ZESZYTY PROBLEMOWE POSTĘPÓW NAUK ROLNICZYCH 1981, z. 211

THE INFLUENCE OF FATTY ACID STRUCTURE ON THEIR WETTING BY AQUEOUS SURFACTANT SOLUTIONS AND THE FRACTIONATION OF FATTY ACIDS

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The wettability of selected solid fatty acids by different surfactants was investigated. On the basis of the measured wetting angles the optimal composition of the wetting solution was established and then separations of rape seed oil fatty acids were performed.

INTRODUCTION

For the last ten years [1, 2, 4-12] separation of fatty acids and triglycerides in two fractions: solid and liquid with the help of surface active agents has found wide application.

The selection of apprioprate agents for the separations has been taken til now exclusively on experimental way. So it seemed obviously, to base the selection of apprioprate surfactants on physical properties of separated phases and applied surfactants.

The wetting of fatty acid crystals by aqueous solutions of surface active reagents plays the main part in the fractionation process.

This wetting depends on the value of wetting angle at the interface: solid fatty acid-liquid fatty acid-aqueous solution of surfactant.

The relatively simplest way to determine the wetting abbilities of a particular surface active agent is the measurement of the contact angle. As it is known the smaller the angle the better the wetting.

EXPERIMENTAL

The measurements of the wetting angle were taken by sessile drop method [3] and the angle was directly calculated from the dimensions of the drop by the following formula:

$$\operatorname{tg}\frac{\Theta}{2} = \frac{2h}{d}$$

where:

h — the drop height,

d — diameter of the contact surface between soild and wetting phase.

The wetting angle was examined for some triphase model systems where the liquid phases were: oleic (C 18 : 1), linoleic (C 18 : 2) or linolenic (C 18 : 3) acids and the surfactant aqueous solution, and the solid phase consisted of palmitic (C 16 : 0), stearic (C 18 : 0), behenic (C 22 : 0), erucic (cis C 22 : 1) or brassidic (trans C 22 : 1) acids.

To compare the wetting of erucic and stearic acid crystals by equeous solutions of surfactants the measurements in following systems were carried out:

erucic acid — oleic acid — aqueous solution of surfactants

and

stearic acid — oleic acid — aqueous solution of surfactants.

The surface active compounds used to the experiments are shown in Table 1.

The results of the wetting angle measurements at the phase boundary as a concentration function are shown at diagrams.

Figure 1 shows the dependence of the wetting angle at the phase boundry: stearic acid-oleic acid-aqueous surfactant solution of the surfactant concentration. It was stated that aqueous solutions of nonionic

Table 1

Surface active agents used to tests

Compounds type	Trade name	Chemical name
Nonionic	Alfenol 710	Alkylphenol polyoxyethylated (10 oxyethylene groups)
Anionic	—	Sodium laureate
Anionic	Marlon-375	Sodium Dodecylbenzene-sulphonate
Anionic	Nansa HS-55	Sodium Dodecylbenzene-sulphonate
Anionic	—	Lauryl Sodium Sulphate
Anionic	Elfan NS-243	Trioxyethylated Lauryl Alcohol Sodium Sulphate

Surface active content — 98%.

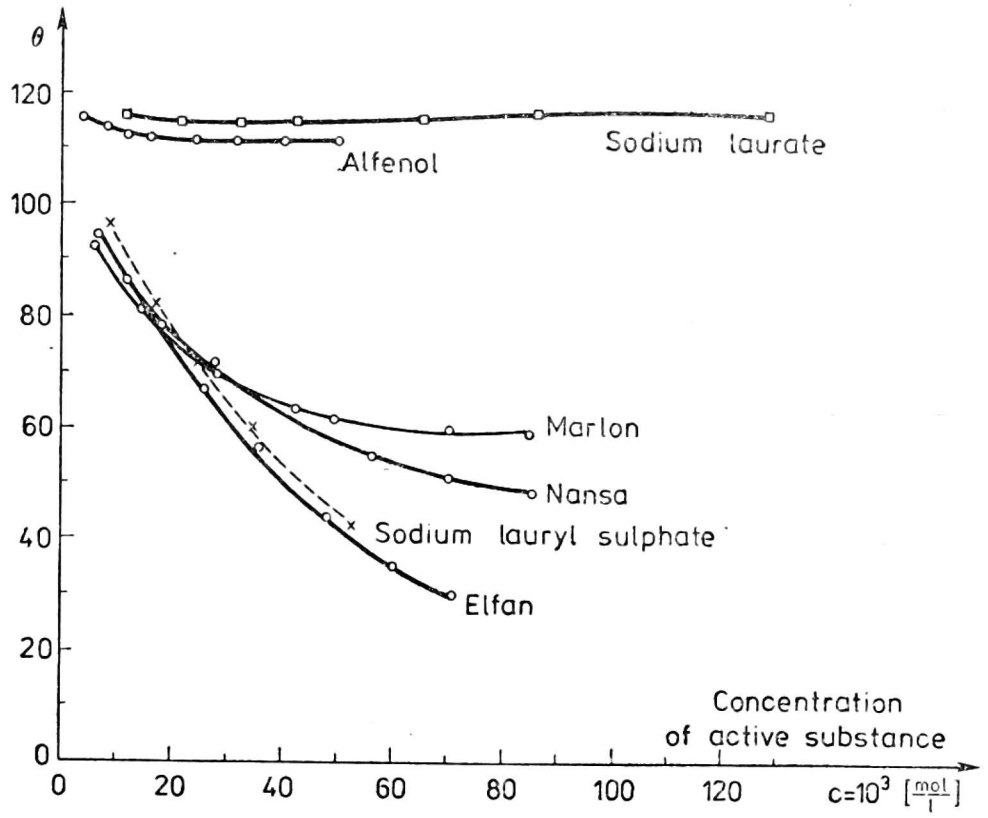

Fig. 1. Dependence of the wetting angle Θ at the phase boundary: stearic acid — oleic acid — aqueous solution of surfactant upon the concentration of surfactant

alfenol and anionic sodium laureate do not wett the solid fatty acid well. The wetting angles of fatty acids by these solutions oscillate in the range of 120-130°. The other solutions of anionic tensides are characterystic of good wetting and the wetting angles approach values even smaller than 90°. These angles diminish with growing surfactant concentration.

