The Potentiometric Titration of Fatty Acids
with Silver Nitrate

OLAVI HARVA and PER EKWALL

Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland

Ekwall and Juup[1] found that the potentiometric determination of the higher fatty acids can be achieved by precipitation of their sodium salts with silver nitrate in aqueous solution. In this manner the individual acids could be estimated quantitatively, the titration error not exceeding — 5 %. These authors calculated the solubility products of the silver salts of different acids from the inflexion points of the titration curves and obtained the following values, which refer to 70° C.

Silver laurate	L Ag L	$= 2.7 \times 10^{-6}$
Silver myristate	L Ag My	$= 4.0 \times 10^{-9}$
Silver palmitate	L Ag Pl	$= 5.3 \times 10^{-10}$
Silver stearate	L Ag St	$= 6.9 \times 10^{-11}$
Silver oleate	L Ag Ol	$= 6.0 \times 10^{-10}$

They also succeeded in the quantitative estimation of fatty acids in a number of binary mixtures. The titration was more difficult when the chains of the saturated fatty acids differed in length by only two CH_2-groups.

The method has been subjected to further study and investigations have been continued in various directions. For example, P. Ekwall, Kjell Andersson-Groth and Margaretha Witting (at the Institute of Physical Chemistry of the University of Uppsala) investigated the method in the case of certain saturated fatty acids and paid particular attention to the titration of binary mixtures. Harva and Ekwall reinvestigated the titration of single acids, extended the study to include capric and lower fatty acids and investigated the possibility of estimating quantitatively the acids in different types of mixtures. The titration of salts and mixtures of salts of the rosin acids has also been studied by Ekwall and Ralph Andresen.

The following is a summary of the results obtained.

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METHODS

The fatty acids were determined as their sodium and potassium salts in aqueous solution. In most experiments a known weight, between 50—120 mg of acid or acid mixture, was dissolved in absolute alcohol and neutralized by an equivalent amount or a slight excess of sodium or potassium hydroxide. After the neutralization, the alcohol was expelled and the salt dissolved in water.

In some experiments the fatty acids were neutralized in aqueous solution with potassium hydroxide, and in others a known amount of the sodium salt of the fatty acid was dissolved in water. All solutions contained a small excess of alkali to prevent hydrolysis.

The electrode used was a silver wire which had been silvered according to the method of Brown [2]. As reference electrode either a saturated or a 1 M calomel electrode was used; this was connected to the titration solution through an agar-agar bridge saturated with potassium nitrate. Titrations were performed with 0.05 N or 0.1 N silver nitrate. The electromotive force (E. M. F.) of the cell was determined with a valve potentiometer. All the E. M. F. values given below refer to a 1 M calomel electrode ($E_{cal} = 0.283$ V). The adherence of the silver soap to the electrode, which resulted in erratic E. M. F. values, was avoided by efficient stirring and by allowing the mixer blade to brush the electrode.

THE TITRATION OF THE INDIVIDUAL FATTY ACIDS

When the sodium salts of the fatty acids were titrated individually at 70° C, the solubility products of silver stearate, palmitate, myristate and laurate calculated from the inflexion points were found to conform with the values given by Ekwall and Juup [1]. The results obtained with sodium stearate, palmitate and laurate were found to be too small by 3—4 %, 2—3 %, and, 0.5—1.5 %, respectively. At 20° C the titration curve of sodium laurate was steeper than at 70° C and hence the accuracy was higher. The calculated solubility product of silver laurate at 20° C was found to be

$$L\ Ag\ L = 5 \times 10^{-10}\ (E.\ M.\ F. = 0.257\ V)$$

This value is slightly greater than the value, 3×10^{-10} reported by Ekwall and Juup [1] but lies in the interval $3—7 \times 10^{-10}$ obtained by Ekwall and Harva [3] with the silver/silver laurate electrode.

