Potentiometric Titration of Viscose*

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POTENTIOMETRIC TITRATIONS

THE means of measuring the degree of ripening of a viscose now at our disposal (Hottenroth, sodium chloride, xanthate sulfur, gamma number) are either too subjective or too inaccurate, and are in all cases insufficient for purposes more exacting than process control.

The chemical reactions occurring during the ripening of a viscose are characterized by progressive conversion of the cellulose xanthate chain molecule into a molecule of hydrated cellulose. An immediate consequence of this process is an increase in the concentrations of salts—specifically, sodium carbonate and sodium trithiocarbonate—in the viscose. Madame Dobry has found, in recent work,[1] that the acetonic solutions of cellulosic derivatives (di- and trinitro-, di- and triacetylcellulose) are always conductive. She terms as "apparent conductibility" the difference between the conductivity of the cellulosic solutions and that of the pure solvent, separated from the former by a semi-permeable membrane. She states that, experimentally, the difference increases to reach a constant value quickly when the solvent is renewed in its cell. This being so, one would expect the electrical conductivity of the medium to vary as a function of degree of ripening, and this variation would indicate, at each instant, the condition of the cellulose chains or micelles.

Before measuring the conductivity proper of a viscose in the process of ripening, a series of potentiometric titrations was carried out, repeating, with amplifications, the work of Neumann, Kargin, and Fokina.[2]

Potentiometric Titration with 0.1 *N* Hydrochloric Acid

A glass electrode was used, with a calomel electrode as reference. The viscose investigated had the following composition: cellulose, 8.10%; sulfur, 2.26%; sodium hydroxide, 6.0%.

In order to be in a position to interpret the titration curves, titrations first had to be carried out under the same conditions on solutions of the pure substances presumably present in the viscose, as well as on solutions of mixtures of known proportions of these pure substances.

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* Translated from the original French. Part II of this paper will appear in THIS JOURNAL under the title of "La Conductivité Électrique de la Viscose."

[1] Dobry, *J. chim. phys.*, 35, 16–20 (1930).

[2] Neumann, Kargin, and Fokina, *Cellulosechemie*, 17, 16, (1936).

The results of the titrations of a viscose during ripening are given graphically in Figure 1. The quantities of 0.1 *N* HCl added to a constant quantity of viscose (20 cc. of a 10% viscose solution) are plotted as abscissas, and the corresponding *p*H values as ordinates; each curve represents a different degree of ripening.

There are three distinct plateaus in the curve of *p*H *vs.* amount of hydrochloric acid added. The first of these corresponds to the neutralization of sodium hydroxide, sodium sulfide, and sodium carbonate; the second, to sodium hydrosulfide and sodium bicarbonate; and the third to the H^+ concentration cell.

Comparison of the curves for the reference substances and for viscose solutions of different degrees of ripening established the following facts. (*1*) The carbonate content increases during ripening. (*2*) The viscose behaves on titration with 0.1 *N* hydrochloric acid as a mixture of sodium hydroxide, sodium sulfide, and sodium carbonate. (*3*) It is impossible, under these experimental conditions, to detect the presence of sodium trithiocarbonate, as its dissociation constant is practically identical with that of the carbonate and of the sulfide. (*4*) As indicated by Figure 1, it would be difficult and rather impractical to use this method to determine the degree of ripening of a viscose. The difference between a young and an old viscose is not easy to detect or to evaluate. (*5*) The magnitude of the slope of the titration curve at *p*H 7 decreases continuously during ripening.

