

## *Degelation of Aluminum Soap-Hydrocarbon Gels*

Several polymeric structures have been proposed for the aluminum soaps,  $\text{Al}(\text{OH})(\text{OOCR})_2$ , both in solid form and in hydrocarbon gels.<sup>1,2</sup> Each has a basic backbone consisting of a linear chain of aluminum and oxygen atoms with the carboxyl groups coordinated with the hexacoordinated aluminum. The carboxyl group may be attached to a single aluminum atom or with two aluminum atoms either intramolecularly or intermolecularly. The latter would be a crosslinked structure. These structures are based mainly upon infrared absorption measurements.

Many polar compounds will peptize or "break" the hydrocarbon gels by altering the Al—O chains. Various mechanisms, again based on infrared measurements, have been proposed for the peptization. Friberg<sup>3</sup> and Yamamoto<sup>4</sup> proposed the formation of hydrogen bonds between the peptizer and the soap molecules. In the case of additives which contain OH or  $\text{NH}_2$ , the hydrogen bond is formed with the OH of the soap molecule. With a peptizer containing a carboxyl group, a new aluminum salt is formed.

During the course of a study of the properties of aluminum soap-hydrocarbon gels,  $^{13}\text{C}$ -nuclear magnetic resonance (NMR) spectra were obtained for gelled and degelled solutions. These spectra show very clearly the two mechanisms involved in degelation.

### EXPERIMENTAL

Aluminum caprylate,  $\text{Al}(\text{OH})[\text{OOC}(\text{CH}_2)_6\text{CH}_3]_2$ , from Pfaltz and Bauer, Inc., was used as the gelling agent. Free acid in the sample was removed by extraction with anhydrous dimethylformamide. An aluminum analysis gave 8.1% Al (calcd 8.2%), and the infrared spectrum agreed with that in the literature.<sup>5</sup>

The solvent, benzene, and additives were reagent-grade chemicals.

The  $^{13}\text{C}$ -NMR spectra were obtained with a Varian XL-100-15 spectrometer at a frequency of 25.14 MHz.

### RESULTS AND DISCUSSION

An NMR spectrum of caprylic acid in benzene is shown in Figure 1(A). The carbon 2 atom is the one adjacent to the carboxyl group which is not included in the spectrum. Assignment of the peaks to individual carbon atoms has been given in the literature.<sup>6</sup> The 4- and 5-carbons appear usually as an unresolved single peak.

Figure 1(B) shows the spectrum of a 6% aluminum caprylate-benzene gel. It is obvious that, when compared with the caprylic acid spectrum, the lines are progressively broadened in going from carbon 8 to carbon 2. This broadening has been shown to arise from a variation in spin-lattice relaxation time ( $T_1$ ) which is a direct measure of the characteristic correlation time for segmental chain motions. Thus, the rapid motions of the free ends of the side-chain units lead to long  $T_1$  values and narrow NMR lines, while the much slower motions of the coordinated ends give short  $T_1$  values and correspondingly broad lines. This indicates that the hydrocarbon chain in the soap has some rigidity and that the main Al—O chain must be quite rigid.

When the caprylate gel was degelled by adding methylamine, the spectrum shown in Figure 1(C) was obtained. The lines are still broadened and the chemical shifts are the same as those for the gel. Obviously, no change has occurred to the carboxyl—Al linkages, and the degelation must be attributed to cleavage of the Al—O bonds. Breaking only a small fraction of the Al—O bonds results in significant reduction in the average length of the polymer units, with a corresponding rapid decrease in solution viscosity.

Figure 1(D) gives a spectrum of a gel saturated with water. The line widths and chemical shifts are the same as for the gel and amine-degelled samples, indicating that peptization in this case also occurs by rupture of the Al—O bonds.

However, when acetic acid was added to a gel sample, the resulting solution gave the spectrum in Figure 1(E). Here the line widths and chemical shifts are the same as those obtained for caprylic acid. Thus, degelation occurs by the cleavage of the Al—carboxyl bonds to regenerate the free acid. The peak at about 22 ppm is due to acetic acid.