The titration curves of sodium caprate (NaCi), sodium caprylate (NaCy) and sodium caproate (NaCo) obtained at 20° C are shown in Fig. 1. In the titration of the caprate a definite jump was observed in the titration curve but the solubility of silver caprylate and silver caproate was so high that a precipitation titration of these acids was not possible. The calculated solubility product of silver caprate at 20° C was found to be

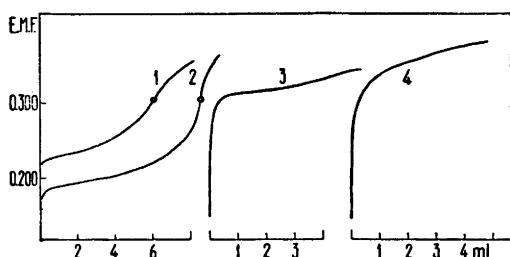$$L\ Ag\ Ci = 1.9 \times 10^{-8}\ (E.\ M.\ F. = 0.303\ V)$$

Fig. 1. 1. *Titration of 0.0118 N NaCi with 0.1 N AgNO₃ at 70° C.*
Error: + 1.4 %.

2. *Titration of 0.01702 N NaCi with 0.1 N AgNO₃ at 20° C.*
Error: — 0.4 %.

3. *Titration of 0.00419 N NaCy with 0.1 N AgNO₃ at 20° C.*

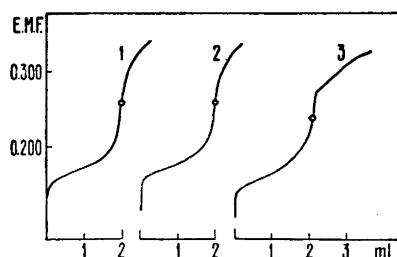4. *Titration of 0.00405 N NaCo with 0.1 N AgNO₃ at 20° C.*

Fig. 2. 1. *Titration of 0.00204 N NaL with 0.1 N AgNO₃ at 20° C.*
Error: — 0.5 %.

2. *Titration of 0.00205 N NaL with 0.1 N AgNO₃ at 20° C; the solution contained 23.3 mol-% NaOH.*
Error: — 0.9 %.

3. *Titration of 0.00207 N NaL with 0.1 N AgNO₃ at 20° C; the solution contained 72 mol-% NaOH.*
Error: — 0.8 %.

The titration error with sodium caprate varied in different experiments between — 1.5 % and + 2.5 % at 20° C.

At 70° C the solubility of silver caprate was so high and the variation of the curve was so slight that the point of inflexion was difficult to determine. The calculated value of the solubility product of silver caprate at 70° C was

$$L \text{ Ag Ci} = 2.7 \times 10^{-7} \text{ (E. M. F.} = 0.304 \text{ V)}$$

The effect of excess of alkali on the titration curves may be seen in the titration of mixtures of sodium laurate and sodium hydroxide (Fig. 2). When the solution contains 20 mol-% sodium hydroxide the titration curve is still quite regular, but when the alkali concentration exceeds 40 mol-% precipitation of silver hydroxide occurs with an accompanying change in the colour of silver laurate from white to grayish brown; at the same time the titration curve is deflected at or above the inflexion point of sodium laurate. Hence an excess of alkali from 10—20 mol-% (pH < 10.8) may be used in the titration without any alteration in the form of the titration curve. Even the theoretical error in the titration of sodium laurate does not exceed — 0.8 % in this case.

If the solution contains sodium chloride, silver chloride precipitates with the silver salts of palmitic, myristic and lauric acids and the amounts of the component acids in the mixture cannot be estimated from the titration curve (Fig. 3, curve 1). In titrating a mixture of sodium chloride and sodium stearate at 70° C a jump corresponding to silver stearate is observed but the titration error is large (Fig. 3, curve 2) owing to the simultaneous precipitation of silver chloride and silver stearate; theoretically the coprecipitation should not occur. Both components of a mixture containing sodium caprate and sodium chloride can, however, be estimated at 20° C (Fig. 3, curve 3).