Comparing the diagrams of stearic and erucic acids it was ascertained that the course of wetting curves is similar but the values of wetting angles for the erucic acid are higher. This proofs that erucic acid crystals are worse wetted than the stearic ones. To lear up the difference in wetting of erucic and stearic acid, and to investigate the influence of the double bond stereoisomerism on the wetting susceptibility, additional measurements of wetting angles were performed for a system where instead of erucic acid (cis Δ-13-docosenoic acid) there were used brasidic acid (trans Δ-13-docosenoic acid) and the saturated acid of the same chain length — it is behenic as well as palmitic acid.

On Fig. 3 we see the comparision of the wettability of palmitic, stearic, behenic, erucic and brassidic acid crystals by aqueous elfan solutions. As it is seen the wetting of erucic acid and the four remaining acids is quite different. So the different wetting susceptibility of discussed acids can be related with different crystalline structures of the acids.

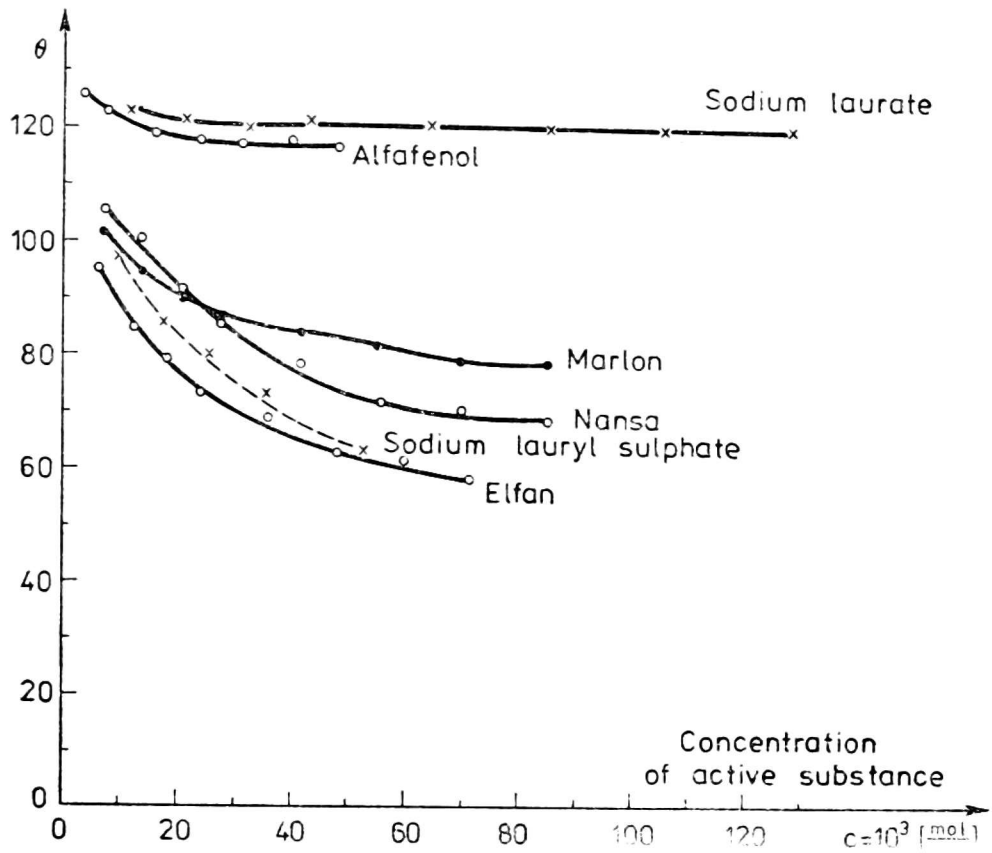

Fig. 2. Dependence of the wetting angle Θ at the phase boundary: erucic acid — oleic acid — aqueous solution of surfactant upon the concentration of surfactant