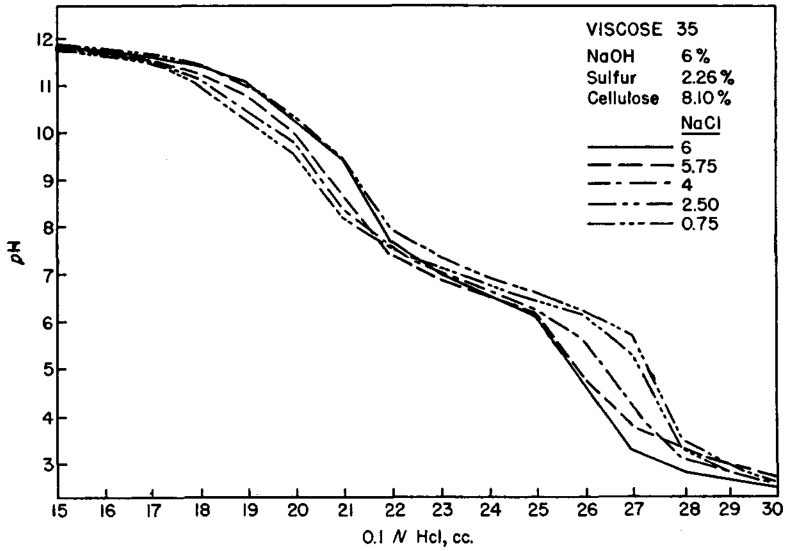

Fig. 1. Change in *p*H of a viscose as a function of the degree of ripening.

Potentiometric Titration with 0.1 *N* Silver Nitrate

In these experiments a cell formed by a silver electrode and a normal calomel electrode was employed. The viscoses varied in composition; in each case compositions are indicated together with the experimental results.

The same quantity of a 10% viscose solution was used for each titration reported. 10 cc. of the solution corresponds therefore to one gram of the original viscose. Potentiometric titrations were carried out at several stages of the ripening process; the experimental curves are reproduced in Figure 2.

As in the case of potentiometric titration with hydrochloric acid, we had previously titrated solutions of the pure substances presumed to be present in the viscose.

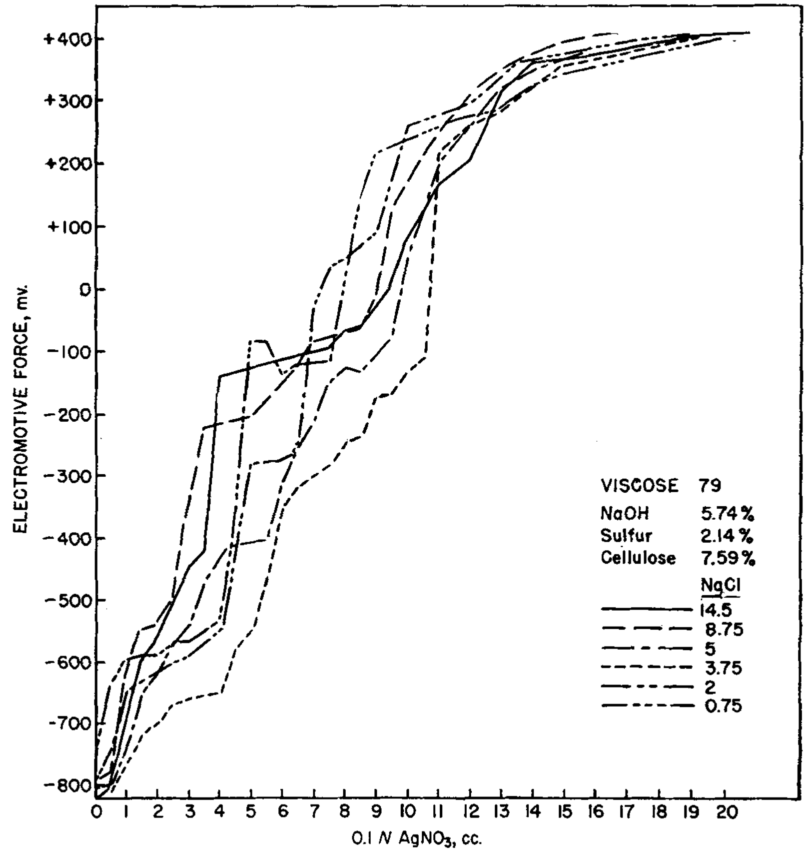

Fig. 2. Change in e.m.f. of a Ag–AgNO$_3$ concentration cell in a ripening viscose.

In Figure 2 the values (in millivolts) of the electromotive force of the silver–silver nitrate half-cell in the 10% solutions of viscose (against the normal calomel electrode as reference) are plotted as ordinates *vs.* quantities of 0.1 N silver nitrate added to these solutions as abscissas. Four plateaus can be distinguished clearly.