An attempt was made to reduce the titration error which possibly arises from the coprecipitation of the soap with the silver salt by using various emulsifiers to effect the suspension of the silver soap. Tylose, mersolate and starch were found to be of no use in this respect.

The effect of added electrolytes in the titration was also studied. Theoretically the titration curve should run higher in the solution containing added electrolytes than in a solution containing no added electrolytes. The addition of electrolyte effects in part an increase in the solubility of the silver soap and in part an increase in the degree of association of the soap; the latter causes a decrease in the fatty acid anion concentration. Both of these effects increase the activity of the silver ion. When the soap has been precipitated the electrolyte effects a decrease in the activity coefficient of the silver ions in excess, and, hence, the titration curve of the solution containing added electrolyte is lower than that of the solution containing no additional electrolyte. In Fig. 4 the extent of the effect of added electrolyte in the titration of potassium stearate is shown. As the concentration of the electrolyte is increased the jump in the titration curve becomes smaller and the curve is flatter. The titration result is not affected by the presence of added electrolyte, although the determination of the end point of the titration becomes less accurate.

THE TITRATION OF BINARY FATTY ACID MIXTURES

As Ekwall and Juup[1] have shown the different values of the solubility products of the silver soaps make it possible to separate quantitatively fatty acids in binary mixtures when these acids differ in structure by more than two CH_2-groups but difficulties are encountered when two successive fatty acids having even numbers of carbon atoms are present.

Theoretically the titration result varies with the relative solubility products of the components, their relative proportions in the mixture, and the total concentration of the solution. When the concentration c_2 of the soap of the lower fatty acid is approximately
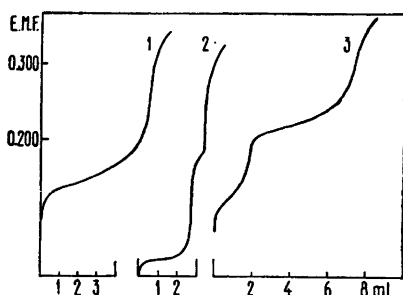
Fig. 3. 1. *Titration of 0.0066 N NaL +*
0.002766 N NaCl with 0.1 N Ag
NO₃ at 43° C. Total titration
error: — 0.6 %.
2. *Titration of 0.00415 N NaSt +*
0.002766 N NaCl with 0.1 N
AgNO₃ at 70° C. Total titra-
tion error: + 3.9 %.
3. *Titration of 0.01081 N NaCi +*
0.003897 N NaCl with 0.1 N
AgNO₃ at 21° C. Total titra-
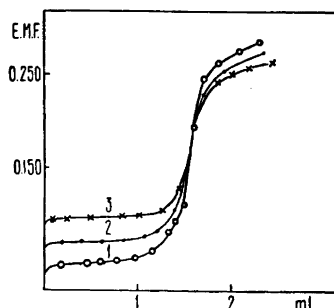*tion error: — 0.65 %.*

Fig. 4. *Titration of 0.00159 N KSt with*
0.05 N AgNO₃ at 65° C:
1. *Without KNO₃;*
2. *Solution 0.02 N in KNO₃;*
3. *Solution 0.2 N in KNO₃. Error:*
—0.8 %.
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$$c_0 = \frac{P_2}{\sqrt{P_1}} \qquad (1)$$

where P_1 and P_2 are the activity products of the silver soaps of higher and lower molecular weight, respectively, the silver salt of the lower acid begins to precipitate at the equivalence point of the higher acid. When the concentration c_2 is less than c_0, its silver salt begins to precipitate only after the equivalence point of the higher acid has been passed and when $c_2 > c_0$ this precipitation occurs before the equivalence point of the higher salt is reached. In these cases the magnitude of the error which arises in the titration of the higher salt also depends on the proportion of the components in the mixture. The magnitude of the error in mol-% ($\triangle$) can be calculated theoretically by using, for example, the equation:

