# MODIFICATION OF THE PROPERTIES OF ESTERS BY SELECTION OF THE ACID RADICAL

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Investigations were carried out on physical properties of esters containing individual or mixed acid radicals. It was found that, in spite of lack of additivness of the values characterizing the melting region, selection of acid radicals leads to significant, from the application point of view, differences in behavior of the esters.

In the past decade there has appeared a tendency to obtain fatty acid chemicalization products after fractionation of the acids into individual constituents. The problem has been exemplified by ester derivatives of fatty acids. The esters have been applied as auxiliary substances in different branches of industry [1]. They are used as softening additives, stabilizers, and as cosmetics and pharmaceutical base substances.

In houshold chemistry preparates and in the rubber industry they act as substitutes for protective or polishing waxes and the like. For many of these applications there are no objective criteria for the evaluation of the utilizable properties of esters and their use is quided exclusively by application-type investigations. Nevertheless, it should be emphasized, that there is a certain set of physical properties virtually responsible for most of the utilizable properties of esters. To these, first of all, belong plasticity and the physical properties associated with the change of the state of aggregation from solid to liquid and conversely [2].

This paper gives results of investigations on the physical properties connected with utilizable feactures of the esters in relation to the kind of acid radical used. Aliphatic alcohol esters were studied. The alcohol constituents were technical-grade tallow alcohols (Table 1, No. 13), the acid constituents were individual saturated and unsaturated acids of

Table 1

Characteristics of raw materials used for synthesis of esters

| No. | Length of hydrocarbon chain | Molecular weight | Name | Purity | Characteristics, chemical, I value | Characteristics, chemical, OH value | Characteristics, physical, m.p., °C | Characteristics, physical, f.p., °C | DTA, °C |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Individual acids | | | | | |
| 1 | $C_{12}$ | 200.0 | lauric acid | reagent-grade | 0.3 | — | 41.0 | 30.6 | 49.5 (36—53) |
| 2 | $C_{14}$ | 227.4 | myristic acid | reagent-grade | 0.5 | — | 52.5 | 52.3 | 60.0 (53—65) |
| 3 | $C_{18}$ | 274.4 | stearine | technical-grade | 8.0 | — | 54.5 | 52.4 | 59.5 (49—63) |
| 4 | $C_{18}$ (unsaturated) | 287.3 | oleine | technical-grade | 92.2 | — | 12.0 | — | —20.0 |
| 5 | $C_{22}$ | 351.1 | erucic acid | 90% purity | 1.0 | — | 75.5 | 74.0 | 72.0 |
| 6 | $C_{22}$ (unsaturated) | 340.0 | behonic acid | 90% purity | 69.4 | — | 30.4 | 28.0 | 33.0 (27—38) |
| | | | | Mixed acids | | | | | |
| 7 | $C_{16}$-$C_{18}$ | 287.0 | animal distilled hardened | | 2.1 | — | 59.5 | 57.4 | 63.0 (55—67) |
| 8 | $C_{16}$-$C_{18}$ (unsaturated) | 282.0 | animal distilled | | 55.9 | — | 40.4 | 41.2 | 53.5 (33—58) |
| 9 | $C_{14}$-$C_{22}$ | 288.0 | mixed distilled hardened | | 4.3 | — | 57.5 | 56.2 | 60.5 (49—67) |
| 10 | $C_{14}$-$C_{22}$ (unsaturated) | 290.7 | mixed distilled hardened | | 76.0 | — | 31.4 | 29.6 | < (20—38) |
| 11 | $C_{14}$-$C_{22}$ | 314.3 | rape oil fatty acids distilled hardened | | 0.9 | — | 63.6 | 56.0 | 64.5 (53—68) |
| 12 | $C_{14}$-$C_{22}$ | 315.6 | rape oil fatty acids distilled | | 97.1 | — | 18.0 | — | — |
| | | | | Alcohols | | | | | |
| 13 | $C_{16}$-$C_{18}$ | 267.7 | tallow alcohols | | 0.6 | 209 | 56.0 | 50.8 | (32—61) |

varying chain lengths (Table 1, Nos. 1—6) and mixtures of saturated and unsaturated acids (Table 1, Nos. 7—12).

Esters were obtained on a laboratory scale; the acid to-alcohol mole ratio was kept constant at 1 : 1.1 and the reaction was continued until the iodine value fell below 5.