From —820 to —780 Millivolts. This plateau corresponds to precipitation of sulfide ion. The potential difference obtained in titration of pure sodium sulfide solutions with 0.1 N silver nitrate remains around —800 millivolts during the precipitation of silver sulfide. The sodium sulfide content of the viscose diminished during maturation.

From —650 to —550 Millivolts. This plateau corresponds to sodium trithiocarbonate. During titration of pure sodium thiocarbonate with silver nitrate, the e.m.f. varies from −700 to −550 mv.

A quantitative interpretation of the variation of the width of this plateau with degree of ripening brings out the following interesting fact:

As the salt index* decreases from 8 to 0.5, we lose, per gram of viscose, 452 mg. of sodium sulfide and gain only 383 mg. of sodium thiocarbonate. In this connection, the literature usually states that sodium sulfide is converted completely into sodium thiocarbonate. Had this conversion really been complete, we should have found 904 mg. of sodium thiocarbonate. There is lost, therefore, an appreciable portion of the sodium sulfide which has not been transformed into sodium thiocarbonate, and which should be recoverable as some other reaction product. This anomaly has led us to study the complete material balance of the reaction between sodium hydroxide and carbon disulfide, which, at least to our knowledge, has never been published. This study will constitute the second part of this article.

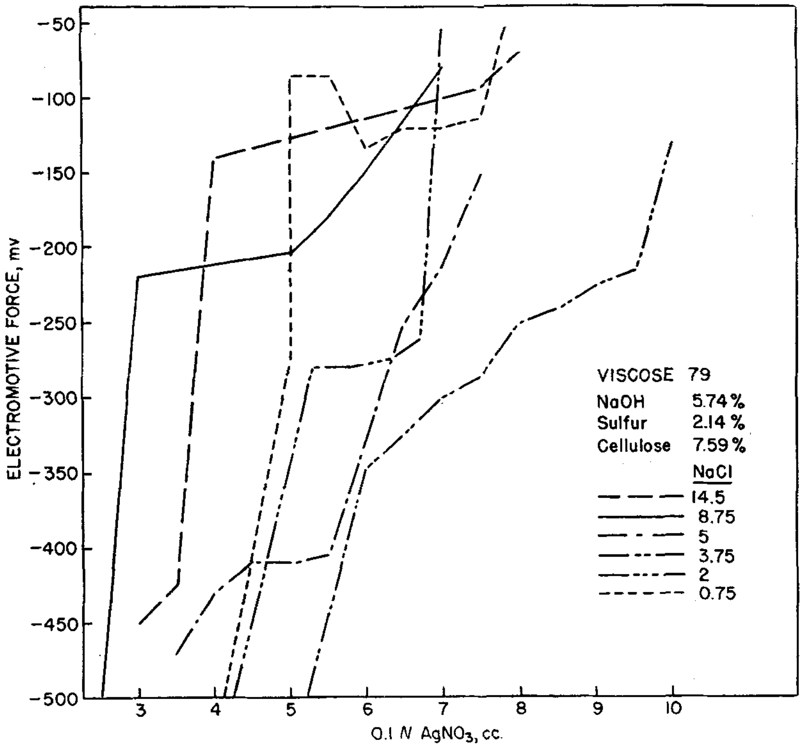

Fig. 3. **Consecutive positions of the xanthate plateau as a function of the degree of ripening.**

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* The salt index is a conventional measure of the degree of ripening of the viscose. It is, in reality, a threshold of coagulation of the viscose, which, because of its ripening, can be coagulated more easily as the solutions of sodium chloride become weaker. The salt index decreases, therefore, as the ripening increases.

From —300 to —50 Millivolts. This plateau is characteristic of silver cellulose xanthate. As was expected, this level is the most important part of the curve. Although its complete interpretation is still difficult at the present stage of our research, we have observed a fact which seems to be quite significant and which we will discuss below.