$$\triangle = \frac{P_1 c_2^2 f_2^2 - P_2^2}{P_2 f_2 c_2 c_1} \cdot 100 \qquad (2)$$

where

$\triangle$, the mol-% of the original amount of the higher soap which is still in solution when the silver salt of the lower soap begins to precipitate;
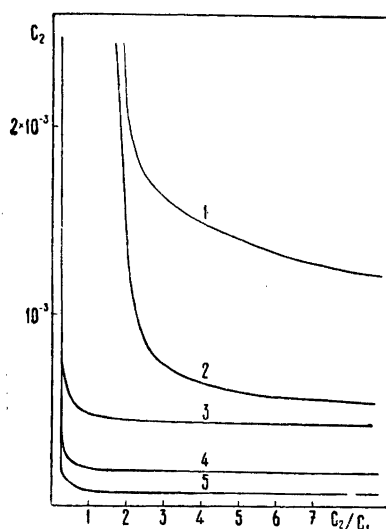
Fig. 5. *Allowed concentration ranges at 70° C in the titration of:*
1. *NaPl + NaL;*
2. *NaSt + NaMy;*
3. *NaMy + NaL;*
4. *NaPl + NaMy;*
5. *NaSt + NaPl.*

P_1 and P_2 are the activity products of the higher and lower soap, respectively; c_1 and c_2 their respective concentrations;

f_2, the activity coefficient referring to the concentration c_2 of the lower soap; the activity coefficient of the higher salt is assumed to be approximately unity.

When the value of $\triangle$ calculated from equation (2) is negative, this means that the silver salt of the lower fatty acid begins to precipitate when the equivalence point of the higher acid has been passed.

From the equation given above it may be seen that only when the concentration of the lower soap is greater than the c_0-value given in Table 1 an error is to be expected in the estimation of the component of higher molecular weight. When the molar ratio of the components is unity the maximum value which this error may attain is that given by the expression P_1/P_2. This error arises when $c_2 \geq 10 \cdot c_0$. It may be seen from Table 1 that the greatest error occurs when a mixture of sodium palmitate and laurate is titrated, in which case the maximum error is — 1.96 mol-%. When the concentration of the lower component increases relative to that of the higher component, and its value is at least ten times c_0, the theoretical titration error also increases in the same proportion.

Table 1. *Maximum titration errors under certain conditions.*

Mixture	c_0	P_1/P_2
NaSt — NaMy	4.8×10^{-4}	1.72×10^{-2}
NaSt — NaL	3.25×10^{-3}	2.55×10^{-3}
NaPl — NaL	1.2×10^{-3}	1.96×10^{-2}

Fig. 6. 1. *Titration of 0.0011 N NaSt +*
        0.00145 N NaPl with 0.1 N
        AgNO₃ at 70° C. Total titration
        error — 2.4 %.
   2. *Theoretical curve for the same*
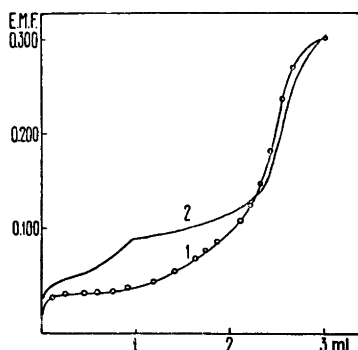   *mixture.*

Fig. 5 indicates in what ranges of the concentration of the lower fatty acid (c_2) and of the concentration ratio (c_2/c_1) of the two components the titration can be conducted at 70° C without incurring a theoretical error exceeding — 3 % in the value of the higher fatty acid. The allowed concentration ranges lie to the left of and below the curve referring to the acid pair in question. The conditions in our experiments have been such that the concentrations and the concentration ratios were in these areas and hence it was found possible to estimate both components in the binary mixtures stearate-myristate, stearate-laurate, and palmitate-myristate, the titration error being between the limits — 3 % and + 1 %. For example, this was the case in the series of titrations of palmitate-laurate mixtures in which the concentration ratio, c_2/c_1, varied from 0.4 to 8, and in a series of titrations of stearate-myristate mixtures in which the ratio varied from 0.14 to 7.

