS

Hydrogen bonded complexes.

The formation of a hydrogen bond



leads to a change in charge distribution which is reflected by the dipole moment vector $\Delta\vec{\mu}$, directed from B to A-H without any exceptions. Its value changes within a wide range, from tenths of D to approx. 10D. ΔpK value of the interacting components ($\Delta pK = pK_{BH^+} - pK_{AH}$) appeared to be a parameter sufficiently well describing the magnitude of $\Delta\vec{\mu}$. Fig. 1 presents the dependence of $\Delta\vec{\mu}$ in function of ΔpK for a model series of phenol-

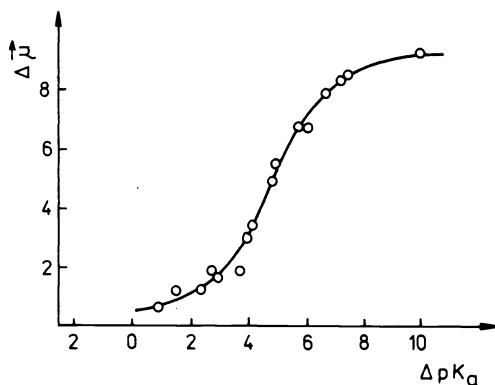


Fig. 1. Hydrogen bond polarity $\Delta\vec{\mu}$ related to $\Delta pK = pK_{BH^+} - pK_{AH}$ for phenol-triethylamine complexes

-triethylamine complexes (1). A similar ΔpK range of the sharp increase of the dipole moment was found for such systems as phenols-pyridines (2,3), phenols-anilines (4), carboxylic acids pyridines (5) or HCl-oxygen bases (6). At the same time it should be mentioned that the inversion range in which the sharp enhancement of $\Delta\mu$ takes place occurs approximately for the same ΔpK values.

The dependence of $\Delta\mu$ versus ΔpK can be explained in the following manner. For low ΔpK values (weak interactions) electrostatic interactions prevail, i.e. an increase of the moment can be entirely attributed to the inductive effect. It is noteworthy that for small ΔpK values $\Delta\mu$ remains constant in a very wide range of ΔpK , although other hydrogen bond parameters (band shift - $\Delta\nu$ (stretch), band intensity (7)) change markedly. Moreover, it is easy to understand high $\Delta\mu$ values for complexes formed by strong acids and bases. They correspond to the proton transfer state, i.e. to ion pairs. It is suggested, that the inversion range of ΔpK from approx. 3 to 7 corresponds to the proton transfer equilibrium. Assuming the existence of tautomeric equilibrium between "normal" hydrogen bonds (HB) and ion pairs (PT) dipole polarizability of the complex can be expressed as a sum:

$$P_{dip} = x_{PT} \cdot P_{PT} + x_{HB} \cdot P_{HB} \quad (1)$$

On the other hand, proton transfer equilibrium can be connected with ΔpK (8): $\log K_{PT} = \Delta pK + \text{const}$. Complete consistency of measurements of dipole moments with P_{PT} equilibrium model is achieved by introducing empirical parameter ξ (1),

$$\log K_{PT} = \xi \Delta pK + \text{const} \quad (2)$$

This general equation describes properly not only changes of the dipole moment but also infra-red (9), NMR (10,11), and NQR spectra (12). The function of the dependence of the resonance frequency NQR ^{35}Cl on ΔpK for pentachlorophenol complexes with amines is presented in Fig. 2.

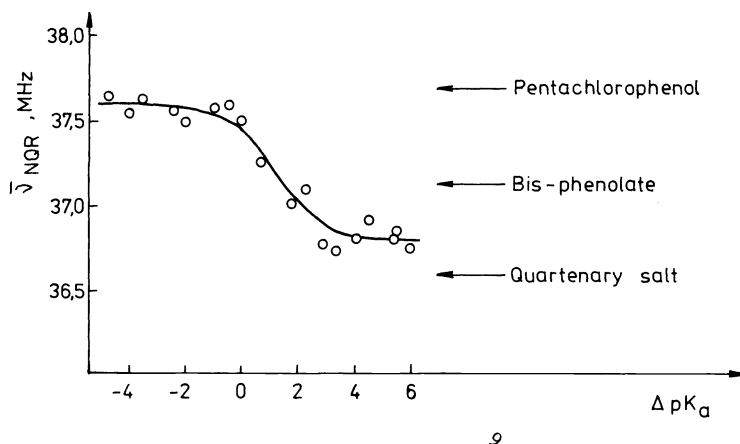


Fig. 2. Plot of $\sqrt{\nu_{NQR}}$ in MHz versus ΔpK_a

As anticipated the inversion range is shifted toward lower ΔpK values since the crystalline state favours a more polar state, i.e., PT. It is significant, however, that in this case ξ parameter is the same found in the measurements of dipole moments in phenol derivatives with triethylamine.

