

Peptization of Aluminium Soap Gels

STIG FRIBERG

*Research Institute of National Defence, Sundbyberg, and Institute of Physical Chemistry,
University of Stockholm, Sweden*

The effect of three different peptizers on gels of aluminium hydroxide-distearate was investigated by means of I.R.-spectrometry and rheological measurements. The peptizing mechanism of octadecanoic acid and octadecanol could be explained by the hydrogen bond mechanism by Bauer *et al.*¹ Octadecylamine on the other hand had a much more pronounced effect on the rheological behaviours of the gels and I.R.-spectrometry measurements gave a strong indication of a nucleophilic reaction of the free electron pair of the nitrogen atom.

The structure of aluminium disoap gels in hydrocarbons has been examined by a number of scientists, who have suggested linear polymers of linked aluminium-oxygen octahedra.²⁻⁴ Later Sheffer *et al.*⁵ gave five bridging structures, partly based on their results from I.R.-measurements on degraded trisoaps and partly on results from measurements by Bauer *et al.*^{6,7} The effect of polar organic compounds was quite thoroughly investigated in the years after World War II and some suggestions concerning the mechanism of the peptizing reactions were given. Later Bauer *et al.* in 1955 presented a theory, by which the peptizer was bonded to the carboxyl ion of the soap by a hydrogen bond. Yamamoto^{9,10} examined several peptizers and their influence on gels of aluminium hydroxide-distearate in Nujol. From the examination of that rich material he came to the conclusion that the hydrogen bond connection was the main mechanism of peptizing. Friberg¹¹ made a literature survey and showed that there is no simple relationship between the changes of rheological behaviour and the changes of absorption in the infrared region, when gels are peptized.

In order to evaluate the influence of some reactive groups on organic compounds three peptizers were selected, namely a carboxylic acid, an alcohol and an amine. Since the chain length of the peptizer has a pronounced effect on the changes of rheological behaviour, which was shown by Jackson,¹² the three peptizers were selected with the same chain length as the soap, in order to obtain the influence of the reactive group alone.

EXPERIMENTAL

Materials. The stearic acid (KEBO, *puriss.*, 69–70°C) used for the preparation of the aluminium soap was recrystallized from ether at –10°C to remove unsaturated contaminants and distilled as methylester in a column at low pressure to remove homologues. Gas chromatographic analysis of the ester showed no impurities to be present to a measurable degree. The ester was saponified with potassium hydroxide in ethanol and the aluminium soap was prepared after Smith *et al.*¹³ and Mysels *et al.*¹⁴ The precipitation temperature was 95°C and the free stearic acid was extracted in an extraction apparatus¹⁴ with dry acetone at 0°C. An analysis of the soap gave a ratio of moles of the fatty acid in comparison to moles of aluminium of 2.01. The stearic acid used as peptizer was prepared from the pure methylester by saponification to potassium soap and hydrolyzing with HCl. The amine and the alcohol were of the *puriss.* grade and repeatedly recrystallized from carbon tetrachloride and benzene, respectively, up to a constant melting point. The cyclohexane used as a solvent was Merck's quality for U.V.-spectroscopy. It was stored and distilled over metallic sodium immediately before use. The carbon tetrachloride was treated the same way with Sikkon.

Gel preparation. Soap and peptizer were dried over P₂O₅ to a constant weight, weighed into dry test tubes and dried again over P₂O₅ for 14 days. After the solvent had been brought into the tubes, the open end was immediately fused. The tubes were transferred to a rotating apparatus provided with a temperature control, described elsewhere,¹¹ and were rotated at a constant temperature for half an hour. After a control had shown that no gelling had begun, the temperature was increased by three degrees and kept constant at the new level for half an hour. This procedure was repeated until the gelation temperature was reached, where the gels were rotated for 24 h. After that the temperature was decreased continuously for 6 h to 25°C, where the gels were rotated 24 h before use.

