

## Gelation of Aluminium Soaps in Hydrocarbons

### I. Infrared and Rheological Investigations

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The gelation of aluminium-hydroxide-distearate in hexadecane was studied by means of IR-spectroscopy and rheological measurements. From the results obtained, it is evident that the gelation is accompanied by a pronounced change in the bonds of the oxygen bridges between the aluminium atoms. On the other hand, the hydroxide and carboxyl groups show only minor changes. The changes in rheological properties take place at the same temperature as those in IR-spectra. Preliminary DTA-determinations show that the gelation is an endothermic reaction and that it occurs in more than one step.

The structure of aluminium disoaps as solids have been examined by means of X-ray investigations.<sup>1,2</sup> The results point to a layer structure, where the long spacings agree very well with those of the C-form of the corresponding acid. X-Ray investigations of napalm gels show a similar pattern.<sup>3</sup> Coordination of the aluminium atom in gels of the soaps was studied by Bauer *et al.*<sup>4</sup> and by Sheffer *et al.*<sup>5</sup> using IR-spectrometry. The results could be explained by assuming a structure of mono- and dinuclear coordinated carboxyl groups to the aluminium atoms, with hydroxide group bridges between the latter. The aluminium octahedra should then be connected by corners only. Aluminium soaps in solid form have been investigated as KBr-pressings and have given spectra similar to those of the soap in gels.

The results from the latter method cannot be compared to the results of investigations in gels, owing to influence of the high pressures involved, and the water which is rather difficult to remove. For that reason, this investigation has been undertaken in order to show the changes in the bonds and in the rheological properties when a suspension of soap passes to a gel when heated. A preliminary investigation on a soap of technical grade in an oil of high purity was made by Atterby and Friberg.<sup>6</sup>

## EXPERIMENTAL

**Materials.** Synthesis of and materials for the soap were described in an earlier paper. The hexadecane was a purum quality (Mercks  $\geq 99\%$ , "olefinfrei"), which was stored in a desiccator over Sikkon and used without further purification.

**Determination of IR-spectra.** The soap and the hexadecane were ground together in a mortar. Complete transparency was not achieved, but the scattering of a 2% suspension was not found to influence the intensity of the absorption to a measurable degree. The suspension was transferred to a Perkin Elmer heatable, demountable cell with a lead spacer of 0.1 mm between the windows. These operations were performed in an atmosphere of dry nitrogen. Determinations of the spectra were made by means of a Perkin Elmer apparatus, Model 221. Spectra were not compensated for the solvent, but this was not considered to be a serious disadvantage, since the spectrum of hexadecane showed little absorption, and no detectable temperature dependence of the absorption in the regions concerned. The spectra were recorded at different temperatures, and equilibrium was assumed when there were no changes when kept at the same temperature for at least 4 h. Results are given as percent transmittance, since calculation of the absorbance could give no further information.

**Rheological measurements.** The soap (5% by weight) and hexadecane were weighed into quartz tubes with tight stoppers pressed into the tubes by a spring. These tubes were kept in a thermostated rotating apparatus<sup>7</sup> for several days, whereafter the flow-curves, shear stress *versus* shear rate,  $\tau = f(D)$  were determined by a Ferranti-Shirley, cone-plate viscometer which was thermostated.  $D$ , the shear rate, was varied continuously from 0 to  $10^4 \text{ sec}^{-1}$  and to 0 again during 80 sec. The period of measurement was made so long in order to reduce influence from the elastic effects. The tubes were charged in an atmosphere of dry nitrogen, and the measurements performed in air saturated with vapours from the solvent.

**Differential thermal analysis.** This was performed in a Perkin Elmer, Model DSC 1, in an atmosphere of dry nitrogen.

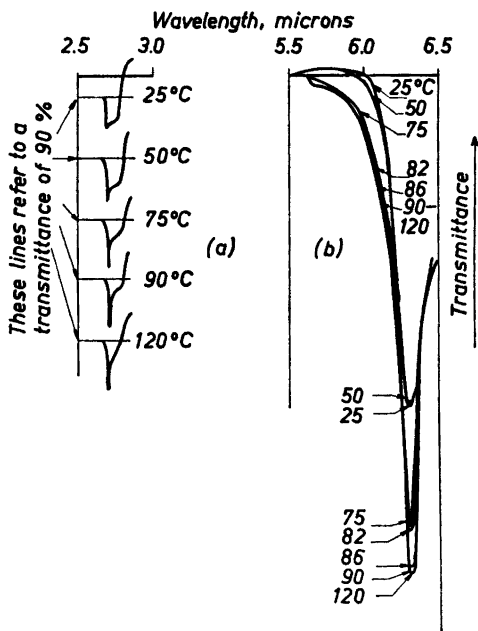


Fig. 1. The transmittance of infrared radiation in the regions of absorption of hydroxide (a) and carboxyl (b) groups.

## RESULTS

*Infrared measurements.* Fig. 1 shows the transmittance in the region of the stretching vibrations of an OH-group with no hydrogen bonds. Gelation occurs between 80 and 90°C, but this has no pronounced effect on the absorption. The changes are gradual over the whole temperature range, and consist of an increase at 2.70  $\mu\text{m}$  and a corresponding decrease at 2.85  $\mu\text{m}$ , which is a quite natural temperature effect on hydrogen bonds. The absorption at 3.0  $\mu\text{m}$ , which is due to hydrogen bonded OH-groups was not of a measurable degree and did not change. The carboxyl band at 6.3  $\mu\text{m}$  increases in intensity to a marked degree between 50 and 75°C. This increase in the absorption is not followed by an increased solvation of the soap or by any other detectable change. It seems probable that it can only be due to changes in the solid soap which give an increased polarity to the carboxyl bonds. The frequency of the absorption did not change.