The fact that the ξ parameter is smaller than 1 indicates that, apart from the electrostatic effect and the proton transfer, the effect of charge transfer (CT) is of some contribution. This contribution increases the closer we get to the inversion point. In other words, dipole moments of PT and HB states are functions of ΔpK .

On the other hand, the existence of proton transfer equilibrium which has been undoubtedly proven using several methods attests to the potential energy curve with double minimum. This fact causes significant consequences. First of all, such systems should be hyperpolarizable. Let us consider, according to Weidemann, Zundel and Janoschek (13,14), the symmetric curve of

potential energy for the proton movement (Fig. 3). The split vibrational

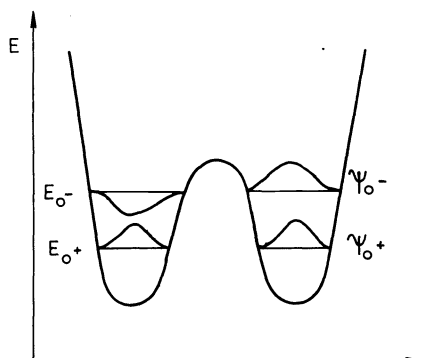


Fig. 3. Split protonic levels for symmetrical double minimum potential energy function

levels described by functions ψ_{0+} and ψ_{0-} are characterized by a symmetric charge distribution but the superposition of such states leads to an asymmetric charge distribution. Applying an external field permits mixing of these states and thus causes polarization. It can be stated that systems with a hydrogen bond of a double symmetric minimum or of a shallow single minimum are exceptionally "soft". Zundel estimates that the polarizability of such systems is greater by approx. 2 orders than the polarizability of other atomic systems.

There is no direct evidence of the hyperpolarizability of hydrogen bonds. Above all, no anomalous field effect has been discovered (compare with the next sub-section). The hyperpolarizability conception proved fruitful while explaining some spectral peculiarities of hydrogen bond systems. The most spectacular phenomenon observed for symmetric and nearly symmetric hydrogen bonds is the occurrence of continuous absorption in infra-red (6,9,14). The continuous absorption finds its justification in hyperpolarizability by two effects. First of all, the hydrogen bond should be exceptionally sensitive to the field fluctuation caused by diffusional motions of dipoles and ions in the environment. Consequently, the diffusion of vibrational levels should take place. The interaction among easily polarizable hydrogen bonds can lead to similar results. Such interaction is referred to as protonic dispersion forces (correlations of proton tunneling). The sensitivity of hydrogen bonds to medium influences is proved by an exceptionally strong influence of the solvent electric permittivity on the proton transfer equilibrium (15,16). Up till now there has not appeared any reports about the influence the external field upon PT equilibrium.

EDA Complexes.

Contrary to the hydrogen bonded complexes, only two effects influence the charge distribution in EDA complexes, namely electrostatic (inductive) as well as the charge transfer effect CT. It appears that for weak EDA complexes, the dominant role is played by electrostatic effects. The charge transfer can be expressed by the following equation, according to the Mulliken's theory:

$$\mu_N = \mu_0 (a^2 + abS_{01}) + \mu_1 (b^2 + abS_{01}) \quad (3)$$

where μ_N indicates the dipole moment of EDA complex in the ground state; μ_0 and μ_1 - are dipole moments of the complex in the state without any charge transfer and with a full charge transfer; S_{01} - is the overlapping integral; a and b are constants of the wave equation $\psi_N = a\psi_0 + b\psi_1$. On the basis of Mulliken's theory a general expression can be formulated combining the enhancement of the dipole moment with formation enthalpy (17):

$$\begin{aligned}
 (\mu_N - \mu_0) \beta_0^2 / (\mu_1 - \mu_0) &= (\mu_1 - \mu_N)(1 - S_{01}^2) \Delta H^2 / (\mu_2 - \mu_0) - \\
 - [2(1 - S_{01}^2) W_0 (\mu_1 - \mu_N) / (\mu_1 - \mu_0) - S_{01} \beta_0] \Delta H + \\
 + (1 - S_{01}^2) W_0^2 (\mu_1 - \mu_N) / (\mu_1 - \mu_0) - S_{01} \beta_0 W_0
 \end{aligned} \quad (4)$$

where $\beta_0 = H_{01} - W_0 S_{01}$; H_{01} - is a resonance integral, and W_0 is the energy of interaction without charge transfer.