Determination of I.R.-spectra. Infrared absorption spectra were determined by means of a Perkin Elmer, Model 221, recording spectrometer with a rock salt prism at 25°C and a relative humidity of 30 %. The cell thickness was 0.1 mm. All the spectra were compensated for the solvent and the values of absorbance are the logarithm of the ratio I_0/I , where I_0 and I are the transmittance of the base-line and of the difference between solution and the solvent, respectively, at given wave-lengths.

Rheological determinations. Flow-curves, shear stress *versus* shear rate, $\tau = f(D)$, where D varied continuously during 15 seconds from 0 to 10⁴ sec⁻¹ and to 0 again, were determined by means of a Ferranti-Shirley cone-plate viscometer in an atmosphere, saturated with the solvent. From the "down branch" of the flow curve the plastic viscosity¹⁶ and its time-dependence were calculated.

RESULTS

Gelation temperature. The gelation temperature of the gels in cyclohexane was 65–68°C and in carbon tetrachloride 55–58°C. The peptizers had no effect on this temperature.

Rheological behaviour of gels in cyclohexane. A striking example of the difference in effect on the rheological properties of gels peptized by the three peptizers is shown in Fig. 1. The three ampoules were kept vertical for some hours and at time 0 they were turned into a horizontal position. As is seen in the figure there is no pronounced difference between the gel without a peptizer and the gel with alcohol or acid, while the gel peptized with amine flows out immediately.

Infrared measurements. These measurements included the effect of the three peptizers on gels in cyclohexane and also some measurements on amine peptized gels in carbon tetrachloride, since the latter solvent has less absorption in the infrared region.

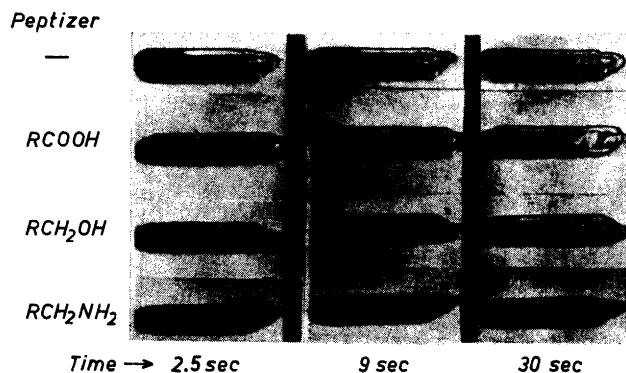


Fig. 1. Flow properties of gels in cyclohexane with different peptizers. Times after the change from vertical to horizontal position.

The variation of absorption *versus* the addition of a peptizer at 2.7 and 3.0 μm is in accordance with earlier results.⁸ At 5.8 μm the alcohol and the acid gave a slight increase, while the amine reduced the absorption to nought even at additions less than one fourth of the number of moles of aluminium soap. The absorption in the region 6.1–6.4 μm differed very much from that of earlier results. Fig. 2 shows that the acid does not change the absorption at 6.33 μm to a measurable degree, while the alcohol reduces the absorption,

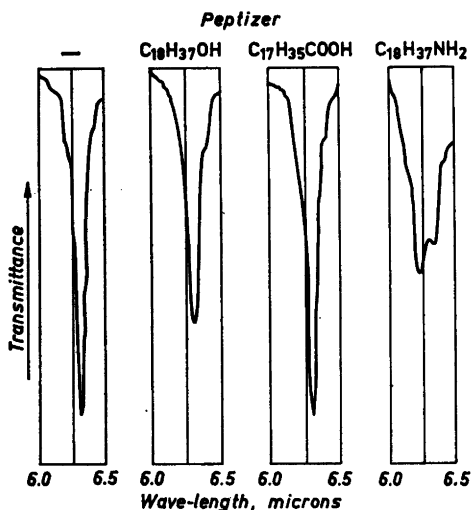


Fig. 2. The transmittance in the region 6.0–6.5 μm with an equimolar addition of peptizers.