If the titration is continued at a lower temperature after the higher soap has been precipitated at a higher temperature the equivalence point of the lower soap can be determined more accurately since the slope of the curve becomes steeper when the solubility of the silver salt of the lower acid decreases (Fig. 7, curve 1).

The theoretical possibility of titrating mixtures containing successive fatty acid salts having even numbers of carbon atoms in the chain is shown by the data given in Table 2.

Table 2. Maximum titration errors under certain conditions.

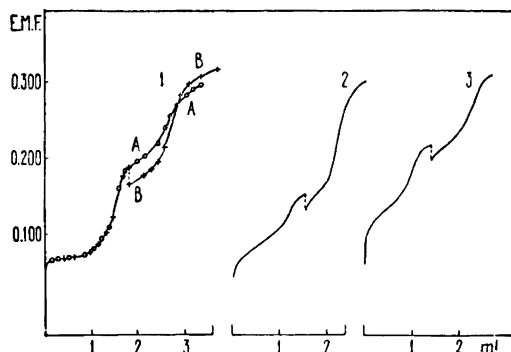| Mixture	c_0	P_1/P_2	Temp.
NaSt — NaPl	6.4×10^{-5}	1.3×10^{-1}	70° C
NaPL — NaMy	1.7×10^{-4}	1.4×10^{-1}	70° C
NaMy — NaL	4.3×10^{-4}	1.5×10^{-1}	70° C
NaL — NaCi	8.5×10^{-4}	2.6×10^{-2}	20° C

Fig. 7. 1. Titration of 0.000795 N KSt +
0.000555 N KMy with 0.05 N
AgNO₃:

    A) at 65° C.   Error in KSt
      — 2.5 %   (theoretical
      — 0.28 %) and in KMy
      — 3.6 %.

    B) KSt at 65° C and KMy at
      45° C. Error in KSt — 2.5
      % and in KMy — 0.3 %.

2. Titration of 0.00064 N KPl +
0.000555 N KMy with 0.05 N
AgNO₃ at 65 and 45° C. Error
in KPl — 4 % (theoretical
— 10 %) and KMy — 6 %.

3. Titration of 0.000555 N KMy
+ 0.00062 N KL with 0.05 N
AgNO₃ at 65° C. Error in
KMy   — 10 %   (theoretical
— 8.6 %) and in KL + 2.5 %.

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A titration error occurs even when the concentration of the lower soap is as small as 6.0 × 10⁻⁵—10⁻⁴ *M*. When the molar ratio of the components is unity, a minimum error ranging from — 10 to — 15 mol-% may be expected in the titration of the higher fatty acid salt. If the theoretical titration error is not to exceed — 3 %, it is necessary, as shown by Figure 5 (curves 3, 4, 5), to conduct the titration in very dilute solution. It may be expected that the estimation of both components in these mixtures is then very difficult and conducted experiments confirm this. When a mixture of sodium stearate and sodium palmitate was titrated no inflexion point corresponding to the stearate was noted, and, hence, the stearate could not be estimated (Fig. 6, curve 1). The calculated titration curve (Fig. 6, curve 2) indicates, however, that it should be possible to separate the stearate and the palmitate. If activities were employed in the calculations instead of concentrations (as we have done above) the jump due to the precipitation of the stearate should be more distinct, as Ekwall and Juup[1] have been able to show. The reason for the discrepancy between theory and practice has not been found. It may be that the concentration of the solution under titration exceeded the critical concentration of the soap mixture for micelle formation and hence the formation
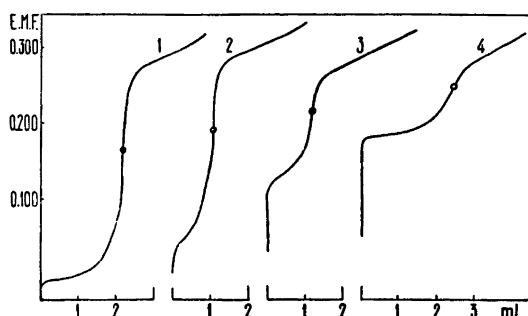
Fig. 8. **1.** *Titration of 0.002288 N NaSt + 0.001488 N NaCi with 0.1 N AgNO₃ at 60° C. Error in NaSt — 2.6 %.*

