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THE STRUCTURE INVESTIGATION OF MAGNESIUM SOAP - HYDROCARBON SYSTEM

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ABSTRACT

The gels of Mg-stearate (2,5-20%) in apolar liquid paraffin media have been prepared with heating the binary mixture to 120-130°C, to reach the critical solution temperature (CST), and subsequently slowly (spontaneously) cooled to room temperature.

The particular components (i.e. Mg-stearate, liquid paraffin), the binary mixture (suspension) and the prepared gels and colloidal dispersions respectively were studied by means of DSC,

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to get the wiev into the system formation course and also to get the information about their thermal characteristics.

These results, in connection with those obtained through rheological investigation, determination of oil number and TEM micrographs, have given the following conception: on heating the metallic soap in liquid paraffin is dissolved in the range of CST and gives on cooling a gel or a colloidal dispersion (considering the Mg-stearate concentration) with spherical and planar (lamelar) structures of inverted type.

From rheological standpoint the gels represent plastic systems with well recognised yield value and thixotropy.

The rewarm of formed gels doesn't give stable ones anymore; their instability is the consequence of the lost water traces what confirms the TG curve.

INTRODUCTION

A soap, as the term is commonly used, is the sodium, potassium or ammonium salt of the higher molecular weight acids, e.g. sodium stearate, potassium oleate, etc. These soaps are soluble in water and have been used as detergents for centuries.

The so-called metallic soaps are the salts with metals other than alkali, e.g. calcium stearate, magnesium oleate, aluminium stearate, etc., and are unlike the ordinary soaps insoluble in water[1], at the most dispersable, if they are wet.

The both sorts of soaps have an extremely low solubility in organic solvents at room temperature. The same is true in polar and nonpolar solvents, even at moderately high ($\sim 50^{\circ}C$) temperatures. It was found that the length of alkyl chain is an important factor in the solubility characteristics of the respective soaps[2]. Metallic alcaline - earth soaps (Mg, Ca, Ba) are

about as soluble in organic solvents as alkali soaps, but their solubilities are greatly reduced in the presence of water. The solubility decreases in the following order Mg > Ca > Ba[2]. The low solubility of soaps and metallic soaps in organic solvents at room temperature is attained at elevated temperatures. Probably the most significant effect of increasing temperature on the soaps solution is the critical solution temperature (CST), at which a great increase in solubility over a small temperature range is observed. The appearance of CST may be in some cases explained through swelling of the soap lattice because of the penetrating solvent, which on heating to CST, causes the soap to disintegrate[2]. The strong van der Waals forces in the hydrophobic part of the acid prevent the formation of solutions in organic vehicles. The solubilisation result of such substances are associates (micelles) with three of more molecules[3].

The low dielectric constant of non-polar solvent prevents the dissociation of ionic surfactant (e.g. soaps and metallic soaps) what was confirmed through conductivity and NMR measurements[4]. So the association of soap and metallic soap molecules can be ascribed only to dipole-dipole attraction between polar groups, hydrogen bonds between them and in some cases, also to coordination of the end groups around a central metallic atom[4].

Systems formed by dissolving of metallic soaps in organic solvents appear in a variety of physical states, some heterogeneous, other apparently homogenous. The behavior of such binary systems was widely investigated. A number of hypotheses have been advanced[2] depending on nature of solute (soap) and solvent (oil vehicles), on temperature, and on impurities presence[2,4]. Homogenous binary systems of soaps and organic solvents

range from true thermodinamically stable solutions to a variety of colloidal dispersions, gels and liquid-crystaline phases[2,4].

The physical properties of these systems can be interpreted in the terms of micellar theory[5]. In the water - surfactant system the CMC is well established (the change of some physical properties e.g. conductivity, viscosity, etc.) what is not the case in apolar media - surfacant system[2,5].

The formed micelles are of reversed or inverted type with a core of non - hydrated or hydrated polar groups, sorrounded with hydrocarbon chains. In many systems as the concentration of surfactant is increased, a transition from these reversed micellar solution to mesophases of the reversed type occurs[2,4]. It is well known, that enthalpic and entropic contributions to formation and to stability of micelles in apolar media are qualitatively and quantitatively different from those in aqueous systems[7]. It was found that the solubilised ions (e.g. H^+, Li^+, Na^+, etc) and polar liquids (e.g. water, glycerol, etc.)in the polar core of micelles increased their stability[8].