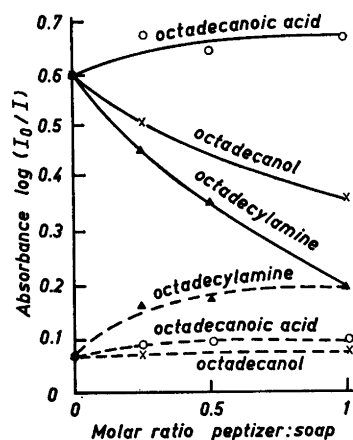


Fig. 3. The absorbance of asymmetric stretching of the carboxyl ion with inter-nuclear (— 6.33 μm) and intranuclear coordination (--- 6.22 μm).

which agrees with the hydrogen bond mechanism. The amine on the other hand gives a fairly pronounced reduction of this absorption and a corresponding increase of the absorption at $6.22 \mu\text{m}$. The absorbance *versus* the addition of a peptizer at these wave-lengths is given in Fig. 3. The figure shows clearly that the alcohol and — to a higher degree — the amine reduces the absorption at $6.33 \mu\text{m}$ and that the amine increases it at $6.22 \mu\text{m}$. The slight increase caused by the acid at $6.22 \mu\text{m}$ probably depends on the broadening of the peak at $6.33 \mu\text{m}$. The absorbance *versus* the addition of a peptizer at $10.15 \mu\text{m}$ is shown in Fig. 4. The results are quite analogous to those obtained at $6.33 \mu\text{m}$, but there is a more pronounced tendency.

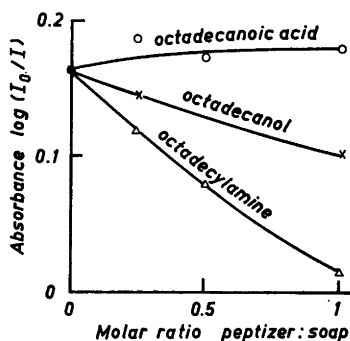


Fig. 4. The absorbance of oxygen bridges between aluminium ions *versus* addition of peptizers.

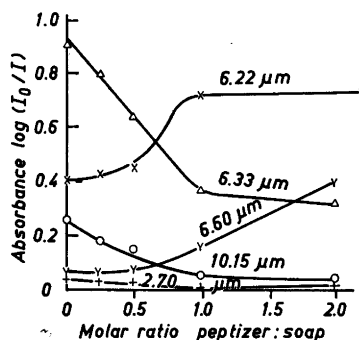


Fig. 5. The absorbance of gels in carbon tetrachloride.

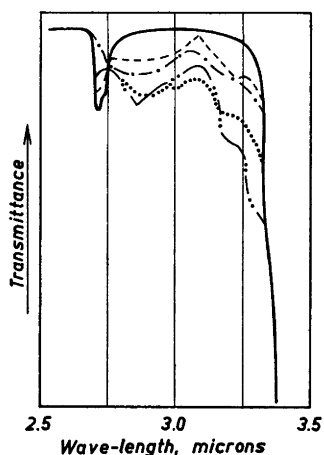


Fig. 6. The transmittance in the region of the valence vibrations O—H and N—H for gels in carbon tetrachloride peptized by octadecylamine. Molar ratio peptizer: soap: 0 —; 0.25 — — —; 0.5 — · — ·; 1.0 ·····; 2.0 — · — · — ·.

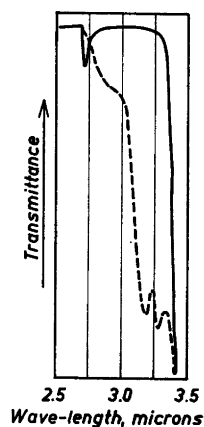


Fig. 7. The transmittance in the region of the valence vibrations O—H and N—H for gels in carbon tetrachloride peptized by NH_3 . Unpeptized gel —; gel peptized by NH_3 — — —.

Gels with the amine as a peptizer were also prepared in CCl_4 to obtain improved spectra, as the absorption of the solvent would be less. Fig. 5 shows the absorbance *versus* the addition of the amine at various wave-lengths which are of special interest. The tendency is the same as that of the gels with cyclohexane but it is striking that the curves of absorption change at the point of equimolarity between the peptizer and the soap. Fig. 6 shows that the absorption at $2.70 \mu\text{m}$ decreases by an increased addition of the amine and that this absorption is replaced by rather a continuous one in the region $2.80 \mu\text{m}$ to $3.35 \mu\text{m}$, with three poorly resolved peaks at 2.85 , 3.2 , and $3.3 \mu\text{m}$. The last two peaks are somewhat better resolved in Fig. 7, where NH_3 is used as a peptizer.