Simplifying assumptions made it possible to find simple correlations between $\Delta \bar{\mu}$ and ΔH . Thus, Guryanova et al. (18) showed that there should exist a linear dependence between these two values, on the other hand, Ratajczak et al. (19), using other simplifications, stated that there should exist a linear relationship between ΔH and $\sqrt{\Delta \mu_{CT}}$. A similar relation seems to be justified for the ionization potential of the donor and $\Delta \mu_{CT}$. Ratajczak provides data for iodine complexes with amines, which satisfy the above mentioned correlation. It seems noteworthy that also $\Delta \mu$ of hydrogen bonded complexes (20) can be described using the same formalism. This fact became the basis to treat both kinds of molecular complexes from the same point of view.

Recently, thorough dielectric and thermodynamic study has been carried out on iodine complexes with oxygen bases (17). Undoubtedly, in this case it is necessary to take into account considerable inductive moments often ranging above 1D. It appears that the inductive moments were underestimated in the cases of iodine complexes with amines. Although the dipole moments for amines are small, even while applying the classical view on point dipoles and polarizable centres, the moments of nitrogen lone electron pairs, which often reach several D, should be considered. In such cases induced moments greatly exceed 1D.

S_{01} in equation (4) is usually much smaller than 1, thus

$$(\mu_N - \mu_0) / (\mu_1 - \mu_0) = (\nabla^2 + \nabla S_{01} \beta_0) / (\nabla^2 + \beta_0) \quad (5)$$

where $\nabla = \Delta H - W_0$. This equation can be applied in numeral analysis.

Fig. 4 presents the results obtained for the dipole moments of iodine com-

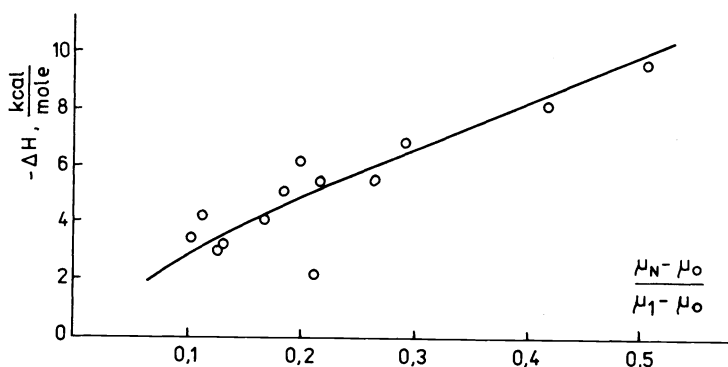


Fig. 4. Dependence of $-\Delta H$ on $(\mu_N - \mu_0) / (\mu_1 - \mu_0)$; theoretical curve (solid line) compared with experimental data

plexes with oxygen bases which are compared with the curve described by equation (5). Parameters S_{01} and W_0 in equation (5) equal respectively 0.22 and -0.2 kcal/mole. While calculating $(\mu_N - \mu_0)$ value, "cyclic" structure of complexes was assumed (Fig. 5). It should be mentioned, that there always exists some uncertainty as far as the spatial configuration of molecular complexes in solutions is concerned, which fact makes it difficult to provide a univocal interpretation of the experimental data.

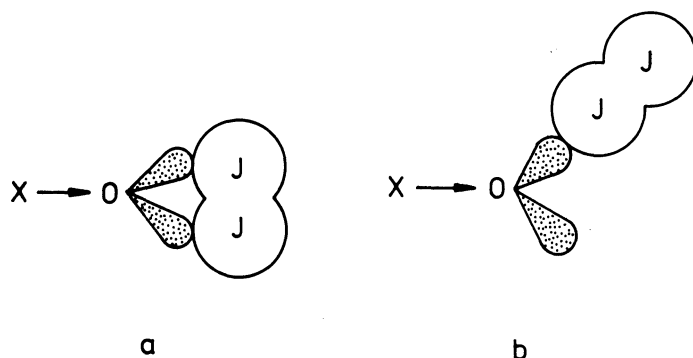


Fig. 5. Two possible structures of iodine complexes:
(a) - cyclic and (b) - inclined

SOLVENT EFFECT ON DIPOLE MOMENTS OF MOLECULAR COMPLEXES

Dipole moments of both HB and EDA complexes are greatly dependent upon the polarity of solvents. Especially susceptible to the solvent action are complexes of medium polarity: in the case of HB complexes - systems with proton transfer equilibrium; for EDA complexes - with approx. 50% of charge transfer (16,22,23).