The stability (e.g. with water inclusion) is followed by reducing the free energy of the aggregate probably by decreasing the mutual repulsion between the polar groups[7,8].

The solubilisation phenomena of the respective micelles have also been the subject of many investigations with respect to both - fundamental and tehnical aspects[7].

The investigated Magnesium stearate is widely used in different industrial production; in pharmacy and cosmetics in powdery preparations, in tablets, as (co) emulsifying agent in creams and as the framer of oil vehicles[1,9,10].

In the previous investigations we were trying to determine the factors regulating the formation of stable Magnesium stearate

gels in apolar liquid paraffine[11,12]. Nowadays we are trying to elucidate the gel formation and its' characteristics by means of thermal analysis and with determination of some rheological properties, further using the TEM technicque to get the visual picture of the formed gel structure.

EXPERIMENTAL

Materials

Mg-stearate, a product of Lek, Pharmaceutical and Chemical Work, Ljubljana, meets the requirements of USP XX regarding the physical properties - bulk volume, moisture content, melting point and chemical properties - Mg in form of MgO content, acid number. Liquid paraffin meets the requirements of Ph.Jug.III.

Preparation of systems (colloidal dispersions and gels)

The white suspension of Mg-stearate (in different concentrations) in liquid paraffin was heated on oil bath to 120-130°C. As Mg-stearate was dissolved and a clear oil solution was formed, the sample was left to cool together with the oil bath to room temperature. On cooling the clearness was lost and the formed systems were opaque white.

The preparation is connected with foaming which stops not until Mg-stearate is completely dessolved and transparency is attained. Foaming is the consequence of in Mg-stearate bound air and water (in form of moisture and crystal water).

Differential Scanning Calorimetry

Samples (20-60 mg) were weighed in platinum pans with holed lids. The samples were heated in air atmosphere (flow of 20 ml/min.) and thermograms were obtained on a Mettler TA 2000 System Differential Scanning Calorimeter. Thermograms were obtained by heating at a constant heating rate of 4°K per

minute, thermogravimetrical (TG) range 10 mg and 1 mg respectively, DSC range 20 μV and recorded at a constant chart speed of 60 cm/h. Areas under the differential scanning calorimeter heating curves were determined by means of weighing.

Rheological measurements

The rheograms were obtained using the "cone and plate" system of rotational viscometer Rheotest 2 (VEB MLW Prüfgeräte, Medingen, GDR).

Oil number determination

The oil number showing the degree of liquid phase fixation in the gel (on solid or other type of structure i.e. liquid crystalline phases) was established gravimetrically using the modified method according to Voigt[8] (modification concerning time). The oil absorbtion into the filter paper (Schleicher-Schüll N° 589, Weissband) was determined after 24 hours.

TEM technique (Freeze - fracture method)

The specimens were prepared in the Balzers BSV 202 freeze-etching unit, according to the method of Moor[13]. The 12,5% Mg-stearate gels were mounted between complementary specimen holders. Each pair was held together with tweezers, while the samples were frozen in liquid freon 22, cooled with liquid nitrogen. The fracturing of the specimen was carried out in the liquid nitrogen container by separating the two pairs of the holders. Platinum carbon replicas were made on cleaved surfaces at 2×10^{-6} torr and at $-100^{\circ}C$ and cleaned by modified tehniques of Bosch and Jacob[14]. The replicas were examined in Jeol 100 CX Electron microscope.

The direction of shadowing is indicated with the arrow at the bottom left corner of the figure.

RESULTS AND DISCUSSION

A gel is formed only when the solubilisation of Mg-stearate is performed in apolar (liquid paraffin) but not in polar (hydrogenated triglycerides) oil vehicles[15,16]. It is probably due to the Mg-stearate small polarity only about 2 - 4 D[2,3]. Additionally it was stated that only the regulated, but not the "shock" colling (on the salt - ice mixture at ~-15°C) enables the formation of stable gels[15]. For the elucidation of gel formation it is therefore important to study the thermal behaviour of particular components in the binary system at first and of the suspension and gel respectively afterwards.

Chemically Mg-stearate represents a hydrate with 1,5 water molecules, which are succesively removed by heating up to 115°C (Fig. 1). The enthalpy changes ΔH_2 (from 50–80) and ΔH_3 (from 80-95°C) undoubtedly interfere with the water loss. The ΔH_4 change is located in the temperature range where the loss of mass is still observed and in which according to literature[3], the polymorph modification of monocline lattice to hexagonal one is to be stated. The low heating rate (1°K/min.) additionally shows, that in this temperature interval two separate heat changes, among which the first is connected with the loosing mass, really exist[17]. The peak temperature of the fourth change (ΔH_4) (Fig. 1) however, doesn't represent the melting point of Mg-stearate, what is usually ment in the literature[3].