Qualitative observations of the viscosity of these gels indicate that degelation with methylamine is extremely rapid, but with acetic acid more of the additive and a longer time are required to attain a solution with the same viscosity. The longer degelation time of water and small concentrations required appears anomalous but can be explained in terms of the solubility of water in the hydrocarbon and the subsequent diffusion of water to the reaction site. These observations and the NMR results suggest that the network is composed of chains in which the carboxyl groups are intramolecularly bonded.

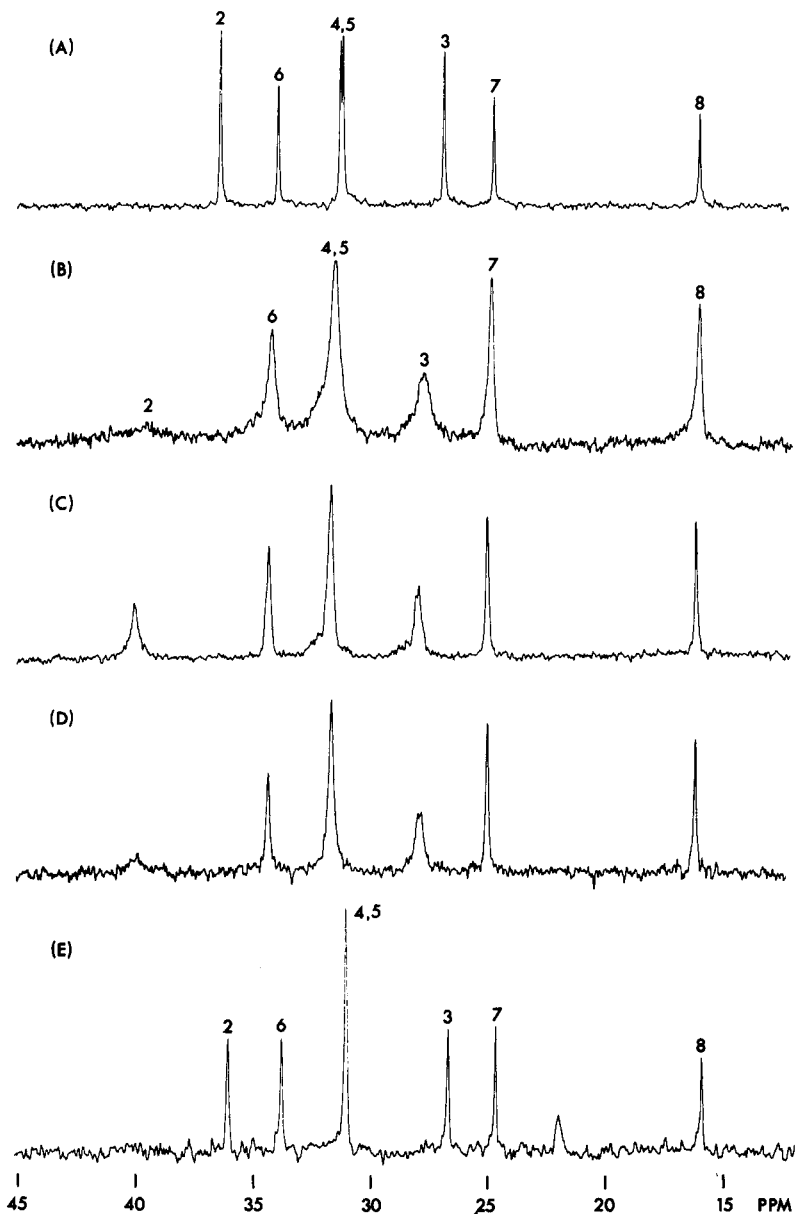


Fig. 1. Alkyl region of  $^{13}\text{C}$ -NMR spectra of benzene solutions of (A) caprylic acid, (B) aluminum caprylate, (C) aluminum caprylate and methylamine, (D) aluminum caprylate and water, (E) aluminum caprylate and acetic acid. The number above each peak is the carbon assignment in the caprylic acid chain.

Thus, two mechanisms of degelation have definitely been established: (1) rupture of the Al—O chains which results in a rapid decrease in viscosity with small amounts of additive, and (2) cleavage of the fatty acid side chain which requires a larger amount of additive to achieve the same viscosity decrease.

#### References

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