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STUDY ON THE EFFECT OF EMULSIFIER ON THERMAL BEHAVIOUR OF CONCENTRATED O/W EMULSIONS

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ABSTRACT

Some investigations on the capability of differential scanning calorimetry (DSC) for the characterization of concentrated mineral oil in water emulsions indicated certain differences in their thermal behaviour depending upon various factors including particularly the emulsifier. In this paper DSC examinations were undertaken in order to assess the influence of the emulsifier solubility properties, i.e. hydrophile-lypophile balance (HLB values), emulsifier concentration and its distribution between the interface, continuous and disperse phase on the thermal behaviour of O/W emulsions and some of their thermal characteristics.

INTRODUCTION

An emulsion submitted to continuous heating undergoes numerous changes in its dispersion state, i.e., flocculation and coalescence of disperse droplets, changes in adsorbed emulsifier layer (distortion and density of the layer, decrease of hydration between hydrophilic moiety of the emulsifier and water, desorption of the emulsifier from the interface), changes in the water phase (size and shape of the micelles, micellar hydration, oil solubilization), appearance of a microemulsion phase, development of a multiphase emulsion structure, phase inversion or separation of the phases.

Theoretically, the energy changes and the heat released associated with the changes of the emulsion can be followed easily by thermoanalytical methods. However, the non-extensive literature data show that differential thermal analysis and DSC have been used mainly to study either the behaviour of freezing droplets (1) or thermal induced phase inversion of emulsions (2-5).

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EXPERIMENTAL

The examinations were performed with the oil/water emulsions containing 70% (mass) paraffin oil and different amounts of tween emulsifiers with various fatty acid moieties and polyoxyethylene chain lengths (tween 20, tween 21, tween 60, tween 61 and tween 65) in the temperature interval from 30° to 150°C.

The investigations were carried out with the differential scanning calorimeter DSC-1B Perkin Elmer with detection of the evolved gas phase (EGD), in the dynamic nitrogen atmosphere using the vessel for volatile samples.

RESULTS AND DISCUSSION

The results obtained show how the tween type, its concentration and the way the emulsifier was added to the emulsion, influence the changes of the emulsion tested during the heating.

Fig.1. shows DSC and EGD curves for the emulsions containing 1% of tween 20, tween 21, tween 60, tween 61 and tween 65 which were dissolved in the water phase prior to the emulsification. The endothermic changes of DSC curves together with the changes of EGD curves represent a breaking process taking place within O/W emulsions comprising a gradual separation of the water.

Different thermal stabilities of the emulsions having the same concentrations of various tweens can be concluded from DSC curves if the temperatures of the peak maxima in the breaking process are compared.

The dependence of the temperature of the breaking process maximum rate on hydrophile-lypophile balance (HLB) of the emulsifier is shown in Fig.2. The temperature tends to decrease with the increase in HLB values of the emulsifier.

A raise in the HLB value brings about a lower thermal stability which may be explained by different changes in hydration between water and hydrophilic moieties of tween molecules and a higher increase of the lipophilic character of tween molecules with higher HLB values upon heating.

Figure 3 shows the influence of the emulsifier distribution among the phase and the interface on the thermal stability of the emulsions which were stabilized with tween 21 and tween 61 added only to the water phase or oil phase, or to both phases, i.e., half of the quantity to water and the other half to oil.

From the DSC curves, it can be seen that the emulsion of tween 21 in oil has the highest stability and that of tween 21 in water the lowest. A similarity of stability change of the emulsion with tween 61 has not been observed.