The second step in the investigation represents the study of liquid paraffin thermogram (Fig. 2). Three well recognised endothermic changes are to be seen. The reason of these changes, wasn't identified but it could be supposed, that changing of hydrocarbon molecules orientation occurs.

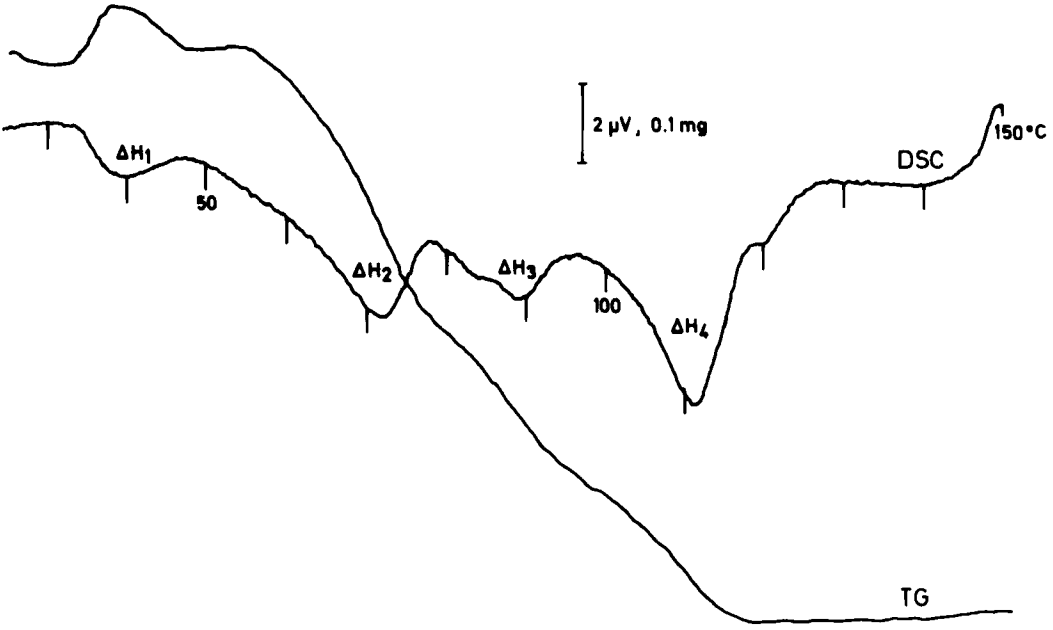

FIGURE 1. Thermogram of Mg-stearate.

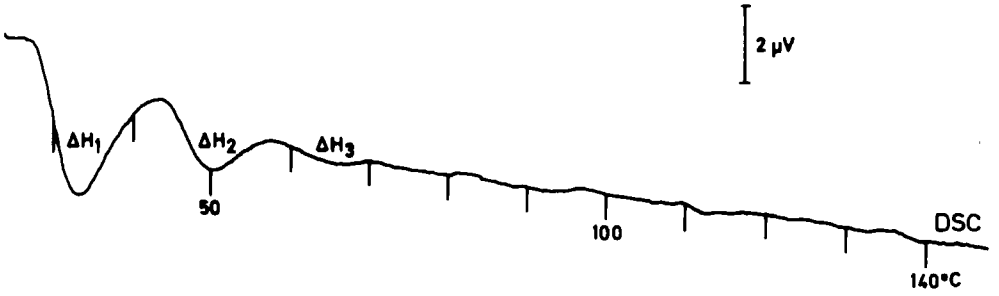

FIGURE 2. Thermogram of liquid paraffin.