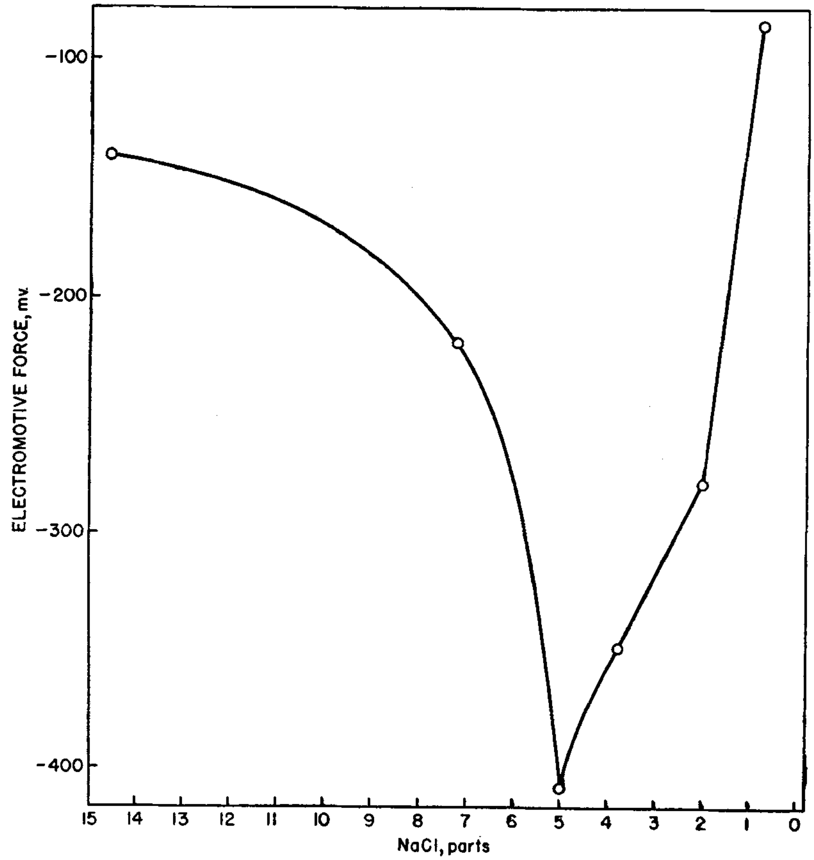

Fig. 4. Change of the inflection point of the plateau corresponding to the silver xanthate in a ripening viscose.

In Figure 3 is reproduced, on a larger scale, that portion of Figure 2 which reveals the change in the position of the plateau corresponding to the xanthate group of the cellulose xanthate molecule as a function of the ripening of the viscose. On closer examination of this group of curves, it may be seen that the ordinate (e.m.f.) of the point of inflection of the curve, marking the beginning of the plateau, changes as a continuous function of the degree of ripening. It decreases first, passing through a sharp minimum, and then increases rapidly as the ripening progresses. Table I gives the numerical values of the ordinate of these inflection points plotted in Figure 4.

TABLE I

ELECTROMOTIVE FORCE OF SILVER XANTHATE IN A RIPENING VISCOSE

E.m.f. at the inflection point beginning the plateau	Salt index	E.m.f. at the inflection point beginning the plateau	Salt index
−140	14.5	−350	3.75
−220	8.75	−280	2.0
−410	5.0	−85	0.75

Now, it will be noted that the sudden change in the slope of the curve in Figure 4 occurs at exactly that degree of ripening which has been established through long experience as optimum for spinning.

This coincidence is more striking since it closely parallels another critical phenomenon occurring at the same stage of ripening observed in a field altogether foreign to electrochemistry. We are at present engaged in a study (as yet unpublished) of the structural viscosity of viscose, and find that if we plot the derivative of the apparent viscosity with respect to the shearing stress as a function of the degree of ripening, a sudden change in the slope of the curve is also observed precisely at the salt index most favorable for spinning.

The existence of these critical changes in physical fields as diverse as viscosity and electrometric titration has led us to suppose that at this precise stage of ripening the cellulose particle undergoes a radical change, either in shape or in degree of molecular aggregation or association, resulting (in spinning) in a product of optimum yarn properties.