Two kinds solvent effects can be distinguished: macroscopic effect, resulting from dielectric permittivity of the environment as a continuous medium, and specific interactions, leading to the formation of defined associates. The first effect seems to prevail whenever the solvent electric permittivity is relatively small and when the solvent molecules do not contain any active donor-acceptor groups. At the same time, the dipole moments of the complexes are large. The Onsager reaction field model can be used for the purpose of the present discussion. If two states for the hydrogen bonded complexes are considered: HB and PT, with dipole moments μ_0 and μ_1 , then the energy difference between these two states can be expressed by the following equation (16):

$$\Delta U/RT = \Delta U_0/RT - A (\epsilon - 1)/(2\epsilon + 1) \quad (6)$$

where ΔU_0 is the energy difference in a vacuum, and

$$A = 4\pi N (\mu_1^2 - \mu_0^2)/3RTV$$

As it follows from the above, the population of the two states strongly depends on their polarity. Moreover, analysis of the $(\epsilon-1)/(2\epsilon+1)$ parameter shows that the system is most sensitive to permittivity changes for small ϵ values, which fact is consistent with the experimental results. In this respect specially spectacular are the results obtained by Jadżyn and Małecki (16) concerning phenol complexes with amines. Fig. 6 sums up those results, presenting the relationship between the hydrogen bond polarity and the generalized $\Delta U/RT$ parameter.

Three groups of authors took up the problem of the solvent effect from a theoretical point of view (24-26). The starting-point for them is the Onsager reaction field model which leads to the non-linear Schrödinger equation:

$$\{H_0 - 2(\epsilon-1)/(2\epsilon+1) \cdot (1/a^3) \mu \langle \psi | \mu | \psi \rangle\} \psi = E\psi \quad (7)$$

where H_0 is the Hamiltonian for the system in vacuum, a - cavity radius; μ - dipole moment operator. If we assume the wave function according to Mulliken's theory $\psi = a\psi_0 + b\psi_1$ (24) then the result is quantitatively consistent with the hitherto obtained observations.

A more general form of the non-linear Schrödinger equation

$$\{H_0 - g \mu \langle \psi | \mu | \psi \rangle\} \psi = E \psi \quad (8)$$

contains tensor g , which is the reaction field susceptibility, i.e. a parameter that in general terms expresses the coupling between the molecular

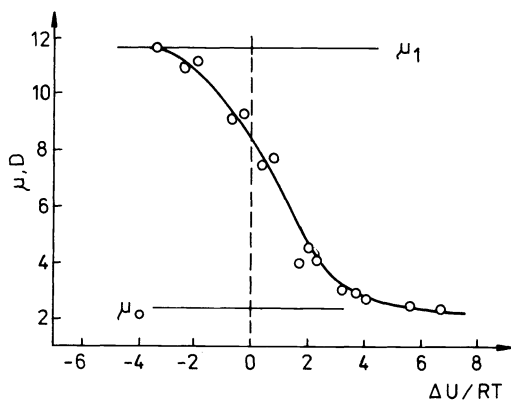


Fig. 6. A plot of $\Delta\mu^\ddagger$ versus $\Delta U/RT$ for phenols-triethylamine complexes in various solvents (16)

system under consideration and the polarizable environment. It is difficult to say whether such a treatment allows us to consider cases of specific solute-solute-solvent interactions.

It seems, however, that in such cases it is more advisable to treat the molecular complex - solvent molecules as a supermolecule and to apply to it the Monte-Carlo method or the molecular dynamics method (27, 28). On the other hand, it is quite effective to use empirical parameters of the solvent activity. We would like to present here two representative examples of HB and EDA complex solutions for which the solvent effect upon the dipole moment should be treated as typically specific. It follows explicitly from the data obtained for p-nitrophenol complex with triethylamine (22) that for a wide group of solvents the Onsager model is not sufficient. For the sake of comparison, Fig. 7 presents the correlation between the dipole moment and Onsager parameter $(\epsilon-1)/(2\epsilon+1)$,* and the macroscopic parameter of the solvent, i.e., the frequency of the $\pi \rightarrow \pi^*$ transition. An equally good correlation