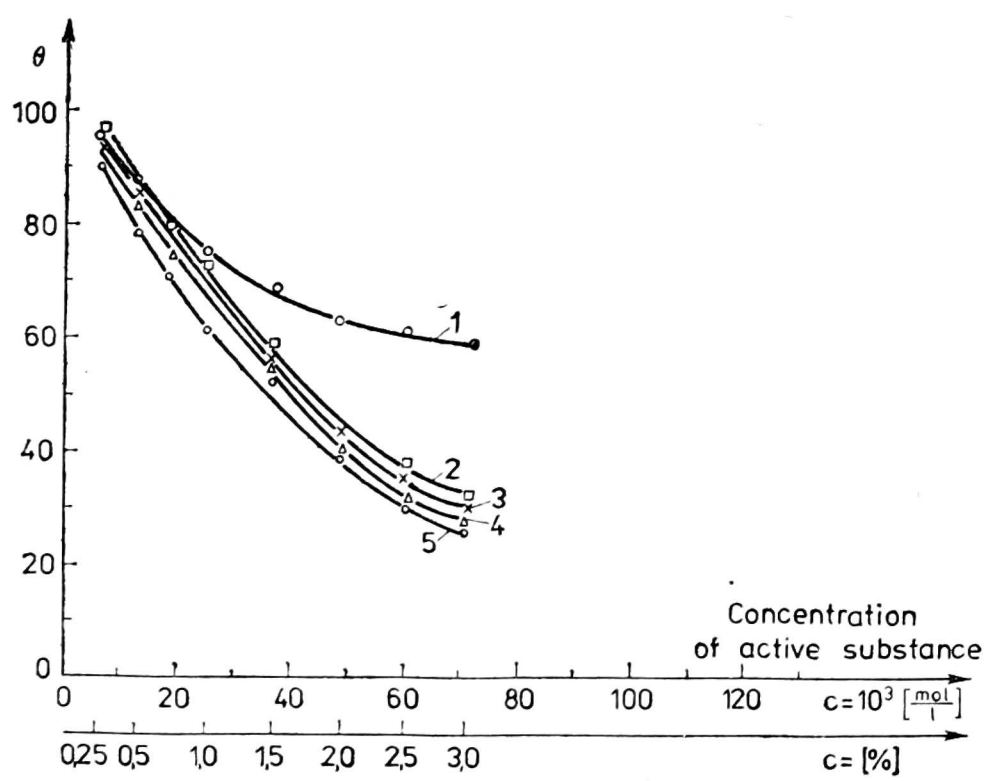

Fig. 3. Comparison of wettability of palmitic (2), stearic (3), behenic (5), brassidic (4) and erucic (1) acids crystals by aqueous Elfan solutions

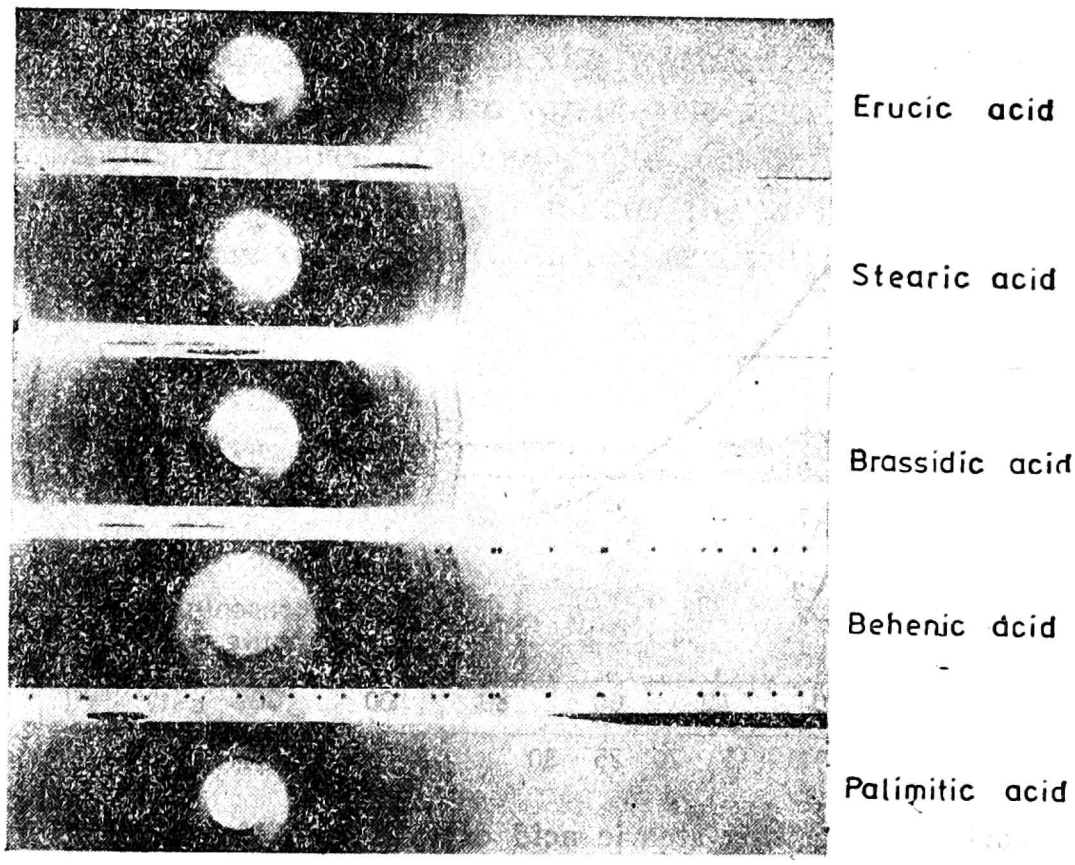

Fig. 4. Powder X-ray diagrams of fatty acids

Powder X-ray diagrams, which are to be seen at Fig. 4 can confirm this hypothesis. Differences on diffraction pictures are distinct and it results from those pictures that the crystalline structure of erucic acid is different from the other acids.

Therefore the conclusion arises that the wettability of fatty acid crystals by aqueous solutions of tensides first of all depends on their crystalline structure, and this in turn qualitatively depends on the structure of fatty acids — it depends namely on unsaturation of the fatty acid and on double bond configuration.

In the mixture of fatty acids being separated aparat from oleic acid there can be other unsaturated acids and because of that, it seemed to be necessary to examine the influence of the liquid phase unsaturation on wetting of solid fatty acid by aqueous solutions of tensides.

For that purpose instead of monounsaturated — oleic acid in the model triphase system the dienoic linoleic acid and trienoic linolenic acids were introduced.

Figure 5 presents the comparison of wetting of stearic acid crystals by aqueous elfan solutions in triphase systems with liquid oleic, linoleic and linolenic acids.

It was ascertained that the highter the unsaturation degree of liquid fatty acids the better the wettability of solid fatty acids by aqueous surfactant solutions.