The next figure (Fig. 3) shows the thermogram of Mg-stearate/liquid paraffin suspension. There are four enthalpy changes, among which the first three (ΔH_1, ΔH_2, ΔH_3) belong to the vehicle and the fourth to Mg-stearate. As it was expected, by heating of Mg-stearate in liquid paraffin, the foaming begins at nearly 80°C, what is, considering the TG curve (Fig. 3),

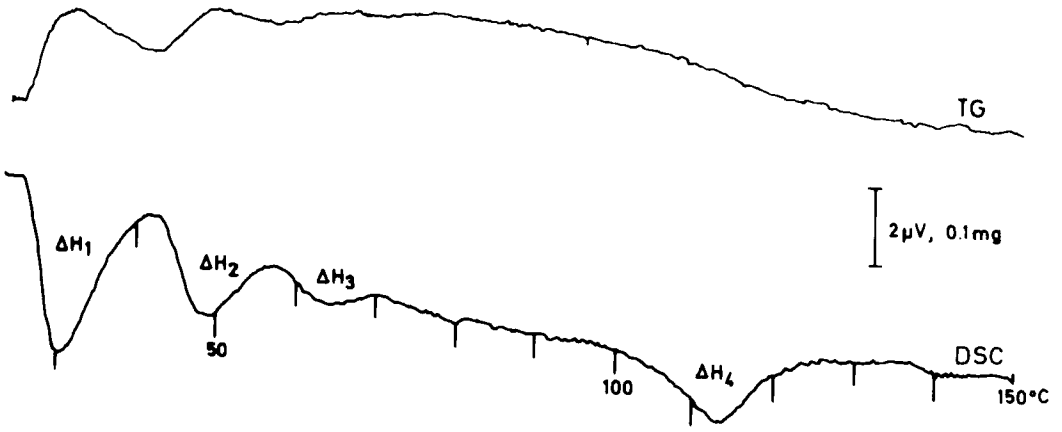

FIGURE 3. Thermogram of Mg-stearate/liquid paraffin (10 w/w%) suspension.

connected with the loss of water. The further very important evident information is the CST.

This temperature ($\sim 115^{o}C$), considering also the literature data[2,3,16], is tightly connected with the loss of water and with already mentioned structure modification[3]. The thermogram of 20% Mg-stearate gel (Fig. 4) is very resembling to that just discussed. Resuming the thermograms informations we are aware that the ΔH_4 change belongs to Mg-stearate part of the gel structure, and the first three to the liquid paraffin, which also specifically contributes to the whole structure.

From until now discussed thermal propertis of the whole system (gel) and of the particular components, it is possible to conclude: by heating of Mg-stearate in liquid paraffin the former dissolves building some kind of gel structure after cooling. The thermal energy required for Mg-stearate to dissolve out of suspension is far greater than that required for Mg-stearate to dissolve out of gel at different concentrations (Fig. 5). This result is undoubtedly an evidence that systems do not represent micro-

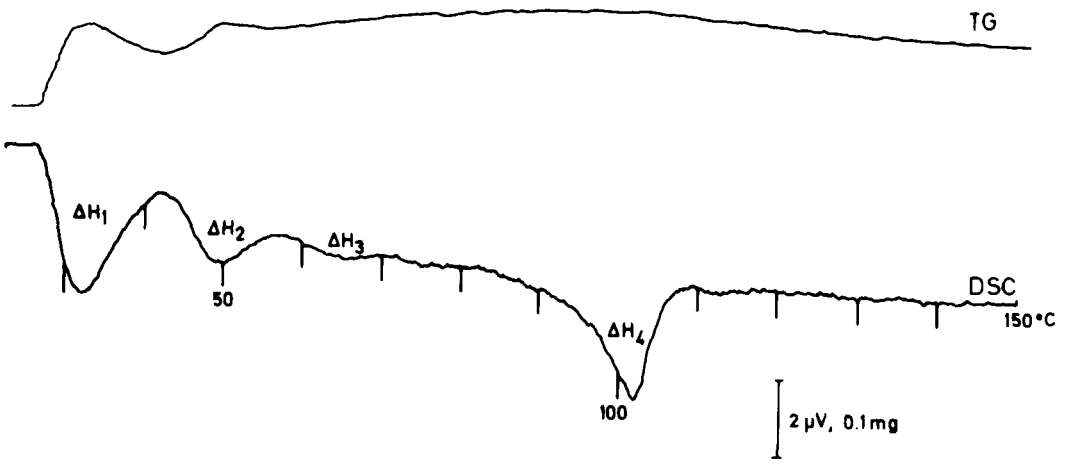

FIGURE 4. Thermogram of gel (20 w/w%).

crystalline suspensions. The TEM micrographs demonstrate this statement once again: the gel structure is ascribed to spherical micelles and to some kind of planar (lamelar mesophases) structure (Fig. 6).

As the temperatures of ΔH_4 change of gels are situated at lower temperatures (comparison with pure Mg-stearate and with suspension) it means, that also the entropy gels' changes are lower. It is however logically, while the pure Mg-stearate and its suspension in liquid paraffin posses crystal structures, or with other words, their structure ordering is far greater.