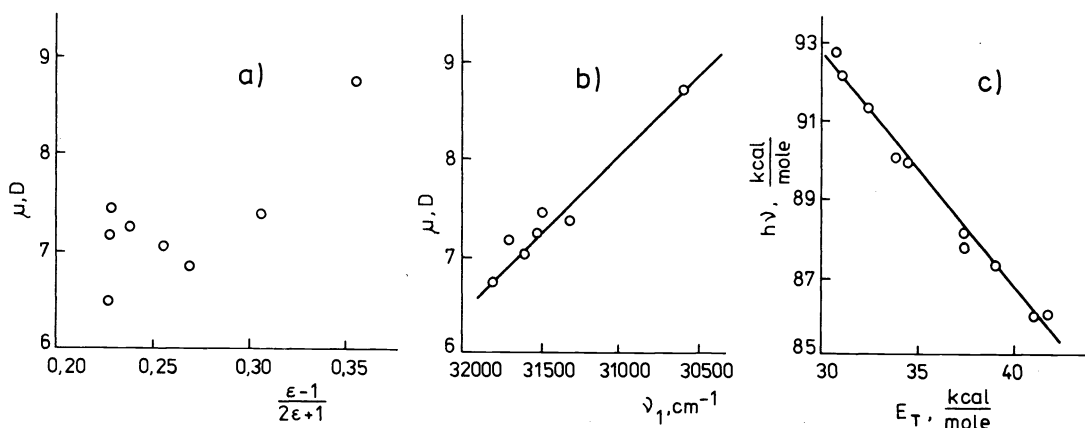


Fig. 7. Dipole moment of PNPB·TEA complex correlated with Onsager parameter (a) and frequency of $\pi \rightarrow \pi^*$ transition (b); correlation between $h\nu$ of $\pi \rightarrow \pi^*$ transition and E_T parameter (c)

can be achieved if other macroscopic parameters of the solvent are considered, eg. E_T or OH stretching frequency in the complex. Most data concerning the solvent effect on the dipole moment of EDA complex were obtained for J_2 -pyridine complex (23). For complexes of iodine with other amines the results are uncertain because of the chemical reactions taking place, especially in more polar solvents. Even in the case of EDA complexes the application of the Onsager reaction field model is not sufficient. On the other hand, the dipole moment correlates well with empirical parameters, among which the most important one is the rate constant of the Menshutkin reaction k_M . Fig. 8 presents this correlation. It is only natural that there exists a good correlation between μ and k_M because the

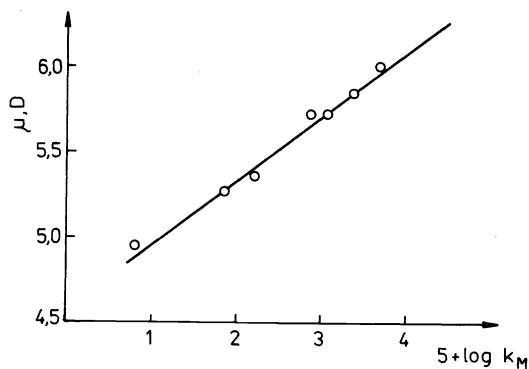


Fig. 8. Correlation between the dipole moment of pyridine- J_2 complex and the rate constant of Menshutkin reaction k_M

transition complex, which is formed in the course of the Menshutkin reaction, has the charge distribution similar to that of J_2 -amine complex.

NON-LINEAR DIELECTRIC EFFECTS (NDE)

The non-linear dielectric effect is characterized by $\Delta\epsilon/E^2$ value, where $\Delta\epsilon$ is the change of permittivity in a strong external field, or by the mole constant of the non-linear effect defined as a derivative of molar dipolar polarization in relation to the square of the local field - F

$$S_{\text{mole}} = \partial P_{\text{dip}} / \partial (F^2) \quad (9)$$

A "normal" non-linear effect for the weakly polar substances with rigid molecules and Debye type dipole orientation are described by the second part of the extension of Langevin function:

$$\langle \mu \rangle_E = (\mu^2/3kT - \mu^4 F^2/45k^3 T^3 + \dots) F \quad (10)$$

where $\langle \mu \rangle_E$ is the mean value of the projection of the moment on the direction of the external field E .

Deviation from a "normal" behaviour of the dielectrics can be best expressed using non-dimensional number R_S , defined as NDE correlation factor

$$R_S = S_{\text{mole}}/S_r ; \quad S_r = -4\pi N \mu^4 / 45k^3 T^3 \quad (11)$$

For an ideal case R_S value should equal unity in the whole concentration range. Even for non-associated liquids, however, a slight deviation from the ideality can be observed as the concentration of the polar substance increases in a non-polar solvent, $0 < R_S < 1$ (curve (i), Fig. 9). In the case of strongly polar substances, such as nitrobenzene, the deviation is so strong that the sign of $\Delta\epsilon/E^2$ changes; R_S for high concentrations becomes negative (curve (ii)). Strong coupling of the dipoles leads to the formation

of less polar aggregates, e.g., anti-parallel pairs which are not rigid: under the influence of a strong field, the aggregates decompose to their initial polar molecules, which fact leads to the enhancement of permittivity (29).