The analytical methods employed in this study can be divided into two groups, chemical and physical. The former included the characteristic values determined according to the Polish Standards, and the latter — in addition to the standard methods for measuring the softening point and the dropping and freezing temperatures — included recording of DTA curves.

The DTA measurements were made on a Fisher Model 260 F apparatus (not equipped with the cooling adjustment). The measurement was started at room temperature with a programmed constant temperature rise of 5°C per minute. The result was expressed as the temperature corresponding to the minimum in the thermogram calculations as read from a standard substance calibration curve. The melting temperature region was taken as the difference of the temperatures fixed by tangents drawn at the minimum in the curve. An example is shown in Figure 1 of the melting curve interpretation for an ester of tallow alcohol and hardened rape oil acids.

Penetration was also determined with a needle penetrometer. This

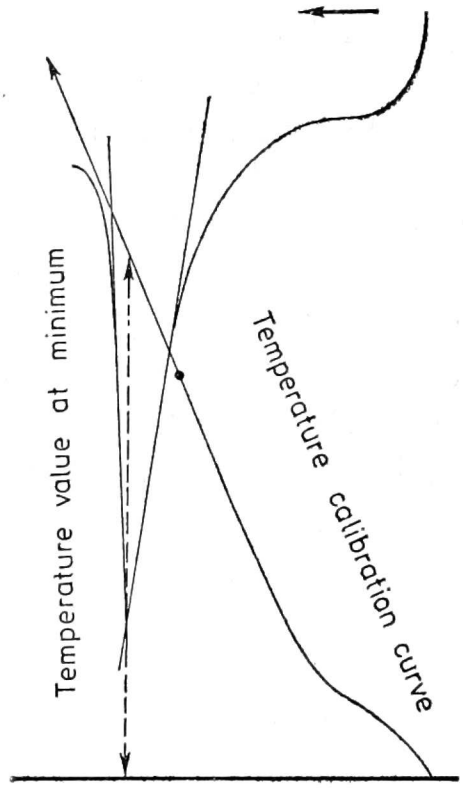


Fig. 1. Example of interpretation of the melting curve (programmed temperature rise, 5°C per/min.)

was executed according to the standard at 25°C (Table 2) and at a temperature 10°C below the freezing point. Results are given in Table 2.

Table 2

Characteristics of esters of tallow alcohols and individual or mixed fatty acids

| No. | Acid in ester | Average molecular weight | Iodine value | Temperature, °C | | | Penetration at 25°C |
|---|---|---|---|---|---|---|---|
| | | Individual | | melting Acids | freezing | DTA | |
| 1 | — $C_{12}$ | 452 | 0.7 | 38.7 | 29.7 | 48 (35—52) | 14.5 |
| 2 | $C_{14}$ | 483 | 0.4 | 46.6 | 37.3 | 53 (42—61) | 6.0 |
| 3 | $C_{18}$ | 528 | 4.1 | 50.6 | 50.3 | 58 (49—62) | 10.3 |
| 4 | $C_{18}$ (unsaturated) | 340 | 45.9 | 19.3 | 17.8 | — | — |
| 5 | $C_{22}$ | 618 | 1.0 | 61.3 | 60.1 | 64 (50—67) | 3.5 |
| 6 | $C_{22}$ (unsaturated) | 593 | 40.8 | 35.8 | 32.3 | 37 (20—42) | 28.5 |
| | | Mixed | Acids | | | | |
| 7 | $C_{16}$ — $C_{18}$ | 537 | 0.7 | 54.5 | 43.8 | 59.5 (45—63) | 4.0 |
| 8 | $C_{16}$ — $C_{18}$ (unsaturated) | 534 | 24.6 | 45.1 | 37.7 | 51 (40—57) | — |
| 9 | $C_{14}$ — $C_{22}$ | 538 | 4.3 | 50.8 | 43.1 | 62 (44—68) | 5.5 |
| 10 | $C_{14}$ — $C_{22}$ (unsaturated) | 540 | 36.8 | 41.4 | 35.8 | — | — |
| 11 | $C_{14}$ — $C_{22}$ | 558 | 0.8 | 58.5 | 57.6 | 6 ((55—65) | 7.0 |
| 12 | $C_{14}$ — $C_{22}$ (unsaturated) | 573 | 43.0 | 30.4 | 19.5 | 40 (22—46) | — |

The study concerned the effect of molecular weight and iodine value of the esters on the parameters characterizing the melting process, i.e. the softening point and the dropping point and the melting minimum (DTA), separately for the individual-acid (Fig. 2) and mixed-acid esters. Fig. 3).

