fore, the self-diffusion coefficient correlates with relaxation rate. In the case of ethanol, however, both the relaxation rates of $-CD_3$ and $-CD_2$ did not show the maximum but decreased with increasing the concentration of methanol.

References

1 D. E. O'Reilly and E. M. Peterson, *J. Chem. Phys.*, *55*, 2155 (1971).

2 E. von Goldammer and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, *73*, 4 (1969).

Dynamical Properties of Pyrrole Dissolved in C_2Cl_4 and CH_3CN

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The aim of this paper is to examine the influence of the 'inert' solvent as C_2Cl_4 and 'active' solvent as CH_3CN on the relaxation time of pyrrole.

On the basis of the line-shape analysis imido protons (scalar relaxation of the second kind) relaxation and correlation times of pyrrole in the mentioned solvents have been calculated.

The dependence of the line-shape on solute concentration and temperature was studied and the activation parameters for molecular reorientation of pyrrole determined.

Influence of the Solvent on the Polarity of Hydrogen Bonded Complexes

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The dipole moments of complexes between carboxylic acids and triethylamine were determined in both binary mixtures and in cyclohexane and benzene solution. If a carboxylic acid is dissolved in pure triethylamine, it forms mainly a 1/1 complex of dipole moment μ_{ab}. This dipole moment and that of the pure base μ_B can be computed in the following way; one determines the experimental quantity Ω_B from the dielectric constant ϵ, the refractive index and the molar volume $\bar{V}$ of the solutions:

$$\Omega_B \equiv \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2+2)^2} \; \frac{\bar{V}}{x_B} \; \frac{9 \cdot 10^{36} kT}{4\pi N}$$

x_B being the mole fraction of the base.

If the dipole moments remain unchanged this quantity must vary linearly with the ratio x_A/x_B accordingly to the equation

$$\Omega_B = \mu_B^2 + (\mu_{ab}^2 - \mu_B^2)\,\frac{x_A}{x_B}$$

Actually the relation is not perfectly linear but shows a slight upward curvature. This can be interpreted as resulting from the influence of the increasing of the *dielectric constant* of the medium *on the dipole moment μ_{ab} of the complex.*

For acetic, propanoic, butanoic and pentanoic acid, the pK_a's of which are very similar, the points of the function $\Omega_B = f(x_A/x_B)$ lie on the same curve, indicating that the dipole moment μ_{ab} of the 1/1 complex at a given value of the dielectric constant is nearly the same for the four acids.

As a first approximation μ_{ab}^2 appears to be a linear function of the reverse of the dielectric constant. The derivative $d\mu_{ab}^2/d\epsilon^{-1}$ is of the order of 13 D^2. The same quantitative relation holds for the complexes dissolved in cyclohexane.

In benzene the derivative is smaller but the moment is markedly higher. This is explained as resulting from specific interactions between the solvent and the ab complex. Presumably these interactions involve the π electrons of benzene and the lone pair of electrons of the C=O group of the complex.

Specific Interactions of Pyridinium Ions and Pyridine Molecules in Nitrobenzene. Substituent Effects

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From conductance measurements of a series of pyridinium picrates in nitrobenzene solutions, the equilibrium constants of the following hydrogen bonding reactions were estimated for each system:

(*1*) the molecular acid–base association constant K_f,

$$\mathrm{HPic} + \mathrm{Py} \xrightleftharpoons{K_f} \mathrm{PyHpic},\; K_f = \frac{[\mathrm{PyHPic}]}{[\mathrm{HPic}]\,[\mathrm{Py}]}$$

(*2*) the ionic association constant K_a,

$$\mathrm{PyH^+ + Pic^- \underset{}{\overset{K_a}{\rightleftharpoons}} PyHPic,\ K_a = \frac{[PyHPic]}{[PyH^+]\,[Pic^-]\,f_\pm^2}}$$

(*3*) the homoconjugation constant K_1^+

$$\mathrm{PyH^+ + Py \overset{K_1^+}{\rightleftharpoons} (PyHPy)^+,\ K_1^+ = \frac{[PyHPy^+]}{[PyH^+]\,[Py]}}$$

In addition to these, the formation of 1:2 complexes between the pyridinium ion and the pyridine molecule is observed in the case of 3,4-dimethylpyridine and 4-dimethylamino pyridine. This may be explained in terms of π–π interactions between the second pyridine molecule and that already bound to the cation by a hydrogen bond.