In future research we plan to investigate the change in the state of the cellulose molecule in viscose that these phenomena reveal, and particularly to seek the connection between this change of state and the optimum mechanical qualities of the thread produced on spinning.

From +300 to +400 Millivolts. This last plateau of the curve represents the formation of silver oxide and silver carbonate, as well as the silver ion concentration cell.

Between the plateau caused by the formation of the silver xanthate and the fourth plateau, we observed a phenomenon apparently unnoticed by Neumann, Kargin, and Fokina. The curves in Figure 2 would appear to indicate a smooth increase in e.m.f. in the region between +100 and +300 mv. upon addition of silver nitrate. Actually, beyond +90 mv., each drop of silver nitrate added to the viscose produced a large transient increase in e.m.f. that disappeared within ten minutes. This phenomenon indicates the formation of an unstable silver compound which, because of its almost immediate decomposition, does not give a characteristic plateau in the titration curve. The proportions of 0.1 N silver nitrate reacting with sodium sulfide, with sodium thiocarbonate, and with this unknown substance were approximately 1:5:1. However, this phenomenon was not observed in a pure cellulose xanthate solution isolated by the Lieser[3] method.

We attempted to identify this compound by the use of the following reactions: carbon disulfide was reacted with hydrated sodium sulfide in alcoholic solu-

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[3] Lieser, *Ann.*, 464, 43 (1928).

tion; the product of this reaction was then added to methyl sulfate, giving an oily liquid which was isolated by distillation and identified as methyl dithiocarbonate. The potentiometric titration with silver nitrate of the solution obtained by saponifying this compound with dilute sodium hydroxide gave, in the same region of the curve, the same e.m.f. variations noted previously in the titration of viscose. This seems to prove the identity of sodium dithiocarbonate and of the unknown compound in the viscose solution.

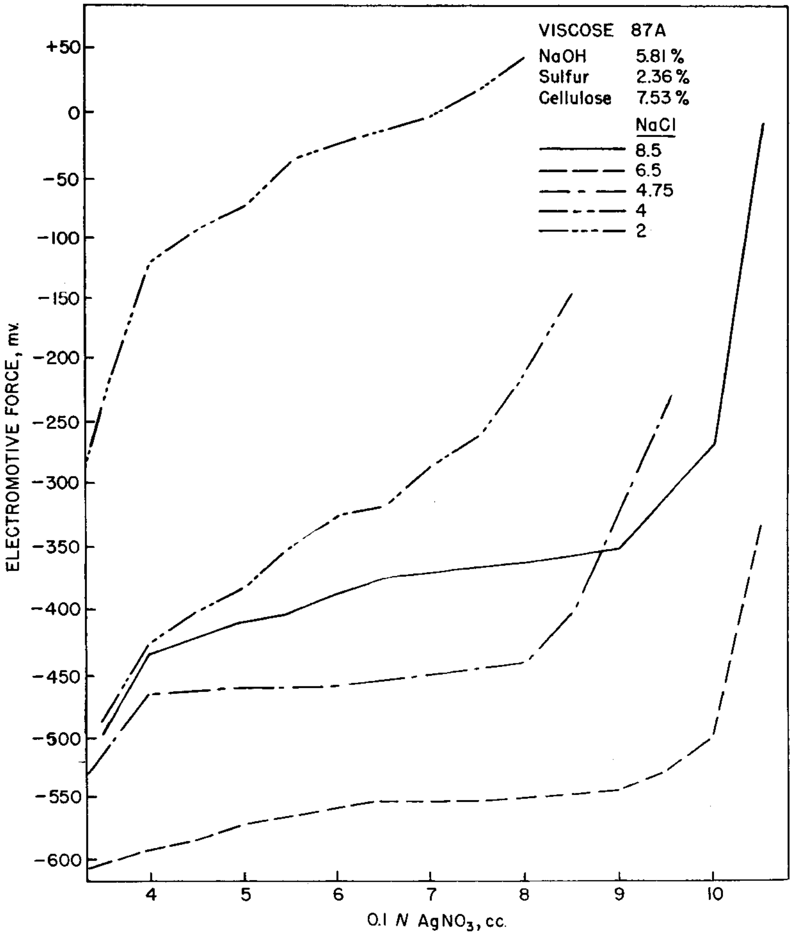


Fig. 5. Change in e.m.f. of a Ag–$AgNO_3$ concentration cell in a viscose of greater sulfur content.

