

# **SEMI-CONDUCTING HYDROCARBON OIL SYSTEMS**

THESIS

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## CONCLUSIONS

The behaviour of magnesium oleate in these investigated mixtures is obviously that of a cationic colloidal electrolyte. On the basis of the previous researches on colloidal electrolytes discussed earlier ("LITERATURE SURVEY"), these anomalous variations in the properties of electrical conductivity, viscosity and refractive index can be explained by assuming various degrees and forms of micellar association of the magnesium oleate ions and molecules.

In general the conductivity and viscosity curves can be divided into four zones distinguished by the abrupt change of the effect measured with the CY1 and BE<sub>2</sub> oil base mixtures. The first, from 2-4% electrolyte concentration, when the conductivity begins to increase rapidly. The corresponding viscosity change in this range is only noticeable at 0°C when it passes through a minimum value, changing the sign of its slope from negative (decreasing) to positive (increasing). The second, at 5-7%, where the conductivity reaches its first maximum value and the viscosity begins to increase more strongly. The third, at 8-10%, where the conductivity levels slightly in its decreasing trend then drops sharply and passes through a minimum value, and the viscosity passes through its maximum value. The fourth, from approximately 9.5 to 11.5%, where the conductivity passes through a second maximum value and the viscosity a minimum value.

The refractive index-concentration curve variations show fair agreement with these zones of change, although not at all clearly, the best agreement being at the higher concentrations.

The D.C.-concentration curves for Test No. 1 are in good agreement with these change zones, the variations in D.C. being quite clear. The capillarity-concentration curves for Test No. 1 are only in fair agreement.

Heavier, more compact micelles forming at the lower temperatures account for the fact that greater variations in the viscosity are noted at the lower measurement temperature of 0°C than at the higher ones, and these viscosity results compare favourably with Umstätter's (see figures 10 and 11).

These sigmoid type curves found for the conductivity, and to a lesser extent, the viscosity, can be considered as composed of three main ranges with respect to micellar aggregation, as follows - the pre-critical (concentration) range, which precedes the critical concentration point from 2 to 4%. At this critical concentration we have the beginning of micelle formation - the formation of small, probably spherical, highly conducting ionic micelles. In this case, that of a non-aqueous non-polar solvent, the Lawrence or inverted McBain micelle (see figure 24), i.e. with the polar groups together, probably exists. The second range, in which the effect

measured changes quickly with concentration, is where these micelles increase rapidly in quantity, and as a consequence, their net charge also, accounting for the great increase in electrical conductivity in this range. The third range from 5-7% where the effect measured changes the algebraic sign of its slope, is the transition area where the large, poorly-conducting, McBain lamellar micelles ('neutral colloid') begin to form from the small micelles, with alternate head-to-head (polar groups) and tail-to-tail (anionic paraffin chain groups) arrangement.

That the results for conductivity and viscosity do not both show just the same values for the critical concentration is not surprising. Previous researchers have experienced similar variations of this value depending on the particular effect measured. In the results here the viscosity (at 0°C) gives a slightly higher critical concentration value than does the conductivity.

This qualitative similarity in the results for the CY1 and BE<sub>2</sub> oil base mixtures is not shared at the same concentrations for the hexaline naphthenate base mixtures. Here, the conductivity and viscosity curves vary much more and are difficult to analyse for corresponding areas of change. As the concentration increases as many as three maxima occur in the conductivity up to 18-20%. But, in general, abrupt changes in one property are matched or followed closely by abrupt changes in the other.

The viscosity curves in these hexaline naphthenate base mixtures are the easiest to analyse. Micelle formation probably begins between 1.5 and 4% electrolyte concentration where the conductivity begins to increase noticeably, and the viscosity changes abruptly the sign of its slope (best seen at 0°C). A change in the nature of the micelle is indicated at between 8 and 10%. Here the viscosity begins a sharp increase and the conductivity passes through a small maximum followed by a minimum in its upward trend. A third area of change occurs from 13.5 to 15.5% where the viscosity curve increases still more sharply upward and the conductivity passes through a high maximum value, indicating transition to a poorer conducting micelle form.

Following this the conductivity passes through one or two more maximum and minimum values, a maximum in the conductivity usually matching a minimum in the viscosity and vice versa. The conductivity remains high and fluctuates between rough limits. This would seem to substantiate the presence of two or more micelle types, the total charge of the better conducting one(s) being almost balanced by the total charge of the poorer conducting one(s), additional colloidal electrolyte forming approximately equal amounts of both better and poorer conducting micelles. The variation in the net charge of these mixtures at these higher concentrations may be due only to slight variations in the number of ions absorbed in the magnesium oleate salt complex during its preparation (see page 20).

As is to be expected, the conductivity, at least up to the concentrations employed here (18-20%), does not diminish to very small values, since the hexaline naphthenate has little tendency to polymerize, resulting in the gradual absorption of the micelles as soap, as is probably the case with the two lubricating oil solvents, CY1 and BE<sub>2</sub>.

Research on colloidal electrolytes at concentrations above, say, 10%, is lacking, but what has been done is in general agreement with the results at higher concentrations obtained here (see pages 26 - 28 and 31). At these higher concentrations evidence has been found for at least some lamellar repeating arrays of long-chain electrolyte molecules in water. But other micellar forms give evidence of their probable presence and rod or plate forms have been suggested (page 27/28).

We may consider that solubilization of our lubricating oil solvents is accomplished by the lamellar micelles, which begin to form at 5-7% concentration, the oil being taken up between the alternate head and tail spacings. The oleate chain being ca 28 Å long, the overall length of one micellar combination of two long-chain electrolyte molecules with solubilized oil in their intramicellar spaces is probably from 70 to 90 Å.

X-ray data on such lamellar micelles has come from investigations of detergent-water and detergent-water-hydrocarbon mixtures. Just what would be the size and form in a detergent-hydrocarbon mixture such as ours, can as yet only be surmised.

The work and conclusions of Harkins, Mattoon and Corrin (pages 31) may quite possibly be applicable to our results at high concentrations. They consider that the soap micelles continue to act as loci in the polymerization reaction of the solvent only up to a certain polymer yield, at which time the micelles will have all disappeared, having changed into absorbed soap. This would result in a reduction of the conductivity with the disappearance of micelles such as was found in Test 1, the conductivity falling off to zero at 20%. The other tests in which CY1 and BE<sub>2</sub> oils form the solvent also tend toward zero conductivity at the higher concentrations from 14 to 16%. Further measurements at still higher concentrations were not made as the mixtures became so thick and viscous as to make the proper handling of the mixtures impossible.

The added substances, tricresyl phosphate, naphthenic acid and ethyl ricinoleate appear to act as peptizers (see page 31) in promoting colloidal conditions, their main effect being a quantitative one on the order of the physical property being measured. From the results with the CY1 oil and hexaline naphthenate base mixtures, ethyl ricinoleate appears to be a slightly better

peptizer than the combination of tricresyl phosphate and naphthenic acid, if we take the (critical) concentration of the beginning of micelle formation as the criterion. The extra naphthenic acid in the naphthenate (Test No. 3) also appears to have a peptizing effect. In BE<sub>2</sub> oil, ethyl ricinoleate and tricresyl phosphate with naphthenic acid appear to have the same amount of peptizing action for the amounts used.

Micelle formation began earlier and higher conductivities were attained in the mixtures in which the BE<sub>2</sub> oil was first refined, and the deterring effect on micelle formation, solubilization and polymerization, of the waxy substances first removed (Test No. 9).