2. *Titration of 0.001093 N NaPl + 0.001204 N NaCi with 0.1 N AgNO₃ at 60° C. Error in NaPl + 0.36 %.*

3. *Titration of 0.001153 N NaMy + 0:002105 N NaCi with 0.1 N AgNO₃ at 60° C. Error in NaMy + 0.8 %.*

4. *Titration of 0.002395 N NaL + 0.001157 N NaCi with 0.1 N AgNO₃ at 60° C. Error in NaL + 1.5 %.*

of mixed stearate-palmitate micelles led to a coprecipitation of both the component fatty acids.

On the other hand, the separation of the components of mixtures of other successive even saturated fatty acids by titration at 70° C was feasible. The precipitation of the silver salt of the lower soap before the equivalence point of the higher soap was reached had in this case a considerable effect on the titration. The titration error is thus great.

In such cases the concentration of the titration at a lower temperature after the higher component has been titrated offers considerable advantages; this procedure was therefore followed in most of the titrations. Using this procedure it was found possible to estimate both components in palmitate-myristate and myristate-laurate mixtures. The concentrations were as a rule so high that the theoretical titration error considerably exceeded — 3 %; the experimentally found titration error was of the same magnitude (Fig. 7, curves 2, 3). It should be noted that in these cases the total concentration of the solution under titration was so low that it did not exceed the critical concentration of the mixture for micelle formation, and, hence, mixed micelles were not formed.

In the case of equimolar binary mixtures of laurate and caprate at 20° C, $c_o = 8.5 \times 10^{-4}$ and $P_1/P_2 = 2.63 \times 10^{-2}$. It should thus be possible to estimate both acids separately; this was confirmed by experiments.
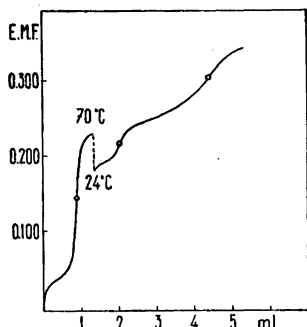
Fig. 9. Titration of mixture containing 0.000975 N NaSt + 0.00105 N NaL + 0.00240 N NaCi with 0.1 AgNO₃ at 70° C and after precipitation of NaSt at 24° C. Error in NaSt — 5 %, in NaL + 2.4 % and in NaCi + 2.2 %.

When the mixture 0.00128 N in NaL and 0.00138 N in NaCi was titrated the error in NaL was + 0.8 % and in NaCi + 0.2 %. According to theory the precipitation of silver caprate should occur 0.5 mol-% before the equivalence point of sodium laurate.

When titrating binary mixtures containing sodium caprate as one component and sodium stearate, palmitate, myristate and laurate as the other component at 60° C the solubility of silver caprate was so great that the titration curve continued almost linearly when the other component had been precipitated, and hence caprate could not be estimated (Fig. 8). However, the other component could be determined quantitatively, the titration error varying from — 2 % to — 3 % with sodium stearate and amounting to — 1 % with the other salts.

The same behaviour was noted with binary mixtures containing sodium caprylate and their titration could be conducted at 20° C without any inflexion point due to the precipitation of silver caprylate being observed.

THE TITRATION OF TERNARY AND POLYCOMPONENT MIXTURES

All fatty acids in ternary mixtures could be estimated separately when two successive fatty acids of the even series C_{14}—C_{18} were not present (Fig. 9). The titration error of each acid was actually larger than in the case of binary mixtures, but in no case greater than 5 %. In order to increase the accuracy of the determination of the inflexion point with the lower fatty acid salts the latter part of the titration was conducted between 20—25° C, whereas the higher salts were titrated at 60—70° C.