The reason of ΔH_4 changes of Mg-stearate in gels considering the different concentrations is still unknown, however they are probably the result of different association (structures) of Mg-stearate molecules. A very interesting fact was unexpectedly stated : the rewarm of gel to 120-130°C (its melting) brings a transparent one with far greater viscosity on cooling: gel shows no spreading properties and is nearly crumbly. The thermal

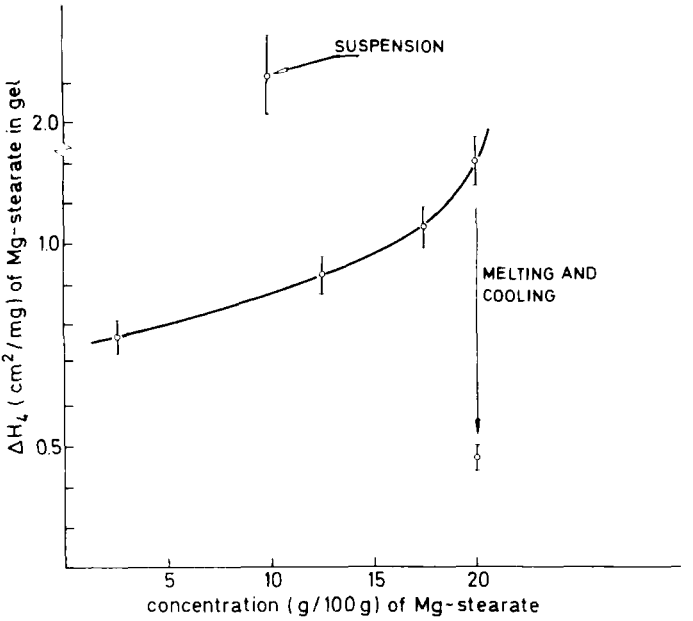

FIGURE 5. Dependence of ΔH_4 (dissolving energy of Mg-stearate) from Mg-stearate concentration.

properties are also different. In comparison with "normal" gels, these gels are highly unstable (syneresis). The reasons of such behaviour are also unknown; but the DSC investigations[17] gave however some indicies, that the water traces loosing on rewarm (TG curves, Fig. 4) play a very important role in the formation and stabilisation of gels, what is in accordance with the statements in literature data[7,8]. A great viscosity and ΔH_4 change (Fig. 7,8) is the evidence of different gel structure.

Otherwise the Fig. 7 and 8 show that between concentration of Mg-stearate and viscosity respectively and the energy needed for gel destruction, a sort of connection does exist: the higher the concentration and viscosity respectively, the greater the energy.

The rheological properties study of investigated systems has shown that gels represent plastic materials with well recognised

FIGURE 6. TEM micrograph (a - spherical micelles, b - disrupted surface of liquid paraffin, c - planar atructures).

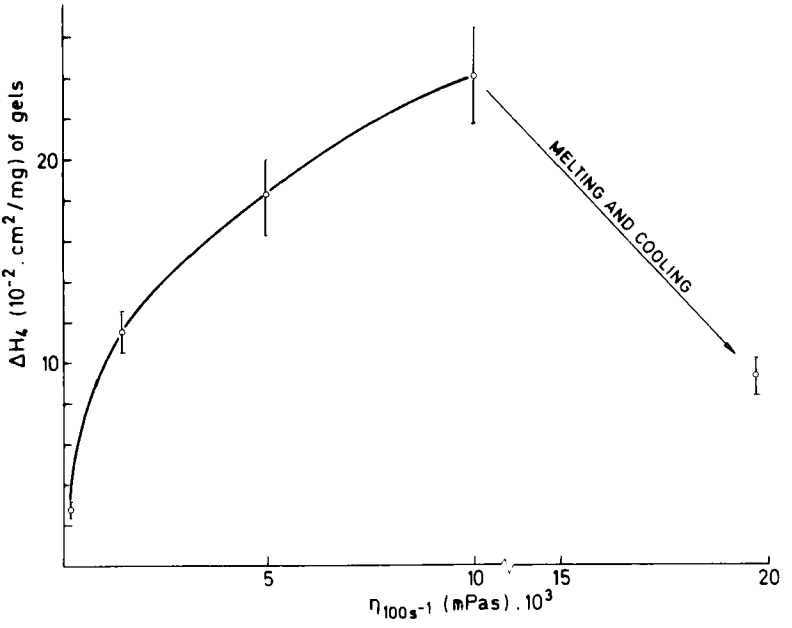

FIGURE 7. Dependence of ΔH_4 (total destruction of gel structure) from gels viscosity.