Also the behaviour of non-rigid molecules with rotating polar groups can be explained in simple terms. The positive non-linear effect, i.e., negative R_s value, in this sort of compounds (curve (iii)) can be described accurately assuming the influence of the electric field upon the trans-gauche conformation equilibrium.

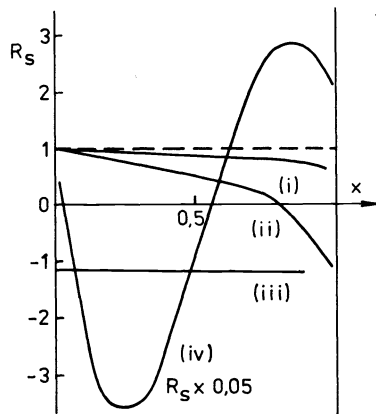


Fig. 9. Four types of the dependence of R_s on molar fraction (36)

Strongly associated liquids, such as water and alcohols, display particular non-linear properties. Curve (iv) illustrates a typical course of R_s following the concentration changes for this type of substances. The first attempt of explaining the "anomalous" behaviour of alcohols in strong fields was to assume the field induced proton transfer (31). According to the studies performed, alcohol dimers should play a particular role in the anomalous non-linear effect. The field induced proton transfer presented in Fig. 10 leads to the formation of a strongly polar species ($\sim 14D$) and this fact should explain the strongly positive non-linear effect.

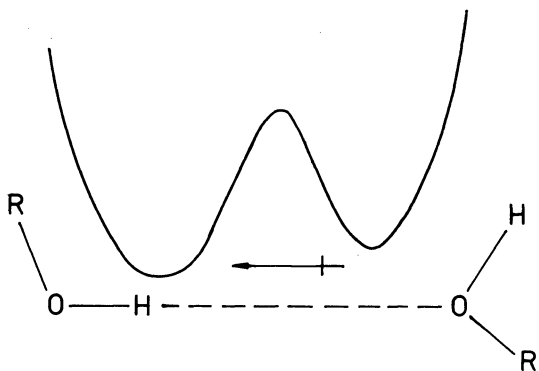


Fig. 10. Field induced proton transfer in alcohol dimers

Recently this view has been a subject of critical analysis. It was stated that one of the basic factors governing the anomalous positive NDE is the field influence on the chemical and association equilibria (33-35). The free energy change caused by an applied electric field is expressed by the equation:

$$F = -\frac{F^2}{6kT} \sum_i N_i \mu_i^2 \quad (12)$$

where N_i - number of molecules with dipole moment μ_i , F - local field. The form of this expression for the dependence of ΔF upon external field E depends on the accepted model of the internal field

$$\Delta F = -f(\epsilon, \epsilon_\infty) \cdot (E^2/T) \sum_i N_i \mu_i^2 \quad (13)$$

where $f(\epsilon, \epsilon_\infty)$ - is a coefficient dependent on ϵ and ϵ_∞ . If the equilibrium compounds differ as far as their dipole moments are concerned then the field shifts the equilibrium toward the more polar components. According to Małeckı (35) the equilibrium model explains all non-linear dielectric phenomena in liquids. Some doubts concerning the role of field induced proton transfers increased after dielectric studies in a strong electric field had been done for phenol-amine complexes where the proton transfer equilibrium had been undoubtedly stated in several cases. It became apparent (36, 37) that such complexes behave normally, with no positive effect that could prove the non-rigidity of the molecule. The most probable explanation of such behaviour is the great rate of proton jumping, considerably higher than the reciprocal of the dielectric relaxation time. Although the chemical model seems to be perfectly adequate for the purpose of describing non-linear effects in various liquid systems, other ways of approaching this problem should not be neglected. Particularly interesting appears to be the approach based on the theory of associated liquids, the so-called theory of significant structures, formulated by Danielewicz-Ferchmin (38). The expression of $\Delta\epsilon/E^2$ has the following form:

$$\Delta\epsilon/E^2 = -(4\pi N/V) \cdot f(\epsilon, \epsilon_\infty) [(V_s/V_l)\varphi + (V_l - V_s)/V_l\kappa] \quad (14)$$

