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

HALINA M. RATAJCZAK

Institute of Chemistry, University of Wrocław, Wrocław, Poland

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

PIERRE HUYSKENS, MARIE-CLAIRE HAULAIT-PIRSON and FRANCOIS KAPUKU

University of Leuven, Department of Chemistry, Celestijnenlaan 200F, 3030 Heverlee, Belgium

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

M. Cl. HAULAIT-PIRSON

University of Leuven, Department of Chemistry, Celestijnenlaan 200F, 3030 Heverlee, Belgium

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,

$$\text{HPic} + \text{Py} \overset{K_f}{\rightleftharpoons} \text{PyHpic}, \; K_f = \frac{[\text{PyHPic}]}{[\text{HPic}]\,[\text{Py}]}$$

(*2*) the ionic association constant K_a,