The results indicate that with the individual fatty acid esters differences between the three characteristic melting values decrease as the molecular weight is raised. The unsaturated bonds in the molecule are distinctly seen to have a decisive effect on the fall or all the temperatures characterizing the change of state. Within the molecular weight range under study, the iodine value effect is much larger than that due to the molecular weight.

Mixed-acid esters (Fig. 3) exhibit the same relations, though much less pronounced.

An analogous method was used to plot the degree of penetration versus iodine value and average molecular weight (Figs. 4 and 5). Here again the iodine value has a decisive effect on the hardness of the product.

The present data deal with only a narrow fragment of the problem of modification of the ester properties. Notice must be made of the

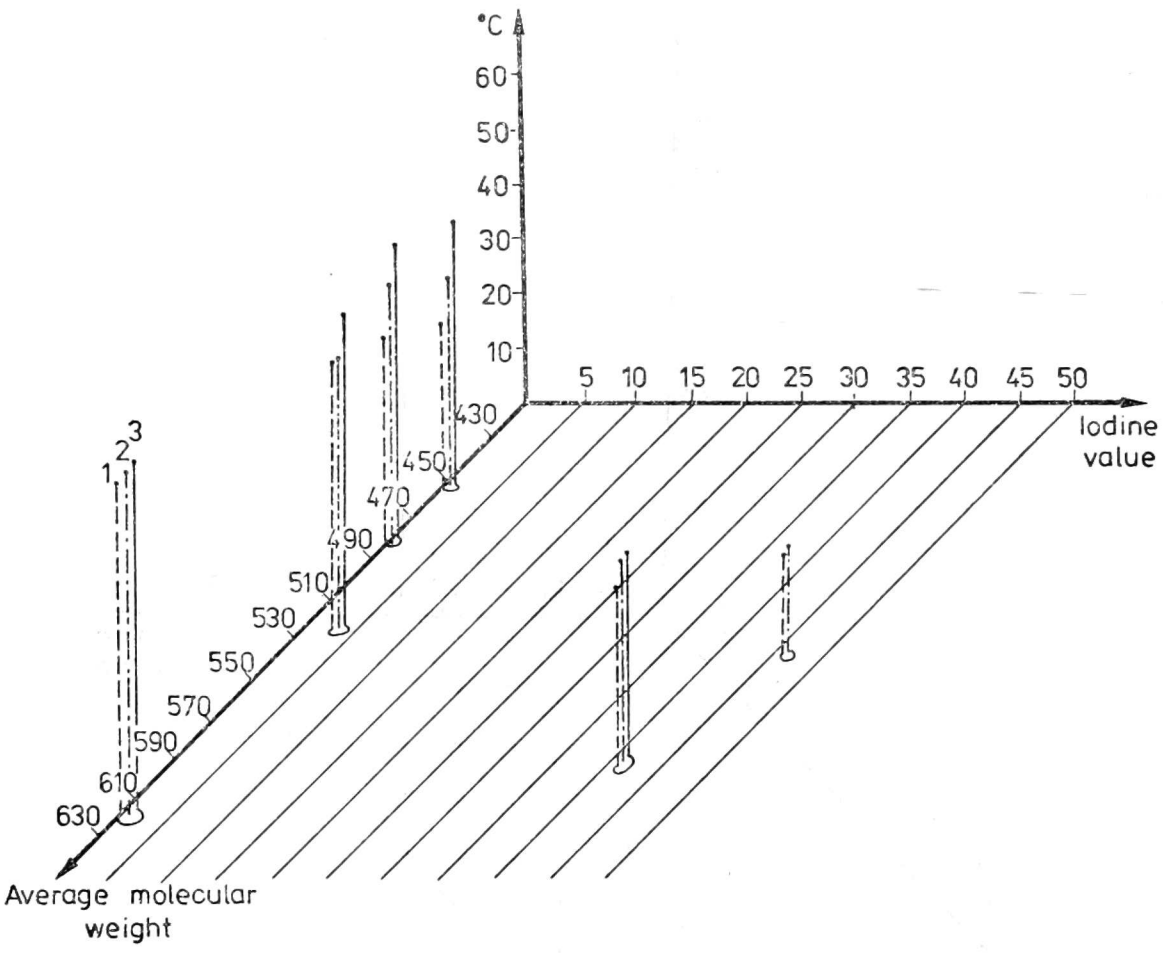


Fig. 2. Relation of softening temperature (*1*), freezing point (*2*) and DTA (*3*) to iodine value and molecular weight for individual acid esters