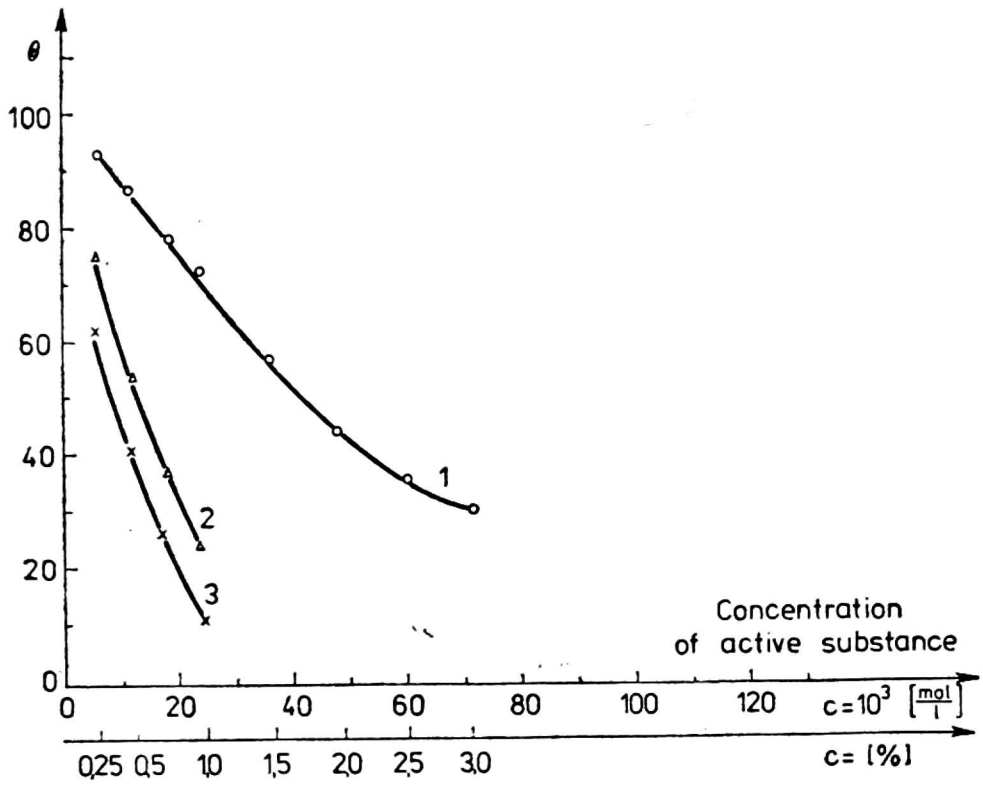

Fig. 5. Comparison of wetting stearic acid crystals by Elfan aqueous solutions in tripphase system with liquid oleic acid (1), linoleic acid (2), and linolenic acid (3)

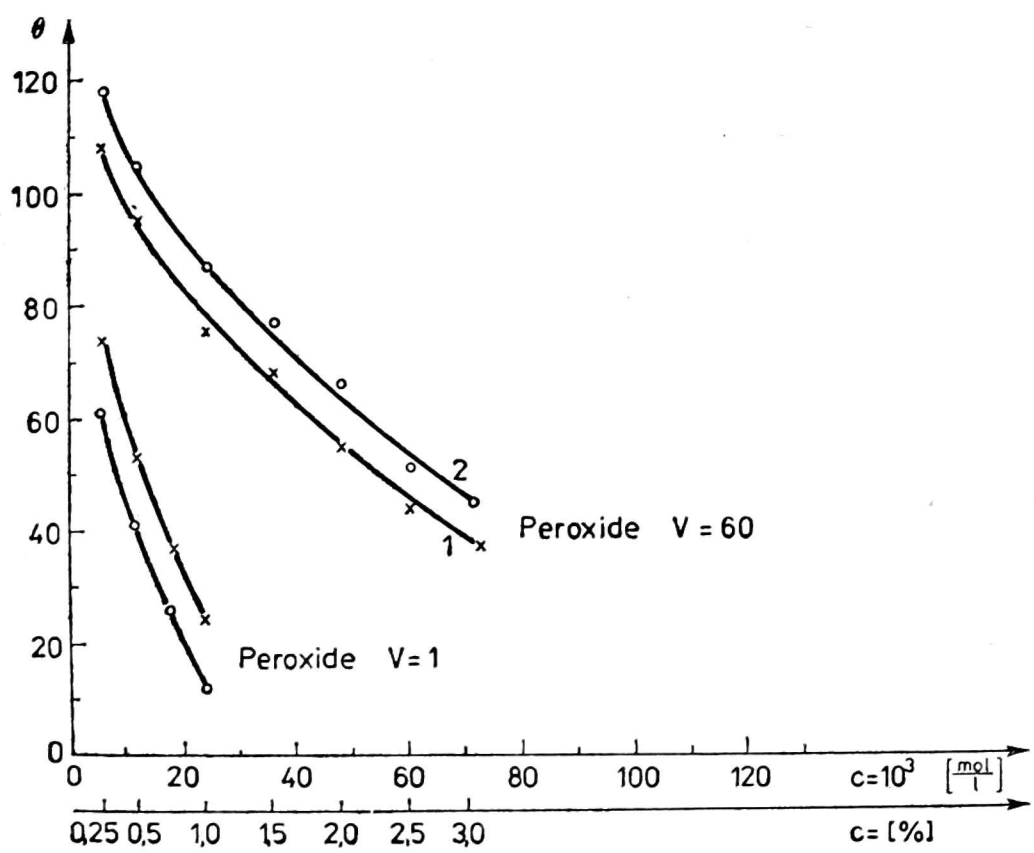

Fig. 6. The influence of oxydation of liquid fatty acid on the wettability of stearic acid by equeous Elfan solution: 1 — linoleic acid, 2 — linolenic acid

It was ascertained also, that the oxidation degree of unsaturated fatty acid is of great influence on the wettability of solid fatty acids.

As it is seen from the diagram for stearic acid the higher the liquid fatty acid oxidation degree the lower the wettability of solid acids by aqueous solutions of surfactants, it means the wetting angle grows up. This dependence was observed for all examined solid fatty acids.