Rheological measurements. Fig. 8 shows the ratio of plastic viscosity of a

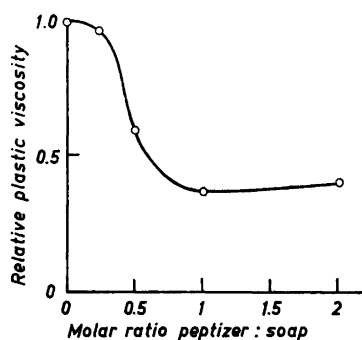


Fig. 8. The ratio of plastic viscosity of peptized gels to the plastic viscosity of unpeptized gels *versus* addition of amine.

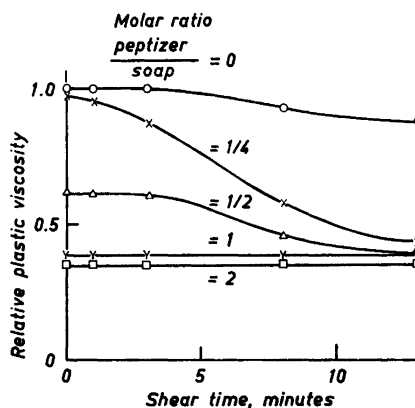


Fig. 9. The ratio of plastic viscosity of gels to plastic viscosity of unpeptized gels at sheartime zero *versus* shear time.

peptized gel in comparison to the plastic viscosity of an unpeptized gel *versus* the addition of the peptizer. It is seen that an addition to a higher degree than that of equimolarity does not effect the viscosity. In Fig. 9 the same ratios *versus* shear time is shown. In similar systems plastic viscosity *versus* the logarithm of shear time usually gives two crossing straight lines¹⁶ but this is not the case here and therefore viscosity was simply plotted against shear time.

DISCUSSION

Fig. 1 shows clearly that there is a great difference between the rheological behaviour at small shear rates of gels peptized with the amine and with the acid or the alcohol. The cause of this phenomenon must be that the forces between the micelles of the gel are weakened either because the peptizer is adsorbed on the faces of the micelles and thus changes the forces between them or because the micelles themselves are less than the critical size. The first condition would not change the I.R.-absorbance of the soap very much while

the second must do so. Fig. 2 shows that the absorption in the region 6.1–6.4 μm has quite a different look as regards the gel peptized with the amine. The absorption at 6.33 μm , which is the wave length of the asymmetrical carboxyl stretching frequency at the maximum damping, corresponds to *internuclear* coordination of the carboxyl ion.⁵ The same authors⁵ give the *intranuclear* coordinated carboxyl ion the assignment 6.22 μm if an OH-group is connected, which will have a dampening effect. Without this effect the carboxyl ion absorbs at 6.1 μm , *e.g.* in a tri-soap. Sheffer *et al.*⁵ give a molecular weight of > 1 000 000 in the first case and about 100 000 in the second. The results of Fig. 1 together with those at Fig. 2 then give evidence of considerable decrease in molecular weight after an amine has been added, while the addition of an acid or an alcohol does not give much difference. The absorbance at those wave-lengths *versus* the addition of a peptizer is given in Fig. 3. In Fig. 4 the absorbance at 10.15 μm is given, which corresponds to the group $\text{Al}-\overset{\text{H}}{\text{O}}-\text{Al}$, *versus* the addition of a peptizer. The amine destroys these bridges more effectively than the alcohol does, and the acid does not seem to have any influence at all.

The changes of absorption with the addition of a peptizer in carbon tetrachloride is analogous, as is seen in Fig. 5. It is evident that the addition of a peptizer to less than the equimolar ratio has a different effect than a further addition has. All the characteristic changes cease at this addition and a new absorption at 6.60 μm increases linearly with a further addition. The absorption at 6.60 μm corresponds to deformation vibrations of the amino group and it is clear that this group absorbs at shorter wave-lengths, when additions are less than equimolar ones.

