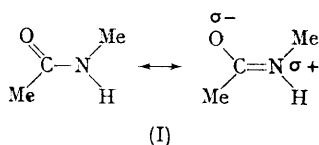


Solvation in Aqueous *N*-Methylacetamide Solutions of Aluminium Chloride: an N.m.r. Study

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PROTON MAGNETIC RESONANCE studies of aqueous *N*-methylacetamide solutions of AlCl_3 have shown conclusively that the organic component of the solvent mixture competes with water in solvating the ions present. *N*-Methylacetamide has a very large dielectric constant,¹ 165.5 at 40°, and is very soluble in water, making it ideally suited for the study of competitive solvation. The resonance structure of *N*-methylacetamide (I) indicates that



the oxygen atom and the amide proton are the most probable solvation sites. Formally, one ascribes the partial positive charge to the nitrogen atom; however, the amide proton is acidic and therefore possesses a certain degree of net positive charge. Due to direct solvation or electrostatic interaction with an anion, the n.m.r. of the amide proton would be expected to undergo the greatest shift in resonance position compared with the proton resonance of the O-C-Me and N-Me groups which are only indirectly affected. In the particular case reported here, the perturbation of the electronic environment around protons of the C-Me group would probably be greater than that around the N-Me groups. This is felt to be true since the charge density of the Al^{3+} ion is greater than that of the Cl^- ion and consequently its influence in the $\text{Al}^{3+}\text{-O-C-Me}$ group in perturbing the electronic environment around the methyl protons would be

greater than the corresponding effect of the Cl^- ion in the $\text{Cl}^-\text{-H-N-Me}$ group. Therefore, using this model, the order of magnitude of the *N*-methylacetamide ^1H -n.m.r. shifts would be $\text{NH} > \text{C-Me} > \text{N-Me}$. This was found to be true experimentally.

Figure 1 compares the n.m.r. spectra of a 40–60%, by weight, mixture of *N*-methylacetamide–water, respectively, with that of a 2.68 m- AlCl_3 solution in 40–60% *N*-methylacetamide–water. These spectra give direct evidence of solvation by *N*-methylacetamide since separate resonance peaks are observed for bulk solvent molecules and for those involved in solvation. The downfield peak of each group is representative of the solvated species. The order of shift in resonance position between solvated and unsolvated molecules is in the predicted order 68 c./sec. $\text{NH} > 12$ c./sec. $\text{C-Me} > 7.5$ c./sec. N-Me .

It is also observed in Figure 1 that the N-Me group proton resonance that appears as a doublet, due to coupling with the amide proton in the non-electrolyte solution, collapses into a singlet in the electrolyte system. This is due to the hydrolysis reaction of the Al^{3+} ion which enhances the chemical exchange of the amide proton.* It should also be noted that the shift in proton resonance of the N-Me group between the solvated and bulk species is 7.5 c./sec., while the coupling constant of the N-Me doublet is 4.7 c./sec. This is further evidence that the N-Me peaks observed are those of the solvated and bulk solvent molecules.

The integrated spectra of the electrolyte solution indicates that approximately 40% of the total organic molecules are involved in the solvation process.

* As added proof, the spectrum of a 40–60% *N*-methylacetamide–water mixture to which HCl has been added shows the collapse of the N-Me doublet into a singlet.

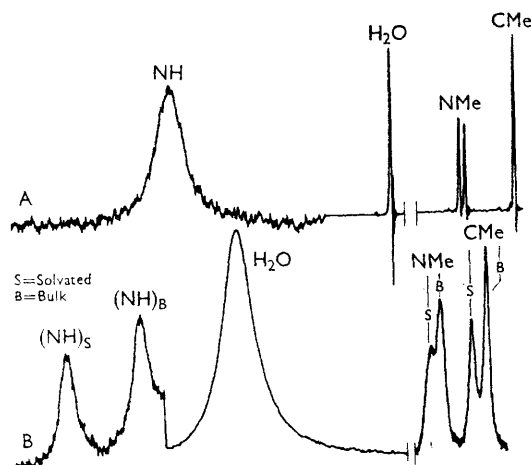


FIGURE 1. (A) *N.m.r. spectra of N-methylacetamide-water, 40—60%, respectively.*

(B) *N.m.r. spectra of 2.68 m-AlCl₃ solution in 40—60% N-methylacetamide-water showing the broadened and shifted water peak and the separate bulk and solvated peaks of the organic component.*

Figure 2 shows the ¹H n.m.r. shifts of water and N-methylacetamide as a function of mole fraction of N-methylacetamide for solution of 0.51 m-AlCl₃. The shifts observed are in the same direction and the order of shift is the same as that observed in the 2.68 m-AlCl₃ solutions.

In both concentrated and dilute solutions, the water peak is significantly broadened, but not split, and undergoes a large downfield shift indicating a high degree of solvation.

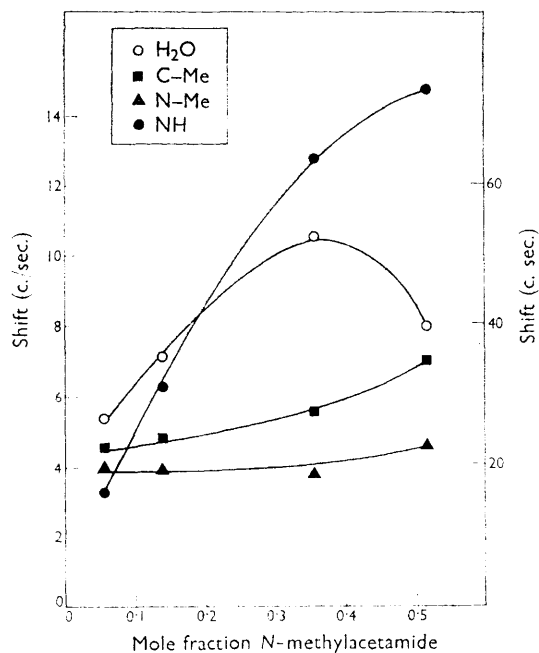


FIGURE 2. *Plots of downfield n.m.r. shift of both solvent components in a 0.51 m-AlCl₃ solution of N-methylacetamide-water as a function of the mole fraction of N-methylacetamide. The right-hand ordinate corresponds to the water shift and the left-hand ordinate to the N-methylacetamide peak shifts.*

Other salts are now being studied in the same solvent mixture to gain more information on specific ion effects.

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¹ L. R. Dawson, E. D. Wilhoit, R. R. Holmes, and P. G. Sears, *J. Amer. Chem. Soc.*, 1957, **79**, 3004.