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COMPETITIVE PREFERENTIAL SOLVATION THEORY AND ITS USE IN THE STUDY OF MOLECULAR ASSOCIATIONS

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When studying weak molecular interactions (charge-transfer complexes) it is frequently necessary to use high concentrations of one of the interacting species in order to determine physico-chemical properties of these associations. Therefore the reliability of the results obtained might be questionable. In fact their concentration dependence has been established and the anomalies observed have been interpreted in various terms such as deviation from ideality, non-validity of Beer's law, presence of higher-order complexes, change of solvent coordination number, contact interactions, etc... (1). We wish to propose here a new theory called "the Competitive Preferential Solvation Theory" (COPS theory), which can easily account for these anomalies. It can be used with any experimental technique. COPS theory is based on the following postulates: 1) In a solvent mixture the constituents (j, k...) compete for the solvation of the solute molecules (i) following their electronic-geometric affinity $\kappa_{i(j)}$ which is constant at constant temperature and pressure. 2) The actual composition of the solvation shell is determined by the affinity constant and the concentration of each solvent component (C_j, C_k...). 3) The real picture may be represented mathematically as if the solute concentration C_i were partitioned between the different solvent components (j, k...): $C_i = X_{i(j)} + X_{i(k)} + \ldots$ where $X_{i(j)} = C_i \dfrac{\kappa_{i(j)} C_j}{\kappa_{i(j)} C_j + \kappa_{i(k)} C_k + \ldots} = C_i P_{i(j)}$. Following this generalized partition there are no "free" solute molecules present in the solution. 4) Since the solvent molecules relax statistically between complexing-solvating states, the definite stoichiometry of complexes cannot be considered explicitly (2). 5) The effects of solvent components on chemical reactivities of the solute are additive. In a binary mixture the reactivity $k_{i(j+k)}$ is the sum of the reactivities in pure solvents, $k_{i(j)}$ and $k_{i(k)}$ weighted by the partitioning factors $P_{i(j)}$ and $P_{i(k)}$: $k_{i(j+k)} = P_{i(j)} k_{i(j)} + P_{i(k)} k_{i(k)}$.

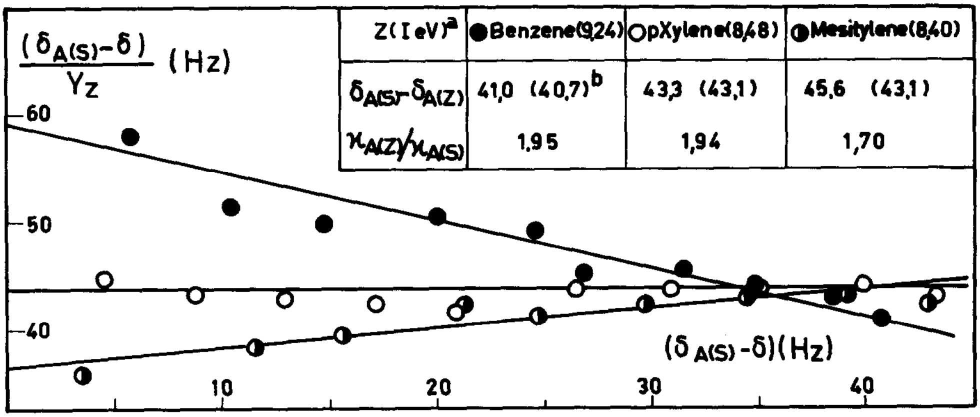
Applications: 1) NMR spectroscopy. The complexation of substituted N-methylphthalimides (A) by aromatic π-donors (Z) is studied in CH_2Cl_2 (S) at T = 25° C. Only one time-averaged solvated species is detected. Therefore the equilibrium chemical shift (δ) of A is :
$\delta = P_{A(S)} \delta_{A(S)} + P_{A(Z)} \delta_{A(Z)}$ i.e. it is the weighted sum of the chemical shifts measured in pure S ($\delta_{A(S)}$) and pure Z ($\delta_{A(Z)}$). The analysis completed following COPS theory leads to the following equation :

$$\frac{(\delta_{A(S)} - \delta)}{Y_Z} = \frac{\kappa_{A(Z)} \nu_S}{\kappa_{A(S)} \nu_Z} (\delta_{A(S)} - \delta_{A(Z)}) - \left(\frac{\kappa_{A(Z)} \nu_S}{\kappa_{A(S)} \nu_Z} - 1\right)(\delta_{A(S)} - \delta) \qquad \text{(I)}$$