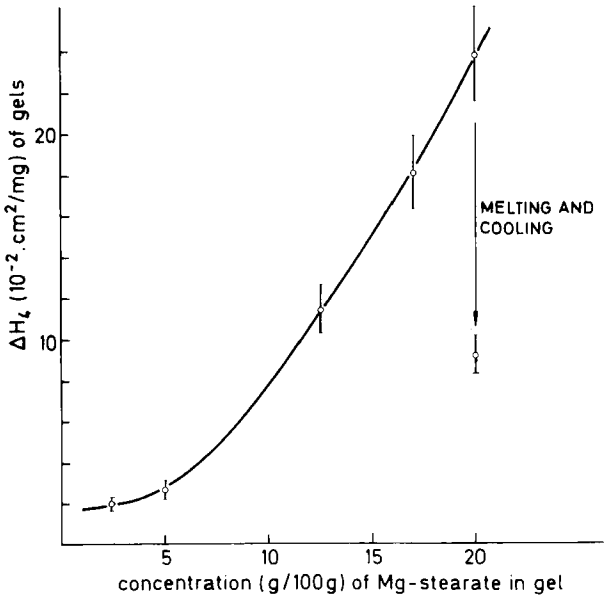

FIGURE 8. Dependence of ΔH_4 (total destruction of gel structure) from Mg-stearate concentration.

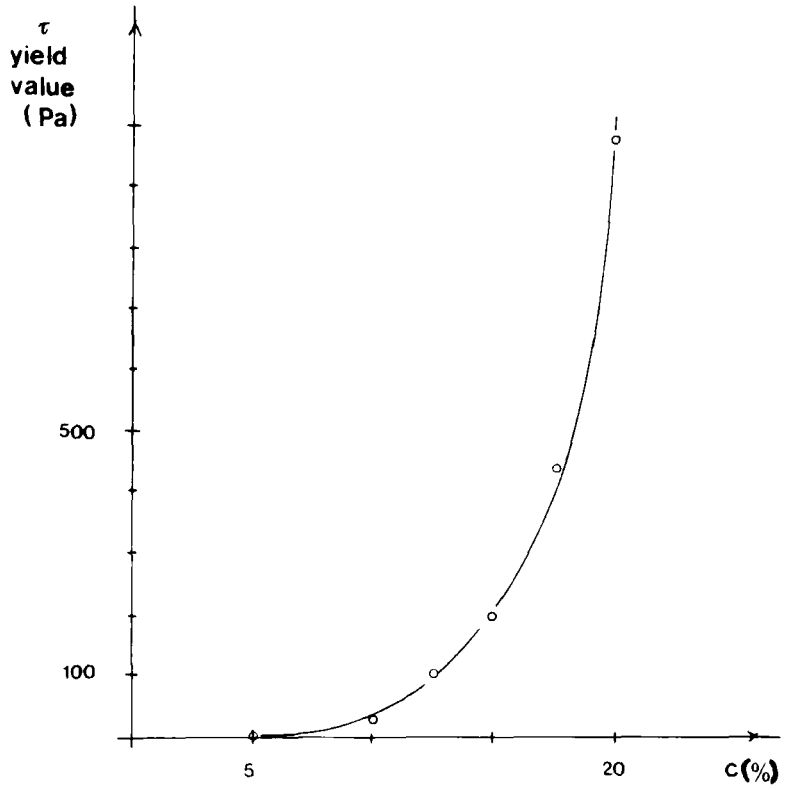

FIGURE 9. Dependence of yield value from Mg-stearate concentration.

yield value (Fig. 9), thixotropy[18] and plastic viscosity (Fig. 10). The raise of Mg-stearate concentration is reflected in the raising values of plastic viscosity, yield value and hysteresis loop surface. These results are in accordance with those obtained through thermal analysis: the greater the gel strength (yield value, plastic viscosity), the greater the thermal energy (ΔH_4) required to deform and to destruct it. The nonisothermal rheological investigation[17] has confirmed the results presented in this report :with raising Mg-stearate concentration the flow activation energy increases and the frequency factor decreases, or with other words:

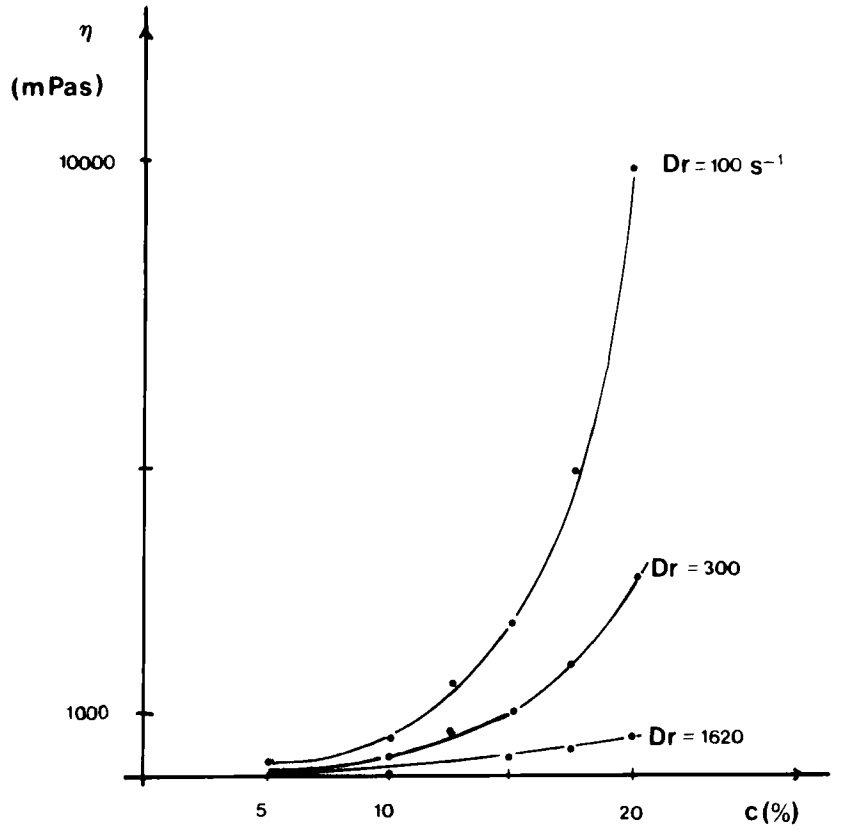

FIGURE 10. Dependence of gel viscosity from Mg-stearate concentration.

gels with higher Mg-stearate concentration are characterised through stronger structure associate connections.

The oil number determination results give us informations about the liquid phase solvation degree in the gel system. However, the liquid phase of a gel can be immobilised not only through solvatation (physical adsorption, energetically connected liquid phase) but also through sterical blocade of the structure forming components[19].

The oil number results (Fig. 11) support the conception, that with the raising Mg-stearate concentration more structural

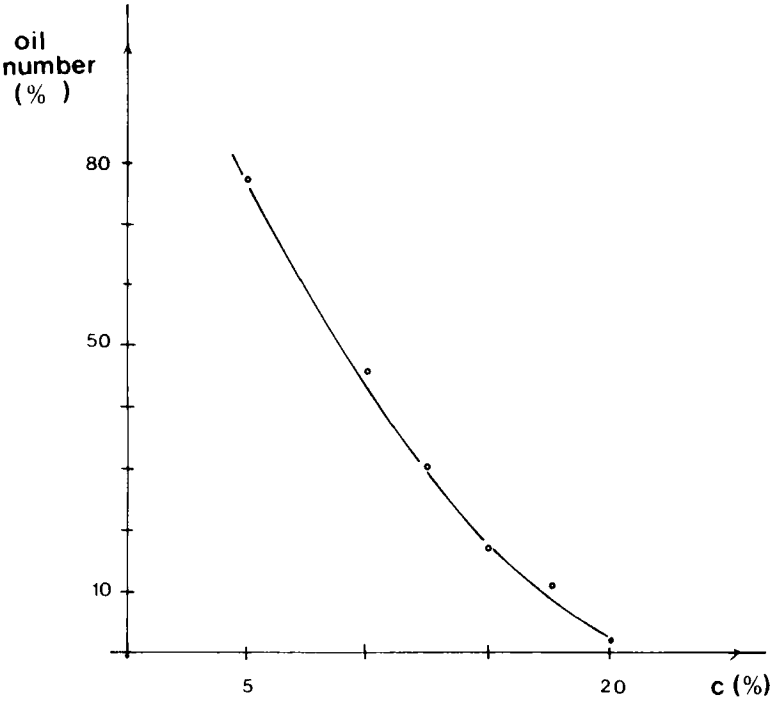

FIGURE 11. Connection between oil number of gels and Mg-stearate concentration.