Plots of $\log K_f$, $\log K_a$ and $\log K_1^+$ *vs.* aqueous pK_a s values of the pyridines yield straight lines with slope of 1.167, –0.218 and 0.061 respectively. The results show that the hydrogen bond formation between pyridine and picric acid in nitrobenzene increases with increasing basicity of the pyridine molecule. The value of the first slope indicates that the proton transfer is important. The ionic association between the pyridinium cation and the picrate anion increases with increasing acidity of the cation. In the case of the formation of the homoconjugate cation $PyH^+\cdots Py$ it was expected that the substituent effects will be small, because the increasing proton donor ability of the cation will be compensated by the decreasing proton acceptor ability of the conjugate base. It is interesting to note that, contrary to this expectation, the stability of the non-*ortho* substituted homoconjugate cation increases, although to a small extent, with the basicity of the pyridine. This is explained by considering the potential energy curve of the proton for the homoconjugate cation. The increase of the depth of the potential well resulting from the hydrogen bond formation is more important when the pyridine is more basic.

A Study of the Solvent Effect on the Raman Parameters of Halogen and Interhalogen Vibration Bands

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The ν_{Br-Br} Raman band of bromine dissolved in several solvents was studied. The observed frequency shifts relative to the gas phase value were correlated with the Krikwood–Bauer–Magat function:

$$\frac{\Delta\nu}{\nu} = C\,\frac{\epsilon - 1}{2\epsilon + 1}$$

Important deviations were observed for the solvents which are known to form specific charge transfer complexes with bromine, and also for CS_2.

The absolute intensity of the bromine Raman vibration band was calculated from relative intensity measurements. Also the depolarization degree ρ was measured. These measurements allowed to calculate the polarizability derivatives $(\alpha'_R)_\parallel$ and $(\alpha'_R)_\perp$.

The ρ factor increases when the polarity of the solvent increases or when specific interactions bromine–solvent occur. Two different relations for the inert solvents and for the interacting solvents were observed on comparing ρ with $\Delta\nu/\nu$. This must be explained by the increase of the parallel polarizability component $(\alpha'_R)_\parallel$ as a result of the specific interaction with the solvent.

The half band width of the bromine band was found to be smaller than the corresponding infrared band and this is explained by the fact that the Raman band is only partially polarized. The relation between the increase of the half band width and the ρ value supports this explanation.

The results for the ν_{Br-Br} band are compared with those of a new study on the ν_{I-Br} band parameters in these solvents.

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Specific Interactions of Trifluoroacetate Ion and Trifluoroacetic Acid in Nitrobenzene

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The conductances of solutions of triethylammonium trifluoroacetate ($Et_3NHCOOCF_3$) in nitrobenzene have been measured in order to study the ionic association:

$$\mathrm{Et_3NH^+ + CF_3COO^- \overset{K_A}{\rightleftharpoons} Et_3NH^+\cdots{}^-OOCCF_3}$$

Using the Fuoss linear relationship [1] for solutions covering the concentration range 10^{-4}–10^{-3} *M*, the association constant K_A has been evaluated ($K_A = 3\cdot10^5$ dm^3 mol^{-1}). This constant is two orders of magnitude greater than that observed for triethylammonium picrate in the same solvent [2] (HPic and CF_3COOH have the same aqueous pK_a's values). For salt concentrations ranging from 10^{-3} to 5.10^{-3} *M*