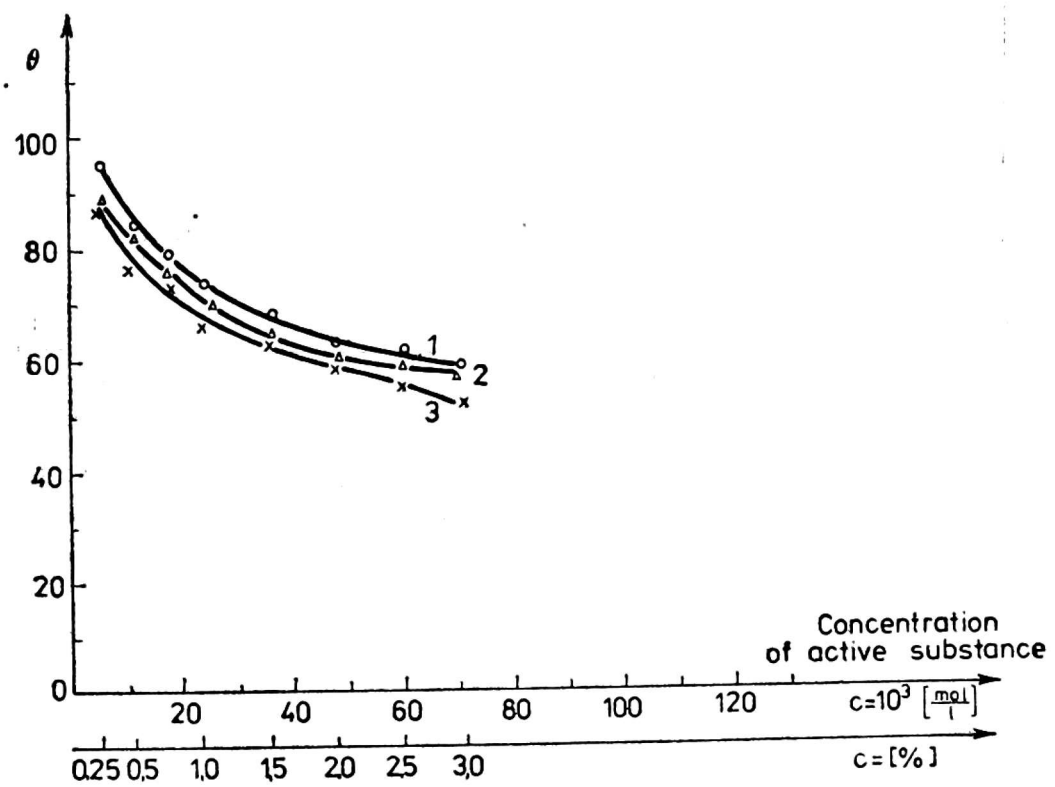

Fig. 7. Comparison of wetting erucic acid crystals by Elfan aqueous solutions in triphase system with liquid oleic acid (1), linoleic acid (2), and linolenic acid (3)

But in the case of erucic acid the influence of liquid fatty acids on wettability of that acid by aqueous solutions of tensides is very small.

Also the oxidation degree of liquid fatty acids is of considerably smaller influence on the wettability of erucic acid.

In the conclusion, it should be stated, that the wettability of the solid phase by aqueous solutions of surfactants depends not only on their chemical and crystalline structure but also on the chemical properties of liquid fatty acids.

The essential meaning plays here the unsaturation degree as well as the possible oxydation of the fatty acids.

It should be stressed that the influence of liquid fatty acids clearly depends on the structure of solid fatty acids.

Surface active agents have besides wetting properties emulsifiable properties too, what is very uprofitable in case of the discussed fractionation method. Addition of electrolyte to wetting solutions is applied

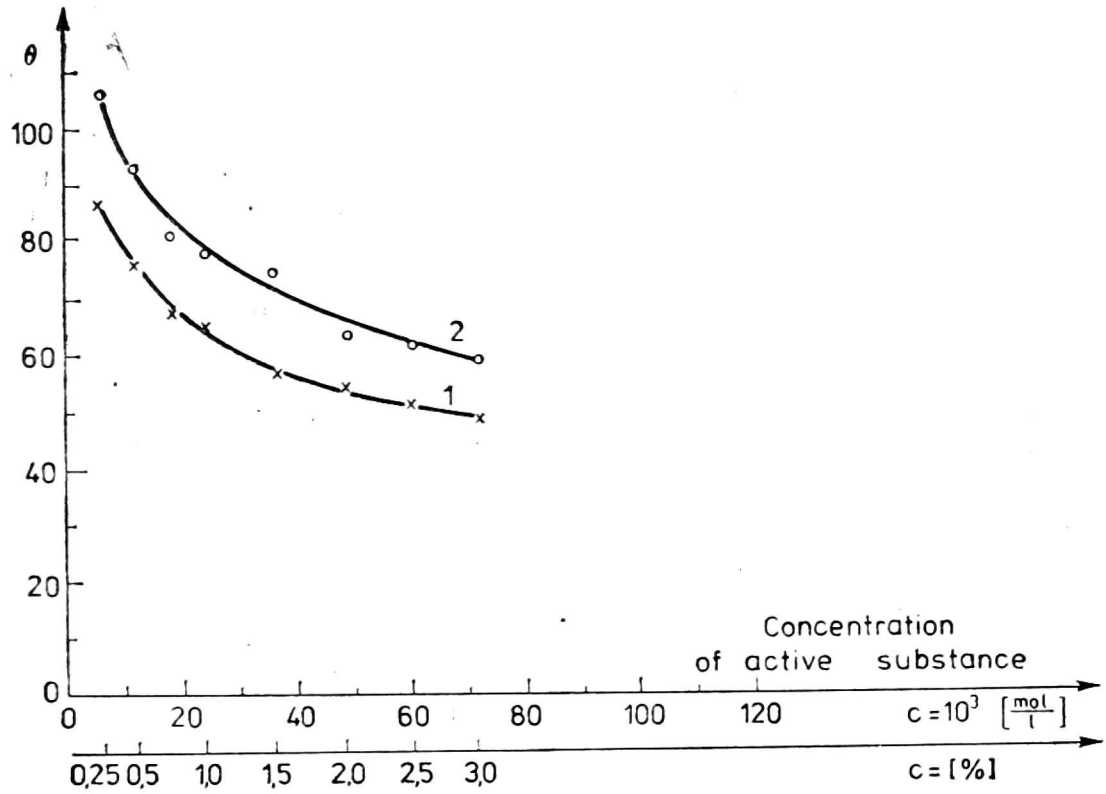

Fig. 8. The influence of oxydation of linolenic acid on the wettability of erucic acid by equeous Elfan solution: PV=1, PV=60