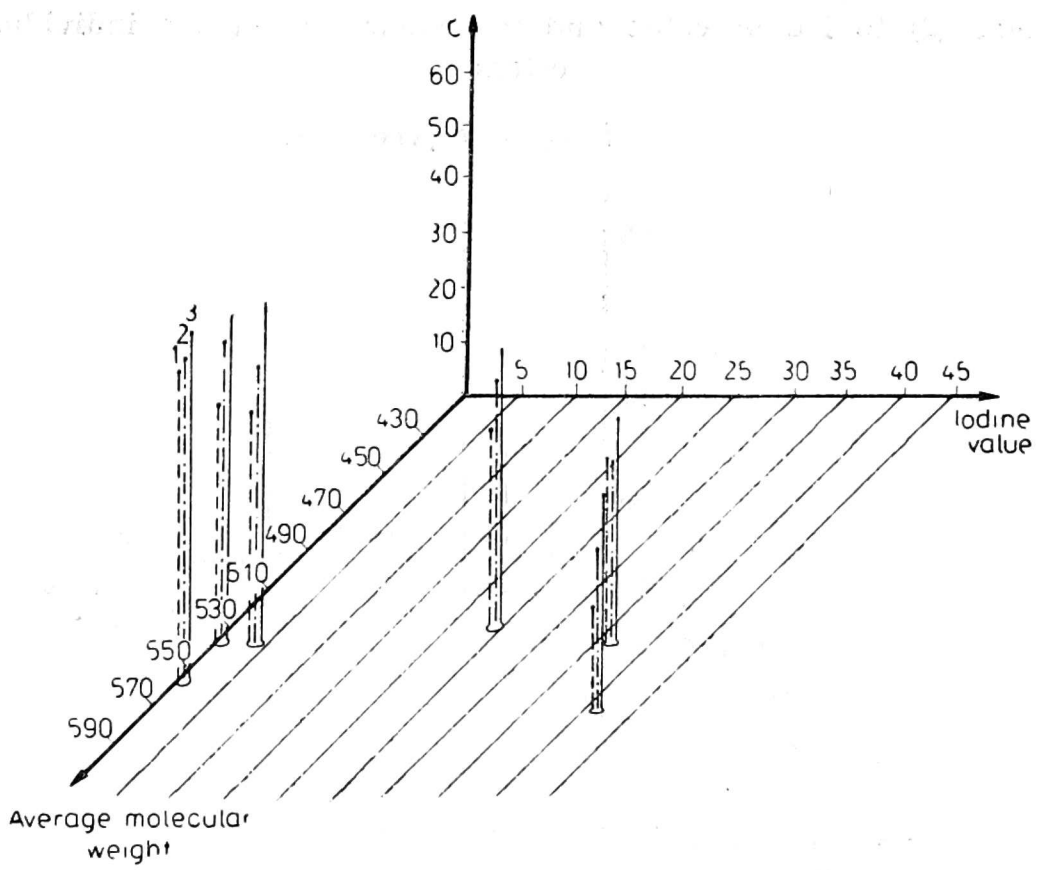


Fig. 3. Relation of softening temperature (*1*), freezing point (*2*), and DTA (*3*) to iodine value and molecular weight for mixed fatty acid esters