The free hydrogen of the OH-group is evidently hydrogen bonded at the addition of the amine (Fig. 6). The two peaks at 3.22 and 3.26 μm correspond to asymmetric and symmetric valence vibrations between nitrogen and hydrogen. Free amine absorbs at 2.85 μm and hydrogen bonding increases this wave-length to about 3.0 μm .¹⁷ When the free electron pair of the nitrogen is occupied, the amine absorbs at a higher wave-length. Complexes of In^{3+} with diethylamine absorb at 3.23 μm ¹⁸ and hydrochlorides of amines at about 3.30 μm .¹⁷

From this it is evident that the amine is bound by its free electron pair and it would not be realistic to assume a bond at any other place than from the aluminium ion. Unfortunately the bond between the nitrogen and the aluminium cannot be detected by the equipment of our institute, since the infrared absorption has a very high wave-length.¹⁹

The results of rheological measurements indicate a compound of one mole amine and one mole of the soap. The form of the curves in Fig. 9 indicates a breaking up of the micellar structure catalyzed by the products of decomposition, but this was not studied further.

Conclusion. The results from infrared absorption spectra and rheological measurements accord and show that the peptizing mechanism of an amine cannot be explained by the hydrogen bond theory. The results give a strong indication that the amine is bound to the aluminium ion by its free electron pair.

Acknowledgements. The author wishes to express his thanks to Professor Arne Ölander for his encouraging interest and valuable advice and to Docent Lennart T:son Larsson for stimulating discussions. He is also most grateful to Mrs. G. Persson at LKB Research Laboratories for her kind assistance in purifying the stearic acid.

REFERENCES

1. Ludke, W. O., Wiberly, S. E., Goldenson, J. and Bauer, W. H. *J. Phys. Chem.* **59** (1955) 222.
2. Gray, V. R. *Trans. Faraday Soc.* **42 B** (1946) 196.
3. Gray, V. R. and Alexander, A. E. *J. Phys. Chem.* **53** (1949) 9.
4. McGee, C. G. *J. Am. Chem. Soc.* **71** (1949) 278.
5. Leger, A. E., Haines, R. R., Hubley, C. E., Hyde, J. C. and Cheffer, H. *Can. J. Chem.* **35** (1957) 799.
6. Scott, E. A., Goldenson, J., Wiberly, S. E. and Bauer, W. H. *J. Phys. Chem.* **58** (1954) 61.
7. Harple, W. W., Wiberly, S. E. and Bauer, W. H. *Anal. Chem.* **24** (1952) 635.
8. Ludke, W. O., Wiberly, S. E., Goldenson, J. and Bauer, W. H. *J. Phys. Chem.* **59** (1955) 222.
9. Yamamoto, M. *Yakugaku Zasshi* **80** (1960) 1524.
10. Yamamoto, M. *Ibid.* **80** (1960) 1530.
11. Friberg, S. FOA I report No. A1046—F160 (April 1963).
12. Jackson, H. S. *Aluminium Soap-Hydrocarbon systems* (Diss.) Rensselaer Polyt. Inst., Troy 1951.
13. Smith, G. H., Pomeray, H. H., McGee, C. G. and Mysels, K. J. *J. Am. Chem. Soc.* **70** (1948) 1053.
14. Mysels, K. J., Pomeray, H. H. and Smith, G. H. *Anal. Chem.* **25** (1953) 1.
15. Friberg, S. FOA I report No. C1043—F160 (October 1963).
16. Green, H. *Ind. Rheol. and Rheol. Struct.* Wiley, London 1948, p. 54.
17. Nakanishi, K. *Infrared absorption spectroscopy*, San Fransisco 1962.
18. Osipov, O. A. and Semenova, I. M. *Zh. Obshch. Khim.* **33** (3) (1963) 720.
19. Heitsch, C. W. and Knisely, R. N. *Spectrochim. Acta.* **19** (1963) 1385.

Received March 3, 1964.