When the acid mixture contained several acids varying in structure by less than two CH_2-groups the individual fatty acids could not be separated as may be seen from Fig. 10. The end point of the titration was difficult to determine

since no distinct inflexion point was evident in the titration curve. If the end point of the titration was taken to be the volume in ml of silver nitrate corresponding to the E. M. F. value of silver laurate at 60° C, the error in the total acid was less than — 2 %.

The fatty acid mixture for which the titration curve is curve 1 of Fig. 10 had an acid value (AV) of 220.2 mg KOH/1 g. 69.92 mg of the mixture consumed 2.75 ml of 0.1 N silver nitrate (to the E. M. F. value 0.268 V), which corresponds to a calculated acid value (AV_p) of 218.8 mg KOH/1 g, the titration error being — 0.2 % when the results are expressed in these units.

The precipitation of the silver salts of capric and other acids of lower molecular weight was not evident in the titration curves obtained at 60° C due to the high solubility of the silver salts of these acids. This made it possible to estimate the total amount of the higher acids in mixtures containing capric and lower acids. (Fig. 10, curves 2 and 3).

Table 3. Titration of some soap mixtures.

|	Solution titrated (normality)	Total acid value (AV) of fatty acid mixtures	Calculated acid value (AV_c) of acids higher than C_{10} in the mixture	AV_p obtained potentiometrically	Error
No. 1.	NaPl : 0.00104 NaMy : 0.000816 NaL : 0.000925 NaCi : 0.000669	256.8	207.0	204.5	— 1.2 %
No. 2.	NaSt : 0.0003231 NaPl : 0.0003435 NaMy : 0.0003945 NaL : 0.0007864 NaCi : 0.0005094 NaCy : 0.000765	279.9	165.6	158.7	— 4.2 %
No. 3.	NaSt : 0.000726 NaPl : 0.000592 NaOl : 0.0004448 NaMy : 0.0003596 NaL : 0.000324 NaCi : 0.0007328 NaCy : 0.0004832	247.1	165.0	165.3	+ 0.18 %
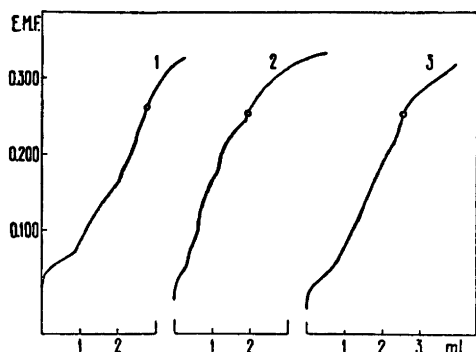
Fig. 10. 1. Titration of mixture containing 0.0003912 N NaSt + 0.000777 N NaPL + 0.0007332 N NaOl + 0.0004418 N NaMy + 0.000404 N NaL with 0.1 N AgNO₃ at 60° C.
2. Titration of mixture No. 2 of Table 3 with 0.1 N AgNO₃ at 60° C.
3. Titration of mixture No. 3 of Table 3 with 0.1 N AgNO₃ at 60° C.

If we take for the end point of the titration at 60°C the volume of silver nitrate corresponding to the E.M.F. 0.253 V (the E.M.F. corresponding to the inflexion point of the titration curve of NaL when capric and lower acids were present) the acid value AV_p calculated from this silver nitrate consumption corresponds to the acid value of the higher acids beginning from C_{12}, as may be seen from Table 3. The difference between the total acid value and AV_p is a measure of the fatty acid C_{10} and lower and can be rapidly determined by this procedure. For example, the fatty acids in cocoanut oil, the total acid value AV of which was 274 mg KOH/1 g, gave on potentiometric titration an acid value AV_p 217.6 mg KOH/1 g. The literature [4] gives for the corresponding average values of cocoanut oil AV 272 mg KOH/1 g and AV_p 218.5 mg KOH/1 g.

