Thermodynamic Properties of Solutions

Self-Association of 4-R-Pyridine N-Oxide Trifluoroacetates in Benzene

M. SZAFRAN, Z. DEGA-SZAFRAN and M. KREGLEWSKI

Institute of Chemistry, A. Mickiewicz University, 60780 Poznán, Poland

A series of vapour pressure osmometry experiments at different temperatures (27–55 °C) was performed on complexes of 4-Cl-, Me-, MeO-, PhO-pyridine N-oxides with trifluoroacetic acid in benzene solutions over the concentration range 0.03–0.6 mol kg^{-1}. The increase in the apparent number average molecular weight with increasing solute concentration was characteristic of a self-association.

The association decreased with increasing temperature and increased with increasing of $\Delta pK_a = pK_{B^+H} - pK_{AH}$. The practical molal osmotic coefficients and molal activity coefficients were determined. The non-ideal behaviour of the investigated systems was interpreted on the basis of an association model including an extended series of multimers. Some results are collected in Table I. The steric effect on associations and structure of associates will be discussed.

TABLE I. Values of Stepwise Self-Association Constant, K_a, for 4-R-Pyridine N-Oxides Complexes with Trifluoroacetic Acid in Benzene at 27 °C.

R	ΔpK_a	K_a mol kg^{-1}	ΔH kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}
Cl	0.13	0.99 ± 0.13		
Me	1.06	4.77 ± 0.44		
MeO	1.82	7.93 ± 0.28	−12.45 ± 0.23	−24.0 ± 0.5
PhO	2.44	2.36 ± 0.17		

Cryoscopic Studies on Amides in Benzene

P. P. RASTOGI*

Alexander von Humboldt Fellow, Physikalisch- Chemisches Institut der Universität München, Theresienstr. 41, D-8000 Munich 2, F.R.G.

and A. K. SHARMA

Department of Chemistry, Lucknow University, Lucknow, India

Molal freezing point depression (ΔT_f°) of N-methylformamide (NMF), N-methylacetamide (NMA), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) have been determined in benzene by cryoscopic measurements. From these results, molecular weight, degree of association and equilibrium constant have been evaluated. The observed deviations from linear behaviour in ΔT_f° *versus* concentration plots appear to indicate the existence of *Monomer* ⇄ *Dimer* equilibrium almost at all concentrations for NMF and NMA as compared to the normal linear feature for DMF and DMA, a novelty explained in terms of hydrogen bonding and supports our previous conclusions [1] drawn from dielectric measurements.

Reference

1 P. P. Rastogi and A. K. Sharma, *Ind. J. Chem., 18,* 67 (1979).