Y_Z is the volume fraction of Z; v_j represents the molar volume of solvent component j. This equation corresponds to the classical Scatchard equation

$$\frac{\delta_A - \delta}{Y_Z} = \frac{K}{v_Z}(\delta_A - \delta_{AZ}) - \frac{K}{v_Z}(\delta_A - \delta) \qquad \text{(II)}$$

where $\delta_A = \delta_{A(S)}$, K is the stability constant of the 1:1 complex AZ and δ_{AZ} is its chemical shift. The plot $(\delta_{A(S)} - \delta)/Y_Z$ vs. $(\delta_{A(S)} - \delta)$ gives a straight line in the whole concentration range. This means that the affinity ratios obtained $\varkappa_{A(Z)}/\varkappa_{A(S)}$ are independent of the medium. The intercepts yield $(\delta_{A(S)} - \delta_{A(Z)})$ values which are the same as the differences of shifts measured in the two solvents separately ! Therefore it is not surprising that the δ_{AZ} values reported in the literature could not be simply interpreted theoretically. The new equation accounts easily also for "negative" or "zero" stability constants in the classical sense (Fig. 1).



$Z(I\,eV)^a$	● Benzene(9,24)	○ pXylene(8,48)	◐ Mesitylene(8,40)
$\delta_{A(S)}-\delta_{A(Z)}$	41,0 (40,7)^b	43,3 (43,1)	45,6 (43,1)
$\varkappa_{A(Z)}/\varkappa_{A(S)}$	1,95	1,94	1,70

FIG. 1. NMR Scatchard plots for the complexes aromatics-N-methylphthalimide (equ. I) in dichloromethane (S) at 25° C (C_A = 5.10^{-2} mole l^{-1}); a) ionization potential of the donor; b) chemical shift differences measured separately in pure solvents.

2) UV spectroscopy. This technique is able to detect several solvated species i.e. "charge-transfer complexed" ($X_{A(Z)c}$) and "uncomplexed" solute ($X_{A(Z)s} + X_{A(S)}$). If the absorbancy ($\mathcal{A}$) is due entirely to the charge-transfer complex ($X_{A(Z)c}$), COPS theory gives the following equation:

$$\frac{\mathcal{A}}{C_Z} = \varepsilon_{A(Z)c}\,\frac{\varkappa_{A(Z)c}}{\varkappa_{A(S)}}\,v_S C_A - \left(\frac{\varkappa_{A(Z)}}{\varkappa_{A(S)}}\,v_S - v_Z\right)\mathcal{A} \qquad \text{(III)}$$

$\varepsilon_{A(Z)c}$ is the molar extinction coefficient of the complexed species ($X_{A(Z)} = X_{A(Z)c} + X_{A(Z)s}$)

The classical Scatchard equation is: $$\frac{\mathcal{A}}{C_Z} = K\,.\,\varepsilon\,.\,C_A - K\mathcal{A} \qquad \text{(IV)}$$

The new equation yields an apparent extinction coefficient $\varepsilon^{app}_{A(Z)c} = \varepsilon_{A(Z)c}\cdot\frac{\varkappa_{A(Z)c}}{\varkappa_{A(Z)}}$ and the affinity ratio $\varkappa_{A(Z)}/\varkappa_{A(S)}$. Despite the fact that the various solvated (complexed) species can be detected and measured separately by UV spectroscopy, the result is the same as for NMR (global measurement): only the partitioning of solute between S and Z can be obtained. By comparing classical and new Scatchard equations (I, II, III and IV) one obtains the following relationships:

$$K = \frac{\varkappa_{A(Z)}}{\varkappa_{A(S)}} \upsilon_S - \upsilon_Z \ ; \ (\delta_A - \delta_{AZ}) = \frac{(K + \upsilon_Z)}{K} (\delta_{A(S)} - \delta_{A(Z)}); \ \varepsilon = \varepsilon^{app}_{A(Z)c} \ \frac{(K + \upsilon_Z)}{K}$$

One can see that ε increases with temperature (K decreases) for weak associations ($K \leqslant \upsilon_Z$) what is explained classically by the presence of contact charge-transfer interactions. The partial molar volume of the donor strongly influences ε and K, this latter may even be negative, positive or zero. The classical intervention of higher order complexes is not necessary. Finally NMR can be successfully used to determine partial molar volumes. It is seen that if one neglects the real structure of solutions (classical treatement), the various techniques (UV, NMR) yield parameters (K, ε , δ_{AZ}) which have not the meaning one attributes to them in the case of weak interactions. This might explain the difficulties met when comparing experiment with theory.