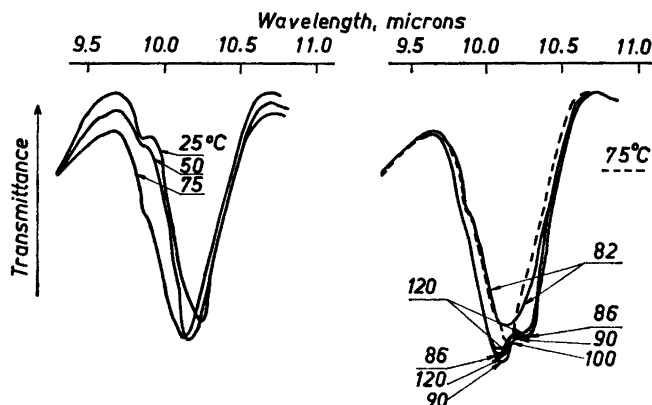


Fig. 2. The transmittance of infrared radiation in the regions of absorption of the Al—O—Al groups.

Fig. 2 refers to the absorption 10.1  $\mu\text{m}$  which is due to the oxygen bridges between the aluminium atoms.<sup>5</sup> Between 50 and 75°C the frequency of the absorption increases, and between 82 and 87°C the intensity increases and at the same time the absorption curve shows two peaks. The increase in intensity between 82 and 87°C cannot be taken too quantitatively since the suspension is transformed into a completely transparent gel here.

*Rheological determinations.* Fig. 3 shows the flow-curves at different temperatures. At temperatures below the gelation temperature, the curves are linear, which is to be expected from a suspension in a Newtonian liquid. Above the gelation temperature the suspension behaves like a pseudo-plastic medium. It is evident from the curves that up to 105°C the shear stress at low shear rates increases, whereas the differential viscosity at shear rates above  $2 \times 10^3 \text{ sec}^{-1}$  changes very little. At temperatures above 105°C both decrease. At these temperatures and in this region of shear rate, the gel showed no sign of thixotropic behaviour.

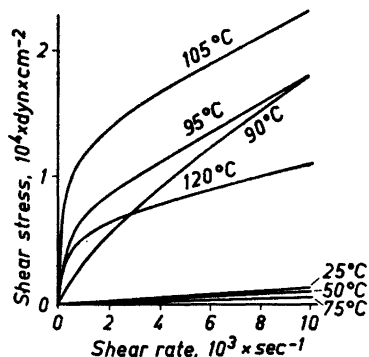


Fig. 3. Flow curves of a suspension of aluminium hydroxide distearate in hexadecane at different temperatures.

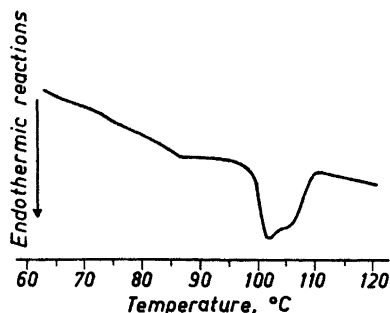


Fig. 4. Differential thermal analysis of aluminium hydroxide distearate in hexadecane.

*Differential thermal analysis.* This investigation is only preliminary and qualitative. Fig. 4 shows a poorly defined peak at 87°C and two rather pronounced but badly resolved ones in the region 100–105°C. Both these temperatures are very significant of the rheological behaviour of the gels. The figure shows also that the curve has a lower gradient after 87°C.

#### DISCUSSION

The results given in this investigation together with those mentioned in the introduction give the following picture of the gelation mechanism. X-Ray investigations make the assumption of a layer structure resembling that of stearic acid fairly reasonable. The changes of the bonds below the gelation temperature can then be explained by the temperature-dependent changes in the solid soap. Increase in intensity of the carboxyl bond between 50 and 75°C is due to a higher level of polarity of the bond. This polarity increase can be explained by the assumption that the bond between aluminium and one of the lone pairs of oxygen is weakened, which would increase the electron density around the oxygen atom. Obviously, this increased density around the oxygen will have no effect on the non-localised three-centre bond of the carboxyl group, which is evident from the unchanged frequency of the carbonyl absorption. The increased frequency of the absorption at  $10.1 \mu\text{m}$  can then be explained by an increased electron density between the aluminium and the oxygen atoms of the hydroxide groups.

The gelation process, which occurs gradually between 75 to 90°C, involves the penetration of the layer structure by the hydrocarbon. This gives an increase in the intensity of the carbonyl bond but no frequency shift. The absorption of the hydroxide bonds are changed to a more definite wavelength of  $2.70 \mu\text{m}$ , which represents a free hydroxide group. From this fact and since there is no difference in the absorption at  $3.0 \mu\text{m}$  it is obvious that hydrogen bonds from the OH-groups cannot explain the forces between the

colloid particles which give the pronounced viscous and elastic properties of these gels. The absorption at  $10.1 \mu\text{m}$ , caused by the bonds between aluminium and oxygen in the chain, is divided into two poorly resolved peaks at this moment. This must be due to differences in the aluminium-oxygen bonds but from this material it is not possible to give an explanation of that fact. A plausible assumption could be increased cross-bondings between the chains, but this is contradicted to a certain degree by the results from the rheological determinations. These suggest increased interactions *between the micelles* up to  $105^\circ\text{C}$  and then a decrease, perhaps depending on some changes in micelle dimensions. The second possibility is to assume two different forms of micelles in a temperature dependent equilibrium, but this question cannot be solved by the methods used in this investigation.

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