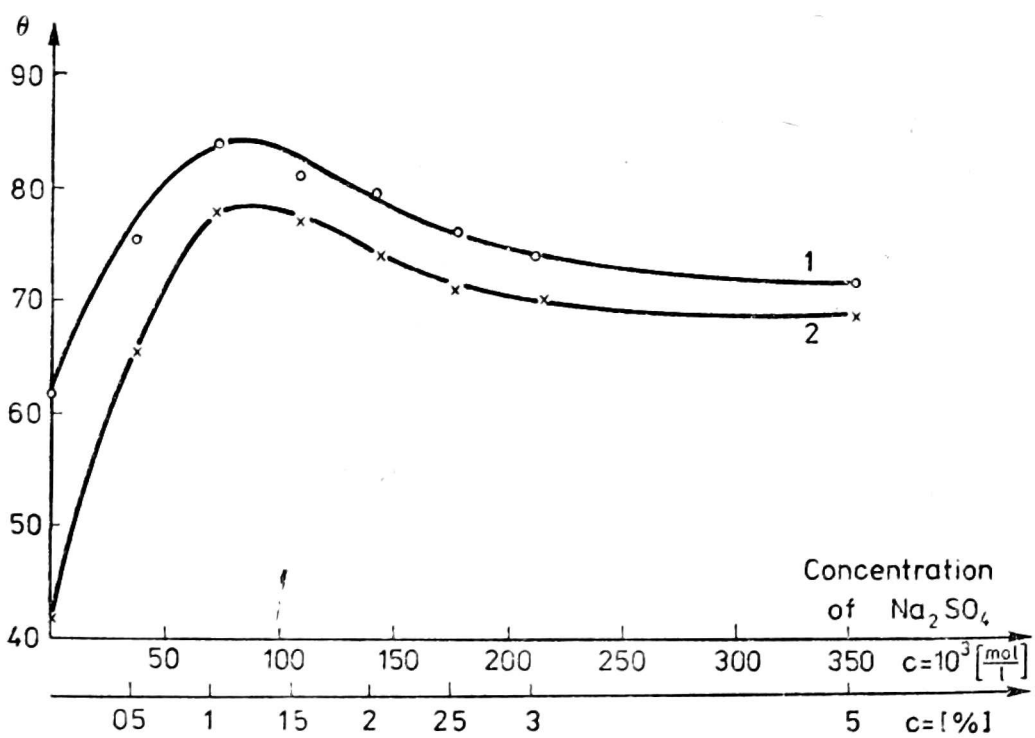

Fig. 9. Dependence of the wetting angle Θ at the phase boundary stearic acid — oleic acid — aqueous solution of lauryl sodium sulphate and Na_2SO_4 upon the concentration of Na_2SO_4: 1 — $35 \cdot 10^{-3}$ $\frac{mol}{dm^3}$ (1%), 2—$52 \cdot 10^{-3}$ $\frac{mol}{dm^3}$ (1,5%)

to diminish the emulsification. So the influence of electrolyte added to the wetting solution on wettability of solid fatty acid was investigated too.

Figure 9 shows the influence of electrolyte addition — Na_2SO_4 on the wetting of stearic acid crystals by aqueous solution of lauryl sodium sulphate. As it is seen from the diagram the electrolyte addition makes the wetting worse.

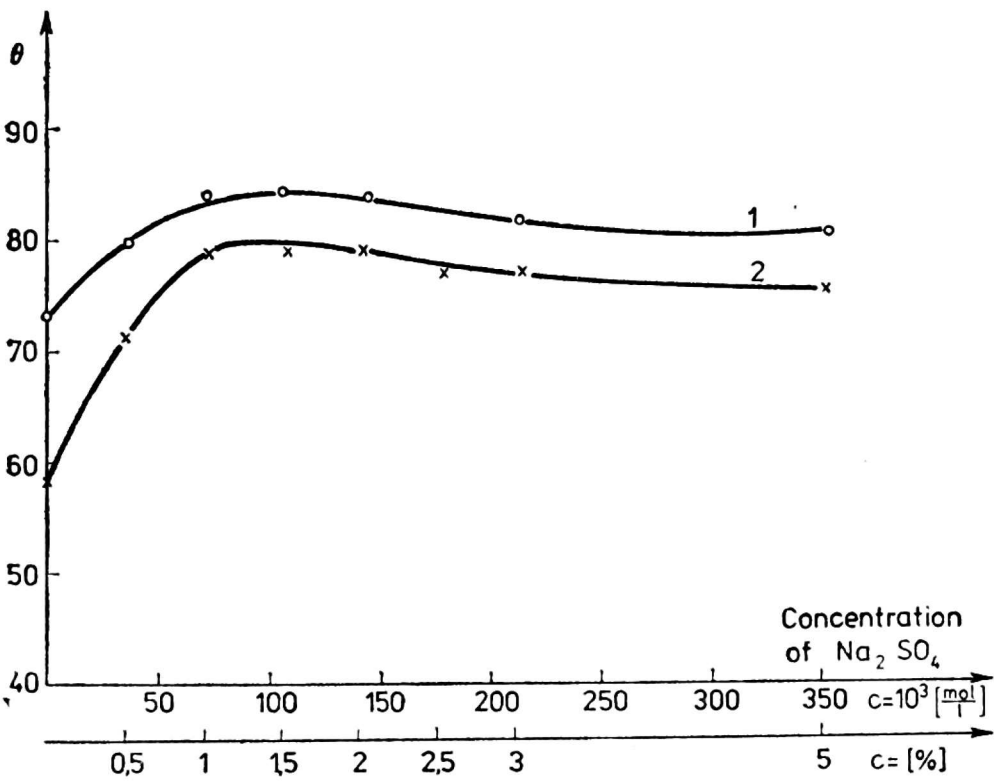

Fig. 10. Dependence of the wetting angle Θ at the phase boundary: erucic acid — oleic acid — aqueous solution of lauryl sodium sulphate and Na_2SO_4 upon the concentration of N_2SO_4 1 — $35 \cdot 10^{-3}$ $\frac{mol}{dm^3}$ (1%), 2—$52 \cdot 10^{-3}$ $\frac{mol}{dm^3}$ (1,5%)