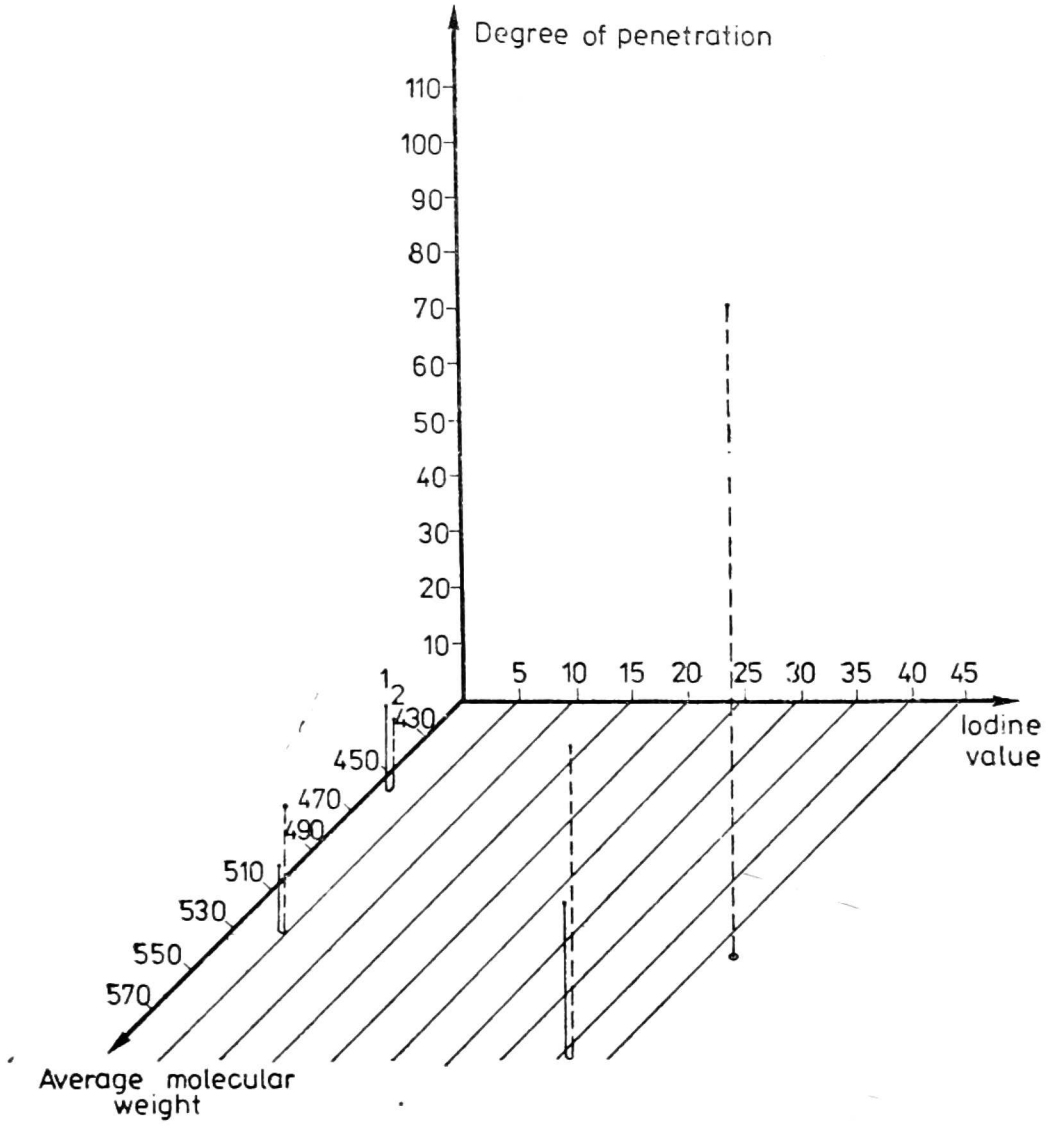


**Fig. 4. Relation of degree of penetration determined at 25°C (*1*) and 10°C below freezing point (*2*) to iodine value and molecular weight for individual acid to esters**