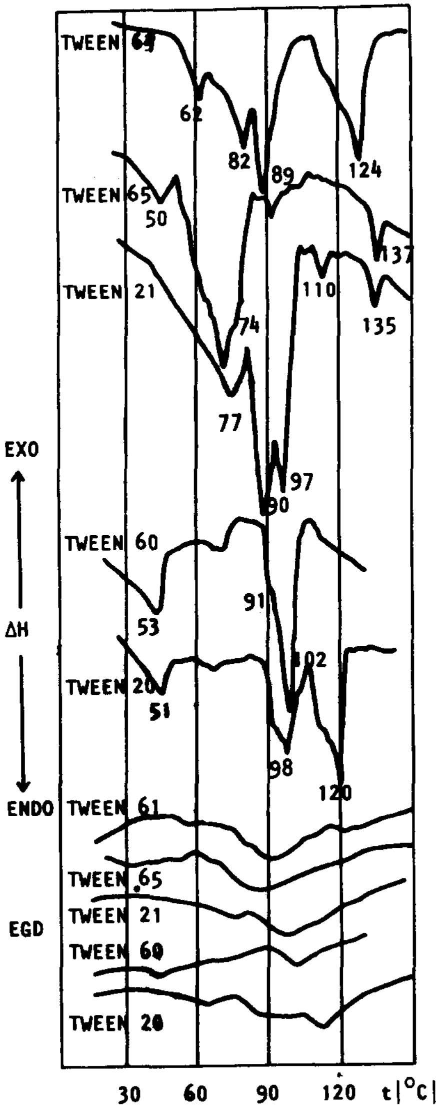

Fig. 1. DSC and EGD curves for emulsions with 1% of emulsifiers.

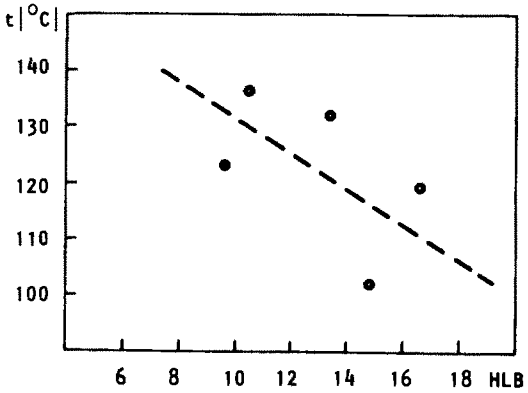

Fig.2. The change of the temperature of the emulsion breaking process of HLB values of emulsifiers.

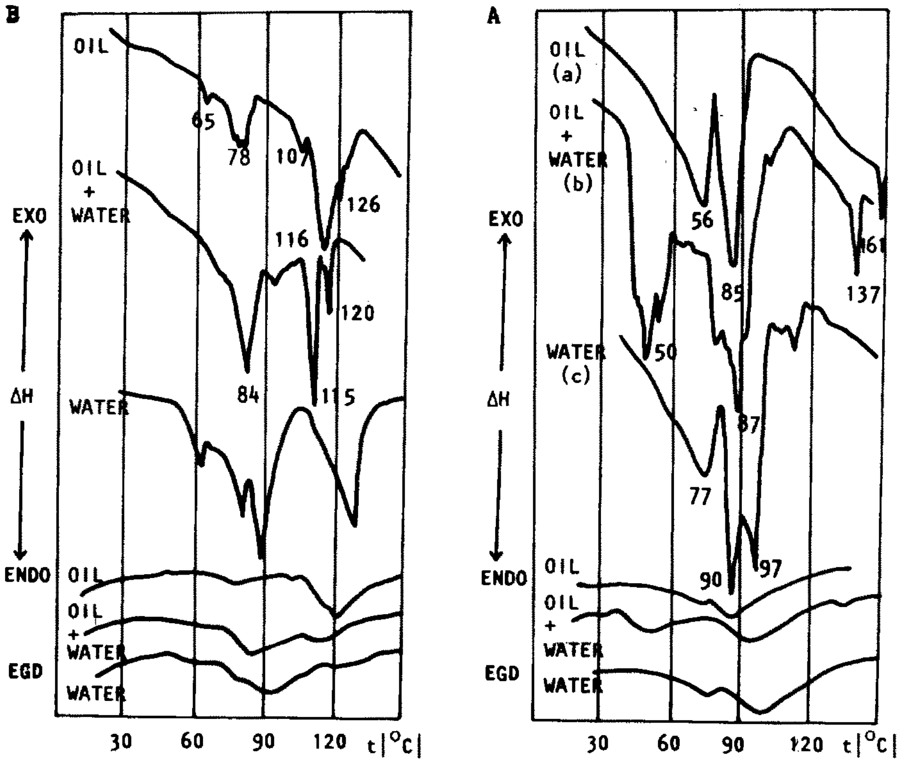

Fig.3. The influence of the process addition of emulsifiers in the emulsion on its thermal stability; A 1% tween 21; B 1% tween 61.

The influence of emulsifier concentration on the thermal stability was investigated on the emulsions containing tween 20 and tween 21 which were dissolved in the water phase prior to the emulsification. The tween concentration varied from 0,5 and 1,0, respectively to 6,0%. The results show that the maximum temperature of the breaking process of the emulsions under the conditions tested has the lowest value at an emulsifier concentration of about 1,5% (Fig.4.)