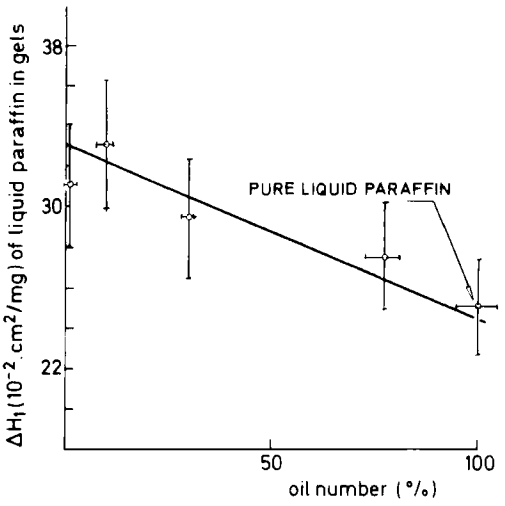

FIGURE 12. Dependence of ΔH_1 (of liquid paraffin) from gels' oil number.

associates are formed enabling the physical adsorption and mechanical blocade of liquid paraffin. The combination of thermoanalytical data and oil number results gives a very interesting information : ΔH_1 of liquid paraffin increases when the oil number decreases (Fig. 12). Assuming that ΔH_1 enthalpy change indicates some kind of hydrocarbon molecules internal orientation[20], it is logically, that the adsorption of liquid paraffin molecules on Mg-stearate associates causes also change in ΔH_1 values. To cause an equivalent conformational change of adsorbed hydrocarbon molecules some energy is needed for desorption at first. The further energy enables the change of free molecules. Increasing ΔH_1 values are therefore the consequence of increasing adsorption of liquid paraffin.

REFERENCES

1. R.G. Bossert, J. Chem. Educ. 27, 10 (1950).
2. P.S.Kertes, H.Gatman, in "Surface and Colloid Science", Ed. E. Matijevič, Vol. 8, John Wiley & Sons, New York, London, Sydney, Toronto, 1976, p. 193.
3. B.W.Müller, Seifen, Öle, Fette, Wachse, 102, 493 (1976).
4. P. Akwall, J.Danielsson, P.Stenius, in "Surface Chemistry and Colloids", Series One, Vol. 7, M.Kerker Ed., Butterworts University Park Press, London, Baltimore 1972, p. 97.
5. N. Pilpel, Chem. Rev. 63, 221 (1963).
6. A.S.Kertes, in "Micellisation, Solubilization and Microemulsions", Ed. K.L.Mittal, vol. 1, Plenum Press, New York, London, 1977, p.445.
7. H.F.Eicke, ibid., p. 429.
8. idem, J.Colloid Interface Sci. 52, 65 (1975).

9. R.Voigt, Lehrbuch der pharmazeutischen Technologie, VEB Verlag Volk und Gesundheit, Berlin, 1975.
10. M.G.deNavarre, "The Chemistry and Manufacture of Cosmetics", vol. 4, sec.Ed., Continental Press, Orlando, 1975.
11. M.Božič, Masters thesis, Faculty of Natural Sciences and Technology, University of E.Kardelj, Ljubljana, 1978.
12. J.Korbar, M.Božič, Parfümerie u. Kosmetik, 58, (1977); M.Božič,J.Korbar-Šmid,J.Lavrič, ibid. 61, 8 (1980); M.Božič, J.Korbar-Šmid, ibid. 61, 12 (1980).
13. D. Branton, Phil. Trans. Roy. Soc. Lond. Sci. B. 261, 133 (1971).
14. M.V.Bosch, W.Jacob, J.Microsc. 122, 2, 239 (1981).
15. A. Kramarič, Diploma work, Faculty of Natural Sciences and Technology, University of E.Kardelj, Ljubljana 1982.
16. G.Büsch,F.Neuwald, J.Soc. Cosmet.Chem. 24, 763 (1973).
17. S.Srčič, unpublished data.
18. J.Korbar-Šmid,S.Srčič,J.Kristl, Vestnik slovenskega kemijskega društva, in press (1984).
19. R.Hüttenrauch, Pharmazie, 23, 400 (1968).
20. R.Hüttenrauch, Pharmazie, 25, 169 (1970).