THE TITRATION OF ROSIN ACID AND ITS MIXTURES WITH FATTY ACIDS

Preliminary titration of rosin soaps with silver nitrate was also conducted at temperatures from 20 to 70° C. The titration curves of sodium abietate and talloil rosin soap were similar to those obtained with sodium laurate. The solubility product of the silver salt of rosin acid at 70° C calculated from the inflexion point of the titration curve was

$$L \ Ag \ Ro \ = 5—9 \times 10^{-8}$$

The titration result is, however, unsatisfactory, since the error is — 30 to — 36 mol-%. A part of the rosin acids evidently are not precipitated, possibly the oxidized rosin acids present in the rosin soap. Although talloil rosin is a mixture of rosin acids, its titration curve resembles that of sodium abietate. Evidently the solubilities of the silver salts of the various rosin acids are of the same magnitude.

When sodium abietate is titrated in binary mixtures containing sodium palmitate, myristate, laurate or oleate, each component causes a jump in the titration curve, but the titration error is greater. A similar behaviour was observed in titrating mixtures of sodium palmitate, oleate and abietate and of sodium myristate, oleate and abietate.

The curves obtained in the titration of the sodium salt of talloil containing 10 % rosin acids revealed jumps due to rosin acid and the various fatty acids and it seems possible that the method might be improved to allow an approximate determination of the rosin acids in talloil.

SUMMARY

1. The solubility products of the silver salts of the higher fatty acids $(C_{18}—C_{12})$ in aqueous solution were redetermined from the inflexion points of the titration curves of the acids obtained by titration with silver nitrate, and the values of the solubility product of silver caprate at 20° C and 70° C were established. The solubility of silver caprylate and silver caproate was so high between 20° and 60° C that the precipitation titration could not be used to evaluate the solubility of these silver salts. A preliminary value of the solubility product of the silver salt of rosin acids (abietic acid and talloil rosin acid) was obtained.

2. The saturated fatty acids ($C_{18}—C_{10}$) and oleic acid can be individually estimated quantitatively by potentiometric precipitation titration with silver nitrate, the titration error not exceeding — 4 %.

3. Both components in binary mixtures of saturated fatty acids containing an even number of carbon atoms can be quantitatively estimated by potentiometric precipitation titration with silver nitrate with an error not exceeding — 4 % if the chains of the two fatty acids differ by more than two CH_2-groups. Both laurate and caprate could also be estimated quantitatively together in their binary mixtures (error ± 1 %). The estimation of both components in binary mixtures of myristate-laurate and palmitate-myristate mixtures is also possible, but in these cases the titration error is rather great (— 10 %). Stearate and palmitate could not be estimated separately in the same solution.

4. The fatty acids in a ternary mixture can be determined separately if the mixture does not contain successive even fatty acids between C_{14} and C_{18}. When the number of components in the mixture is increased it is no longer possible to obtain a separation of the acids but their total amount can be evaluated with an accuracy of 2 % when the E. M. F. of the inflexion point of (sodium) laurate at 60° C is taken for the end point of the titration. (E. M. F. = 0.268 V with reference to the calomel electrode + 0.283 V.)

5. Owing to the relatively high solubility of the silver salts of capric and lower acids at higher temperatures the presence of these acids in the fatty acid mixtures has very little effect on the titration curve obtained in the titration with silver nitrate at 60° C. The total amount of C_{12} and higher acids can in this case be determined by titration to the E. M. F. value of the inflexion point of laurate (E. M. F. = 0.253 V). When the results are expressed in terms of the acid value (AV) the maximum error found was — 5 %. The difference between the total acid value of the acid mixture and the potentiometrically determined acid value gives a measure of the fatty acids C_{10} and lower contained in the mixture and their amount can thus be rapidly evaluated by this method.

REFERENCES

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