Figure 10 gives the influence of the addition of Na_2SO_4 on wettability of erucic acid crystalls by aqueous lauryl sodium sulphate solution. Here also one observes the worsening of wetting properties but the differences in wetting with and without the electrolyte addition are considerably smaller than in the case of stearic acid.

Basing on above discussed experiments to the fractionation process such wetting solution concentrations were estimated where the solution could wet the erucic acid best.

The separation of rape seed-oil fatty acids by aqueous surfactant solutions were achiewed by using periodic centrifuge of 3000 rotations per minute.

The separation was carried out according to Fig. 11. The separation temperature 16° was found on experimental way.

The fatty acid to be separated were cooled down to the tempera-

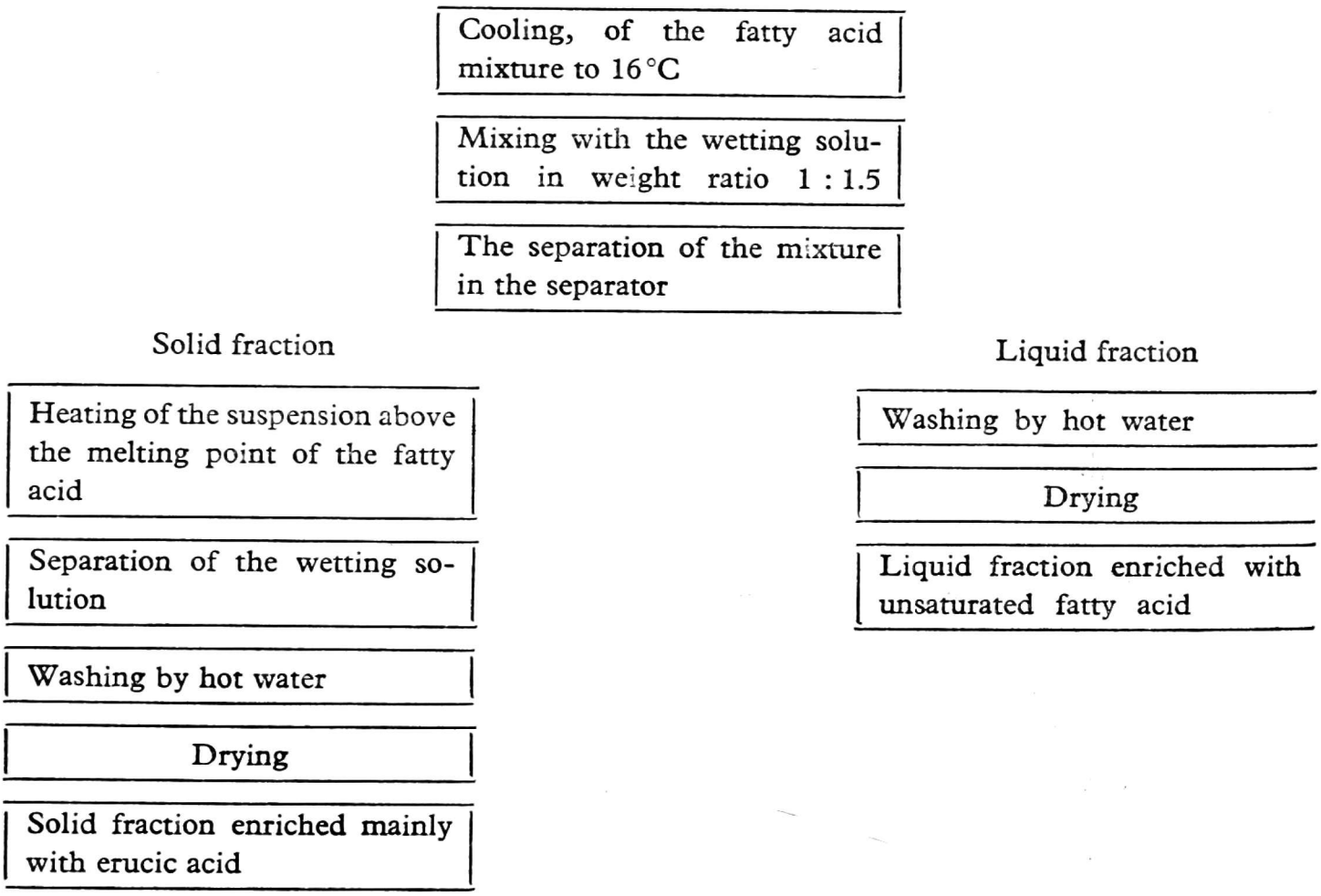

Fig. 11. Of rape-seed oil fatty acid separation

ture of 16°C. At this temperature mainly saturated and erucic acids were cristalized. The partially crystalized mass was mixed with the wetting solution of the same temperature in amount of 150%, by weight in ration to fatty acids.

Such prepared mixtures were separated in the separator and two fractions were obtained:

— aqueous suspension — the suspension consisted mainly of solid fatty acids in wetting solution,

— liquid fatty acids — mixture mainly consisted of unsaturated fatty acid.

The aqueous suspension was heated above the melting point of fatty acids and the molten fatty acids were separated from the wetting solution.