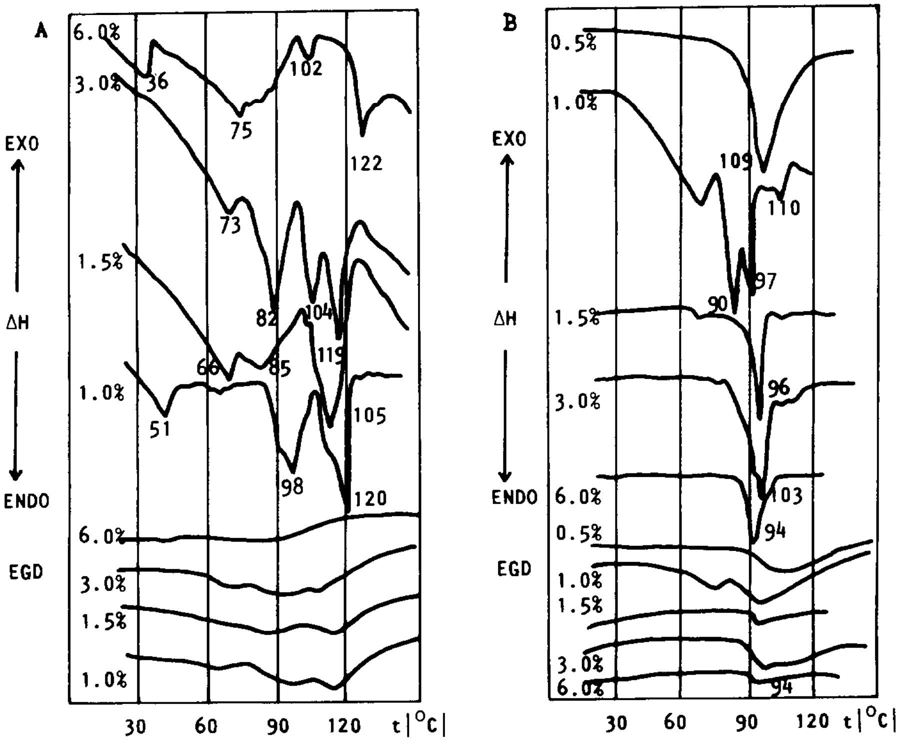

Fig 4. The influence of the emulsifier concentration on the thermal stability of the emulsion: (A) tween 20; (B) tween 21.

In Fig.5. the concentration dependence of the temperature corresponding to the maximum rate of breaking process as concluded from DSC curve can be seen. The influence of the emulsifier concentration change on thermal stability can be less pronounced than that of the emulsifier distribution among the phases or the change in HLB values.

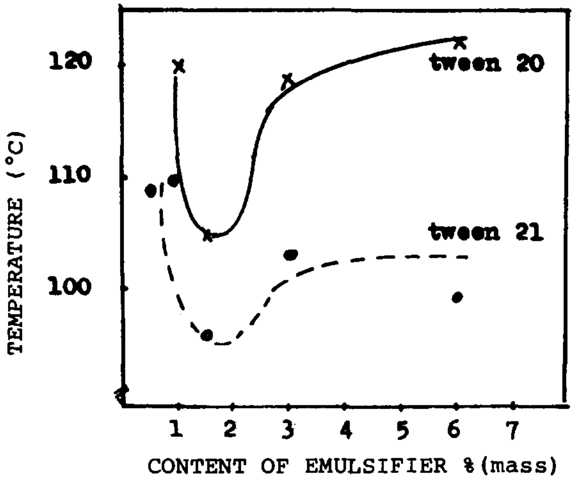

Fig. 5. The influence of emulsifiers concentration on the temperature of maximum rate of emulsions breaking.

CONCLUSION

The examinations on thermal behaviour of the emulsions stabilised with different concentrations of tween 20, tween 21, tween 60, tween 61 and tween 65 and with various distribution of the tween between the phases and the interface have shown:

1. In the tested interval of temperature the registered endothermic processes, as well as the changes in EGD curves, i.e. separation of water phase represent a breaking process of the given emulsions.

2. If the same conditions are used for the preparation of the emulsions, the type of tween, i.e. its HLB value influences their thermal stability.

3. The way of adding emulsifiers to the emulsion phase influences thermal stability.

4. The dependence of the temperatures of maximum rate of breaking process on the emulsifier concentration was noted.

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