3) Kinetics: The rate and mechanism of the n-butylaminolysis of substituted N-alkyl phthalimides in organic aprotic media (pure and mixed solvents) can be characterized by the following facts: the reaction is of first order in imide (A) and of third order in amine (B); the n- π type charge-transfer complex (AB) formed between the reagents is a true reaction intermediate (3). When the dielectric constant is maintained at a fixed value, these characteristics remain the same in the whole amine concentration range (amine profile determined up to volume fraction Y_B = 0, 8). This lack of sensitivity of kinetic parameters (k_S, k_Z, $\varkappa_{AB(Z)}/\varkappa_{A(Z)}$, $\varkappa_{AB(S)}/\varkappa_{A(S)}$) to amine concentration shows a complete independence from the bulk polarizability of the medium. The amine does not seem to play an important role in the solvation shell. By gradually replacing an "inert" solvent (cyclohexane, S) by a π-donor solvent (aromatic, Z), the pseudo-first order rate constant $k_{1(S+Z)}$ decreases with increasing aromatic solvent concentration (C_Z). The usual linearizing procedure (plot of $k_1^{-1}{}_{(S+Z)}$ vs. C_Z) results in a upward curvature. However theory predicts only downward curvatures or a straight line ! Following COPS theory the rate constant in a solvent mixture (S+Z) may be written:

$$k_{1(S+Z)} = \frac{(k_S \varkappa_{AB(S)} C_S + k_Z \varkappa_{AB(Z)} C_Z) \ C_B{}^3}{(\varkappa_{A(S)} + \varkappa_{AB(S)} C_B) C_S + (\varkappa_{A(Z)} + \varkappa_{AB(Z)} C_B) C_Z} .$$

This equation can be easily linearized in function of C_Z. It turns out that k_S and k_Z are the same as the rate constants measured separately in the respective pure solvents ! For example one obtains for the reaction of tetrachloro-N-butylphthalimide in mixed solvent: $k_{1(S)}$ = 0, 429 min^{-1} and $k_{1(Z)}$ = 0, 050 min^{-1} ; the values obtained separately in pure solvents are 0, 433 min^{-1} and 0, 050 min^{-1} respectively (T = 20° C; Z = benzene).

4) The various affinity constant ratios obtained from kinetics were confirmed by partition constant measurements (classically: $C_{A(Z)} / C_{A(S)}$; COPS theory: $\varkappa_{A(Z)}/\varkappa_{A(S)}$; non-miscible

partner: formamide S):

$$\frac{C_{A(Z)}}{C_{A(S)}} = \frac{\varkappa_{A(Z)}\, C^*_Z}{\varkappa_{A(S)}\, C^*_S}$$

where asterisk designates molar concentration of pure solvent. The affinity constant ratios decrease as expected with increasing ionization potential (I) of aromatic solvents. Fig. 2 shows good agreement between the results obtained by various techniques supporting the validity of COPS theory.

The present treatment is valid for regular solutions (volume of mixing $\Delta V = 0$). Therefore the deviations from COPS theory permit the detection of anomalies such as the variation of partial molar volumes and affinity constants with solvent composition. For example in the case of the systems benzene-mesitylene and benzene-1-methylnaphthalene neither the kinetic nor the NMR equations can be linearized.

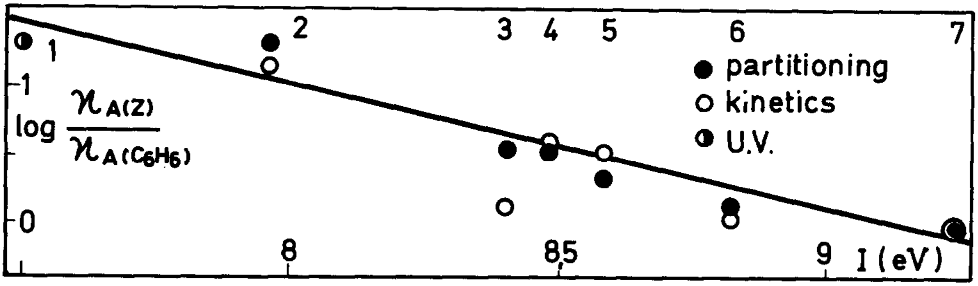


FIG. 2. Dependence of relative affinity constants on donor ionization energies for the complexes aromatics-tetrachloro-N-butylphthalimide at 20° C (1: pyrene; 2: 1-methylnaphthalene; 3: mesitylene; 4: p.xylene; 5: m.xylene; 6: toluene; 7: benzene).

+ Taken in part from Ph. D. Thesis of MUKANA wa MUANDA, U. C. L., Louvain-la-Neuve, (1974).

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