The fatty acids of rape-seed oil containings 48.5% erucic acid were the raw material. The yield of erucic acid and the acid composition were studied in obtained fractions. The best separation results from each series are given in Table 2.

The acid composition analysis of the fractions proves that best separation results were obtained by using elfan and lauryl sodium sulphate. The amount of erucic acid in the solid fraction was 75.0 and

Table 2

Characteristics of products obtained from fractionation of rape-seed oil fatty acids by aqueous solutions of surfactants

No.	The composition of the wetting solution	Fraction	Yield %	Erucic acid enrichmet factor	Acid composition						
					$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:1}$	$C_{22:1}$
1	1.0 Lauryl sodium sulphate	Liquid	70.1	0.83	4.2	1.6	17.8	16.9	8.5	10.7	40.3
	5% Na_2SO_4	Solid	21.1	1.51	2.1	0.9	7.0	6.6	3.4	6.6	73.5
2*	1.5 Elfan	Liquid	80.1	0.90	3.7	1.3	16.6	16.9	7.9	11.3	42.3
	1% Na_2SO_4	Solid	15.5	1.61	2.1	0.8	5.4	5.7	3.9	6.6	75.5
3	1.5 Marlon	Liquid	68.2	0.84	4.3	1.8	17.2	16.4	7.9	11.3	41.1
	1% Na_2SO_4	Solid	30.1	1.40	2.1	1.0	8.3	7.9	4.4	7.9	68.2
4	2.0 Nansa	Liquid	58.8	0.85	3.6	1.8	16.9	16.1	8.6	11.5	41.5
	2% Na_2SO_4	Solid	38.7	1.31	2.4	0.9	10.6	9.2	5.2	8.0	63.7
5*	1.0 Alfenol	Liquid	54.2	0.96	4.1	1.3	13.5	14.0	8.7	11.7	46.7
	2.5 Na_2SO_4	Solid	40.0	1.20	3.8	0.7	12.5	10.8	5.2	8.6	58.4
6*	0.25 Sodium Laureate	Liquid	55.2	0.95	4.4	1.3	14.8	14.3	8.2	11.2	46.4
	2% Na_2SO_4	Solid	38.8	1.19	3.8	0.7	13.0	10.6	5.3	8.4	58.2

* At separations 2, 5, 6 there occurs an intermediate fraction.

Table 3

The analysis of products obtained by repeated fractionation of rape-seed oil fatty acids by using the wetting solution of the following composition: 1% lauryl sodium sulphate and 5% Na_2SO_4

Separation degree	Separation temperature °C	Fraction	The erucic acid content	Yield %
I	16	Solid	63.4	35.2
	22	Liquid	60.6	72.2
		Solid	80.3	26.2
II	23	Liquid	60.3	68.8
		Solid	81.8	23.0
I	16	Solid	67.7	28.0
	22	Liquid	63.2	54.2
		Solid	81.1	40.3
II	24	Liquid	66.2	64.5
		Solid	85.1	25.0
I	16	Solid	74.7	26.0
	22	Liquid	65.1	49.2
		Solid	81.4	48.7
II	24	Liquid	65.3	71.8
		Solid	86.9	27.7
II	24	Solid	84.8	31.8
III	28	Liquid	77.5	46.5
		Solid	88.6	50.2

73.3% respectively. The worst results were observed when sodium laurate and alfenol were used.

As it is seen from Table 3 the II step, fractionation gives the enrichment of the solid fraction with erucic acid up to 80.3 or 86.9% depending on applied separation temperature. The III step separation enables obtaining fractions of 88.6% of erucic acid.

The presented results reflect the influence of fatty acid structures and applied surfactants on the composition of obtained fractions and their yield.

It must be also stressed that the studies on wettability of solid fatty acids by solutions of surface active agents in presence of different liquid fatty acids show the role of the chemical structure while the fractionation process of those compounds.

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WPŁYW BUDOWY KWASÓW TŁUSZCZOWYCH NA ICH ZWILŻANIE WODNYMI ROZTWORAMI ŚRODKÓW POWIERZCHNIOWO-CZYNNYCH ORAZ FRAKCJONOWANIE

Streszczenie

Określono zdolność zwilżania stałych kwasów tłuszczowych wodnymi roztworami różnych detergentów oraz wpływ struktury tych kwasów na zwilżanie. Jako kryterium stosowano pomiary kąta zwilżania na granicy faz: stałe kwasy tłuszczowe — ciekłe kwasy tłuszczowe — roztwór detergentu. Zbadano również wpływ ciekłych kwasów tłuszczowych oraz wpływ dodatku elektrolitu na zwilżanie.

Opierając się na uzyskanych wynikach określono przydatność wodnych roztworów detergentów do procesu frakcjonowania kwasów tłuszczowych oleju rzepakowego. Frakcjonowanie prowadzono, stosując roztwory detergentów o różnych własnościach zwilżających. Za pomocą chromatografii gazowej badano zmiany składu kwasowego otrzymanych frakcji.

В. Звежиковски, Э. Ледуховска

ВЛИЯНИЕ СТРУКТУРЫ ЖИРНЫХ КИСЛОТ НА ИХ СМАЧИВАНИЕ ВОДНЫМИ РАСТВОРАМИ ПОВЕРХНОСТНО-АКТИВНЫХ СРЕДСТВ И ФРАКЦИОНИРОВАНИЕ

Резюме

Определяли способность смачивания твердых жирных кислот растворами разных детергентов, а также влияние структуры этих кислот на смачивание. В качестве критерия использовывали измерения угла смачивания на границе фаз: твердые жирные кислоты — жидкие жирные кислоты — раствор детергента. Исследовали также влияние жидких жирных кислот и влияние прибавки электролита на смачивание.

Основываясь на полученные результаты, определяли пригодность водных растворов детергентов для процесса фракционирования жирных кислот рапсового масла. Фракционирование проводили с использованием растворов детергентов с разными смачивающими свойствами. С помощью газовой хроматографии исследовали изменения кислотного состава полученных фракций.