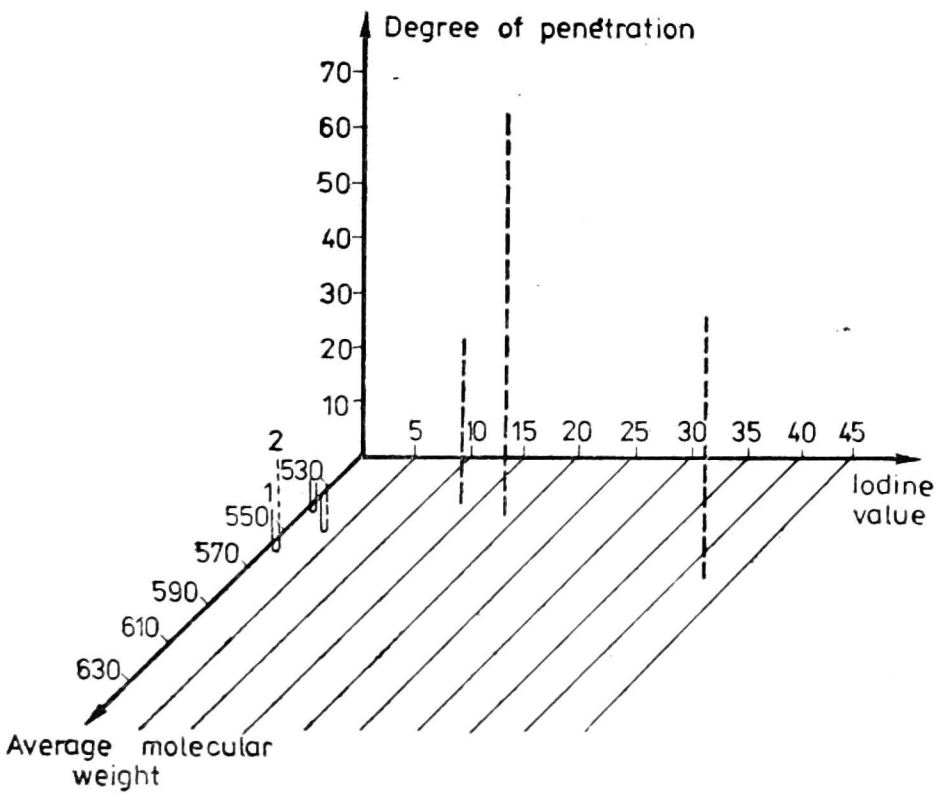


**Fig. 5. Relation of degree of penetration determined at 25°C (*1*) and 10°C below freezing point (*2*) to iodine value and molecular weight for mixed acid esters**

fact that analogous esters derived from individual fatty acids permit differentiation of the utilizable properties of the compound in a much wider range than is possible for multicomponent acid mixtures.

Further changes in ester properties can be obtained by applying modifying additives like solid hydrocarbons. An example of possible modification of properties of some wax esters by changing the composition of the mixture is shown in Fig. 6. This is a projection on the dropping temperature vs. mixture composition plane. The mixture has