where V_l and V_s are molar volumes of liquid, and solid states,

$$\varphi = \mu^2 p^3 \cos^4 \nu / k^3 T^3, \quad \kappa = \mu^2 / 15k^3 T^3;$$

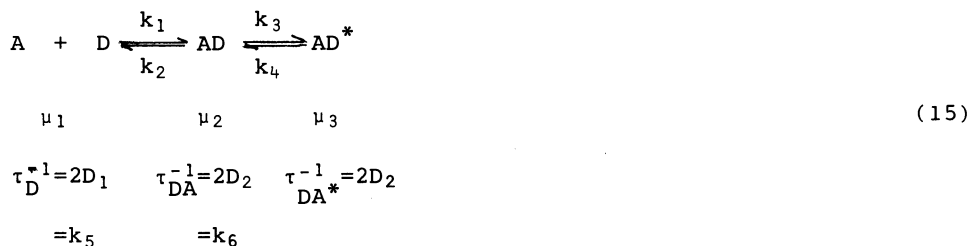
ν is a mean angle between the dipole and the direction of maximum domain polarization; p - number of orienting molecules.

It appears that for more diluted solutions the equilibrium conceptions is more appropriate but for pure associated liquids the use of liquid models taking into consideration quasi-crystalline molecule order proves to be of greater value.

DIELECTRIC RELAXATION AND MOLECULAR INTERACTIONS

Many reviews have appeared recently discussing in detail the theory of dielectric relaxation in regard to molecular interactions and properties of associated liquids (39,40). So far there exists no clear interpretation for the measurements of dispersion and dielectric absorption of alcohols. There are arguments both for the conception of ordered domains and for the conception of association equilibria between defined associates. As it has been already demonstrated in the previous sub-sections, the controversies include also the non-linear effects. The present survey is limited only to chosen aspects of complex electric permittivity, mainly in regard to the problems discussed in previous sections.

Let us consider an interaction leading to the formation of simple molecular complexes AD (in general, A indicates an acceptor, D - donor), including the "chemical exchange" (44-47) as an active relaxation process:



Let us assume that the dipole moment of the acceptor equals zero, then μ_1 indicates the moment of the donor. Six rate constants define the dynamics of the system, where the last two constants k_5 and k_6 are defined by diffusion reorientation constants of the dipoles μ_1 and μ_2 . In general,

AD* is the conformational state of AD molecule differing as far as the dipole moment is concerned e.g. it can be a state of a hydrogen bonded complex in the form of an ion pair. The assumption that the reorientation rate constant k_6 for AD is the same as for AD seems to be well-substantiated. Let us assume that there is no correlation between dipoles, except for those which are introduced by the process of chemical exchange, and finally that the local field effect can be neglected. These assumptions make it possible to formulate the dipole moment autocorrelation function and to undertake the numeric analysis. Such an analysis displays the fact that dielectric properties depend on the relation between chemical exchange rate constants and reorientation rate constants. Therefore, most often, when the reorientation rate constants are much higher than the exchange rate constants, only dispersion ascribed to the dipole reorientation can be observed and, at the same time, the dielectric increment is proportional to the concentration and to the square of dipole moments. Let us, consider, however, a more general case, when $k_1, k_2 < 2D_2$ and $k_3, k_4 > 2D_1$. It should be emphasized that other combinations are reduced to this case because of very large or very small equilibrium constants for both stages of the reaction expressed by equation (15). Thus, dielectric losses are described by the equation:

$$\begin{aligned} \epsilon''/(\epsilon_0 - \epsilon_\infty) = & [C_1^0 \mu_1^2 / (C_1^0 \mu_1^2 + C_2^0 \mu_2^2 + C_3^0 \mu_3^2)] \cdot \omega \tau_1 / (1 + \omega^2 \tau_1^2) + \\ & + \{ [1 / (C^0 - C_1^0)] \cdot (C_2^0 \mu_2 + C_3^0 \mu_3)^2 / (C_1^0 \mu_1^2 + C_2^0 \mu_2^2 + C_3^0 \mu_3^2) \} \cdot \omega \tau_2 / (1 + \omega^2 \tau_2^2) + \\ & + \{ [C_2^0 \cdot C_3^0 / (C^0 - C_1^0)] \cdot (\mu_3 - \mu_2)^2 / (C_1^0 \mu_1^2 + C_2^0 \mu_2^2 + C_3^0 \mu_3^2) \} \cdot \omega \tau_3 / (1 + \omega^2 \tau_3^2) \end{aligned} \quad (16)$$

which means that there may appear three relaxation times: $\tau_1^{-1} = 2D_1$, $\tau_2^{-1} = 2D_2$, $\tau_3^{-1} = 2D_2 + k_3 + k_4$, where $C^0 = C_1^0 + C_2^0 + C_3^0$, and C_1^0 , C_2^0 and C_3^0 are equilibrium concentrations D, DA and DA*. Contributions of these relaxation processes to the total losses depend on the concentrations of two forms and their dipole moments. For the cases when stable AD complexes are formed (low concentration of the donor) equation (16) is reduced to:

