

Interaction of Acrylonitrile-Zinc Chloride Complex with Benzene

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EARLIER we reported that acrylonitrile (AN) formed both a 2:1 and a 1:1 complex with $ZnCl_2$ and that the former complex showed anomalous dissolution in benzene or toluene.¹ With a molar ratio of benzene:monomer of less than unity incomplete dissolution of complex was observed. With the ratio near unity one liquid phase was observed at room temperature whilst two liquid phases appeared with the ratio greater than unity. Analysis showed that the upper layer contained monomer and benzene, and the lower layer monomer, $ZnCl_2$, and benzene. Figure 1 shows that the

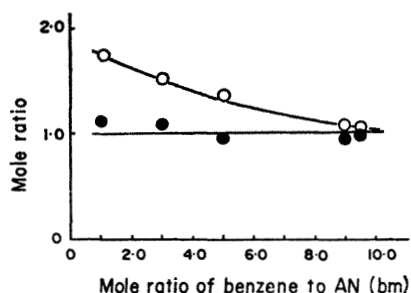


FIGURE 1. Changes of the mole ratios of AN to $ZnCl_2$ (○) and AN to benzene (●) in the lower layer of benzene solution of the 2:1 AN- $ZnCl_2$ complex.

molar ratio of monomer to benzene in the lower layer is constant. Similar behaviour was observed both for methacrylonitrile (MAN) and a methyl methacrylate complex.

An n.m.r. spectrum of the lower layer showed that the chemical shift of methylene proton *cis* to the nitrile group

moved to lower field with an increase in the benzene:monomer ratio ($\Delta\tau$ 0.05 p.p.m.). In the i.r. spectra the absorption band of the nonplanar vinyl protons ($=CH_2$ and $=C-H$) at 965 cm^{-1} split into a doublet for the AN- $ZnCl_2$ complex and shifted to higher frequencies for the MAN

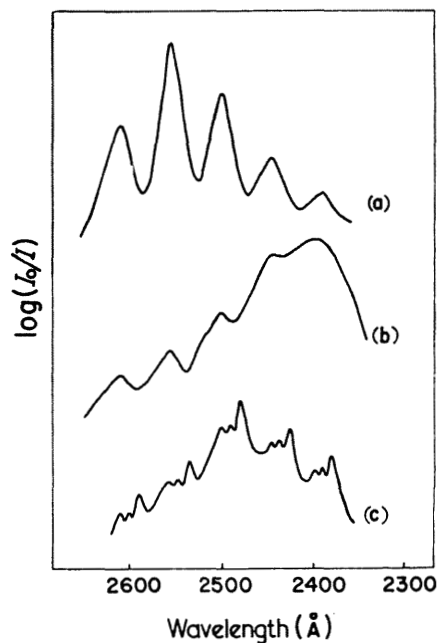


FIGURE 2. Absorption spectra of (a) pure benzene, (b) benzene in the lower layer of benzene solution of the 2:1 AN- $ZnCl_2$ complex at benzene:monomer ratio of 1:1 and (c) 9:5:1.

complex ($\Delta\nu = 5 \text{ cm.}^{-1}$). Further small hypsochromic shifts were observed in the bands at 1475, 1820, and 1976 cm.^{-1} ($\Delta\nu = 5 \text{ cm.}^{-1}$). The bands near 2500 \AA were quite different from those of benzene (see Figure 2). Fine structure appeared when the benzene: monomer ratio was greater than 5. The peak-to-peak interval of the fine structure was *ca.* 10 \AA . These observations indicate interaction between the AN-ZnCl₂ complex and benzene.

A complex of ZnCl₂ with a saturated nitrile such as propionitrile showed neither anomalous dissolution characteristics nor spectral changes. It is possible that the electron acceptability of AN increases as the result of its

co-ordination to ZnCl₂ and the observed behaviour is due to a donor-acceptor interaction of benzene with AN. Recently, Kemula and Watanabe² reported that the complex of ester of aliphatic carboxylic acid with SnCl₄ formed collision complexes with benzene.

Copolymerization of these complexes [e.g. ZnCl₂(AN)₂] with styrene showed³ that the resulting 1:1-copolymer was always obtained and was independent of the monomer feed ratio. This is also in accord with the possibility of the formation of a 1:1 complex of styrene-(AN-ZnCl₂).

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¹ H. Hirai, S. Okuzawa, T. Ikegami and S. Makishima, *J. Fac. Eng., Univ. Tokyo*, 1967, **B**, **29**, 115; H. Hirai, T. Ikegami, and S. Makishima, *J. Polymer Sci.*, to be published.

² A. Kemula and R. T. Iwamoto, *J. Phys. Chem.*, 1968, **72**, 2764.

³ T. Ikegami and H. Hirai, *J. Polymer Sci.*, to be published.