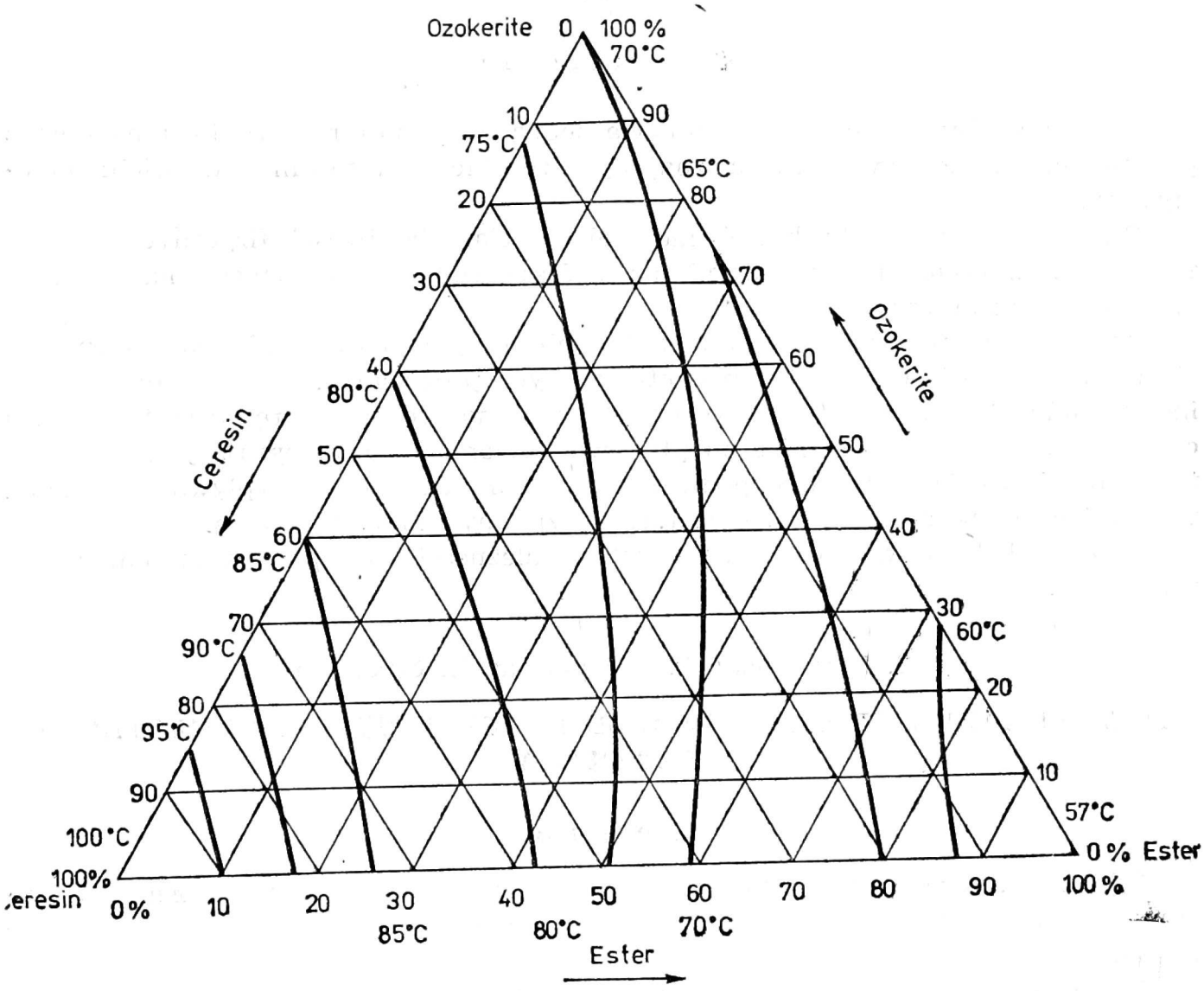


Fig. 6. Effect of composition of the three component mixture on the dropping value

three constituents, one ester and two hydrocarbons. The figure shows that it is possible to anticipate the dropping temperature of the mixture, or conversely, to determine the dropping temperatures for a composition. The same procedure can be applied to other properties of the esters.

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## MODYFIKACJA WŁAŚCIWOŚCI ESTRÓW DROGĄ DOBORU RODNIKA KWASOWEGO

Streszczenie

Estry kwasów tłuszczowych stanowią jedną z liczniej reprezentowanych grup pochodnych tłuszczowych, które znajdują szerokie zastosowanie w wielu przemysłach.

Praca zawiera wyniki badań nad zależnością właściwości fizycznych estrów, związanych z cechami użytkowymi, od rodzaju rodnika kwasowego na przykładzie estrów alifatycznych alkoholi.

Zastosowany w pracy zespół metod analitycznych obejmował charakterystykę chemiczną oraz właściwości fizyczne otrzymanych preparatów. W przypadku estrów indywidualnych kwasów tłuszczowych stwierdzono, że w miarę wzrostu ciężaru cząsteczkowego maleją różnice między wartościami charakteryzującymi przebieg topnienia. Natomiast obecność podwójnych wiązań decydująco wpływa na spadek wszystkich temperatur, charakteryzujących zmiany stanu skupienia.

W estrach kwasów mieszanych podobne zależności występują w stopniu mniej wyraźnym.

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## МОДИФИКАЦИЯ СВОЙСТВ ЭФИРОВ ПУТЕМ ПОДБОРА КИСЛОТНОГО РАДИКАЛА

Резюме

Эфиры жирных кислот представляют собой одну из многочисленно представленных групп жирных производных, которые нахорят широкое применение в многих промышленностях.

В труде приводятся результаты исследований по зависимости физических свойств эфиров, связанные с полезными качествами, от вида кислотного радикала на примере эфиров алифатических алкоголей.

Использованный в труде комплект аналитических методов охватывал химическую характеристику и физические свойства полученных препаратов. В случае чфиров индивидуальных жирных кислот установлено, что по мере роста молекулярного меса снижаются разницы между величинами характеризующими ход таяния. Наличие же двойных связей влияет решительным образом на снижение всех температур характеризующих изменения агрегатного состояния.

В эфирах смешанных кислот подобные зависимости выступают менее четко.