$$\begin{aligned} \epsilon''/(\epsilon_0 - \epsilon_\infty) = & [(1/C^0)(C_2^0 \mu_2 + C_3^0 \mu_3)^2 / (C_2^0 \mu_2^2 + C_3^0 \mu_3^2)] \cdot \omega \tau_2 / (1 + \omega^2 \tau_2^2) + \\ & + [(C_2^0 \cdot C_3^0 / C^0)(\mu_3 - \mu_2)^2 / (C_2^0 \mu_2^2 + C_3^0 \mu_3^2)] \cdot \omega \tau_3 / (1 + \omega^2 \tau_3^2) \end{aligned} \quad (17)$$

which means that there should be only two relaxation times: τ_2 and τ_3 . Cases when chemical exchange rate constants k_1, k_2, k_3 and k_4 contribute considerably to the dielectric losses seem to be rare. Let us first consider cases where intercomplex transition $AD \rightleftharpoons AD^*$ leading to the increase of the dipole moment is possible, and omit those when k_3 and k_4 are comparable with D_2 because then the dispersion ranges related to τ_2 and τ_3 relaxation times overlap. Furthermore, the contribution of the process with τ_3 depends on dipole moment μ_{DA^*} and on the mole fraction x_{DA^*}

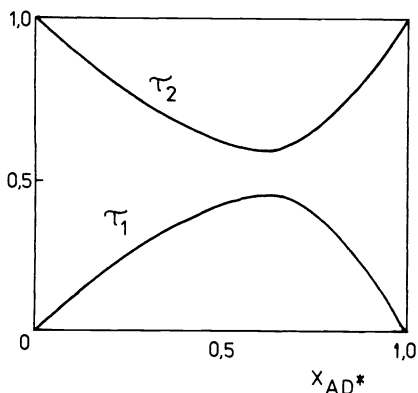


Fig. 11. Contributions of two relaxation mechanisms in relation to molar fraction of AD*

Calculations done for $\mu_{DA} = 2.6D$ and $\mu_{DA}^* = 11.6D$ (an actual example for the complex of phenol with triethylamine) resulted in plots of relative contributions of losses shown in Fig. 11 (47).

The diagram proves that losses ascribed to the τ_3 mechanism are always smaller than those connected with reorientation of AD molecules and that the systems with equilibrium constant for the process $AD \rightleftharpoons AD^*$ ranging between 0.1 and 1 display highest contribution on the dielectric absorption. At the same time, the analysis shows that the maximum contribution of the τ_3 mechanism to the absorption occurs for the condition $k_3/k_4 = \mu_{DA}/\mu_{DA}^*$. As it follows from the discussion in the first section, complexes of phenol with amines from inversion range $\Delta\mu$ fully satisfy the conditions for the greatest contribution of the proton transfer mechanism to the total dielectric absorption. Experimental facts seem to support this conclusion (47). In the case of weak complexes, when their life-time is shorter (or comparable) than that of reorientation relaxation, there can occur an absorption defined by the kinetics of complex formation. The relationship between the complex permittivity and frequency, when the complex components are non-polar, assumes the form (42)

$$(\epsilon^* - \epsilon_\infty) / (\epsilon_0 - \epsilon_\infty) = [K / (1+K)] \cdot 1 / (1+i\omega\tau_{DA}) + [1 / (1+K)] \cdot 1 / (1+i\omega\tau_2) \quad (18)$$

where K is the equilibrium constant of reaction $A+D \rightleftharpoons AD$; τ_{AD} is the reorientation relaxation time of complex AD ; $\tau_2^{-1} = \tau_{AD}^{-1} + \tau_{chem}^{-1}$; the chemical exchange relaxation time, τ_{chem} is defined by k_1 and k_2 . This equation shows that for small K values the contribution to the absorption of the reorientation process AD is not detectable, i.e., the dielectric absorption results from the chemical exchange process. For intermediate equilibrium constants the life-time of the complex and the relaxation time are comparable so that one absorption range is observed in practice. In two cases described up to date the conditions are fulfilled for the "kinetic" contribution to the dielectric absorption process, namely in solutions of such electron acceptors as TCNE in mesitylene and dioxane (48), as well as chloroform in non-polar proton acceptors (mesitylene, dioxane) (49). In such a case, however, it is necessary to consider also the reorientation relaxation of non-complexed chloroform molecules.

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