By its plateaus, therefore, the silver nitrate titration curve of a ripening viscose indicates the presence and the approximate quantity of sodium sulfide, sodium thiocarbonate, xanthate, sodium hydroxide, and sodium carbonate, and by its oscillations, it indicates the transient existence of sodium dithiocarbonate.

Before leaving this phase of the work, we also investigated viscose solutions of different compositions. Figure 5 shows the cellulose xanthate plateaus obtained in the silver nitrate titration of a viscose of greater sulfur content.

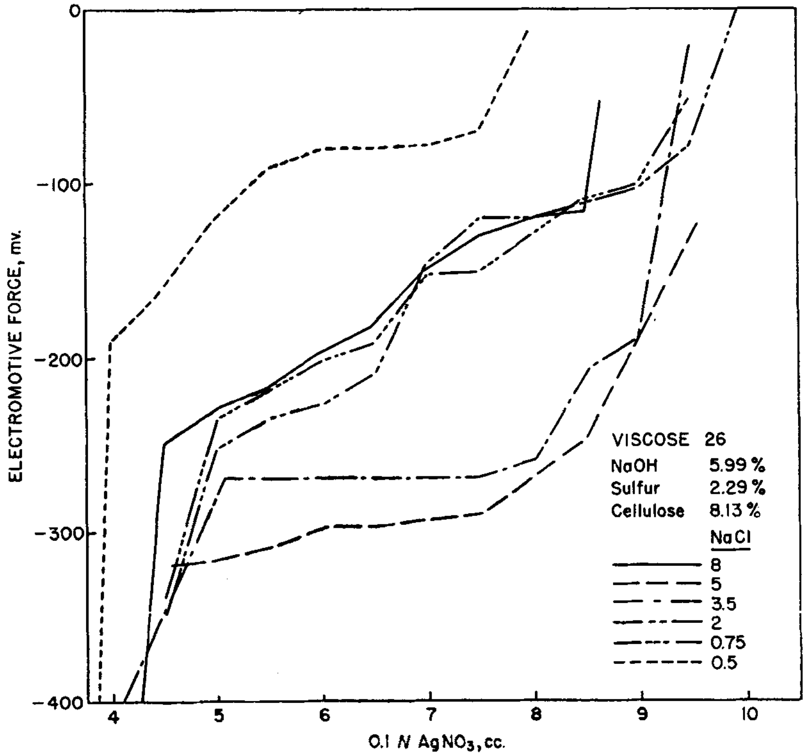


Fig. 6. Change in e.m.f. of a Ag–AgNO$_3$ concentration cell in a viscose of completely different composition.

TABLE II

CHANGE IN ELECTROMOTIVE FORCE OF THE INFLECTION POINT[a]

Analysis	Viscose					
	A		B		C	
Cellulose:	7.59%		7.53%		8.13%	
NaOH:	5.74%		5.81%		5.99%	
Sulfur:	2.14%		2.36%		2.29%	
	Salt index	E.m.f. of inflection point	Salt index	E.m.f. of inflection point	Salt index	E.m.f. of inflection point
	14.5	−140	8.5	−430	8.0	−250
	8.75	−220	6.5	−600	5.0	−320
	5.0	−410	4.75	−462	3.5	−270
	3.75	−350	4.0	−425	2.0	−253
	2.0	−180	2.0	−120	0.75	−235
	0.75	−85			0.50	−190

[a] Marking the beginning of the silver xanthate plateau, as function of degree of ripening.

The general appearance of the curve is the same as those previously obtained. A change in the inflection point beginning the xanthate plateaus may again be seen to exhibit a sharp minimum, as in Figure 4. However, the increase in sulfur content—all other conditions being kept constant—greatly lowered the e.m.f. at which the plateau started.

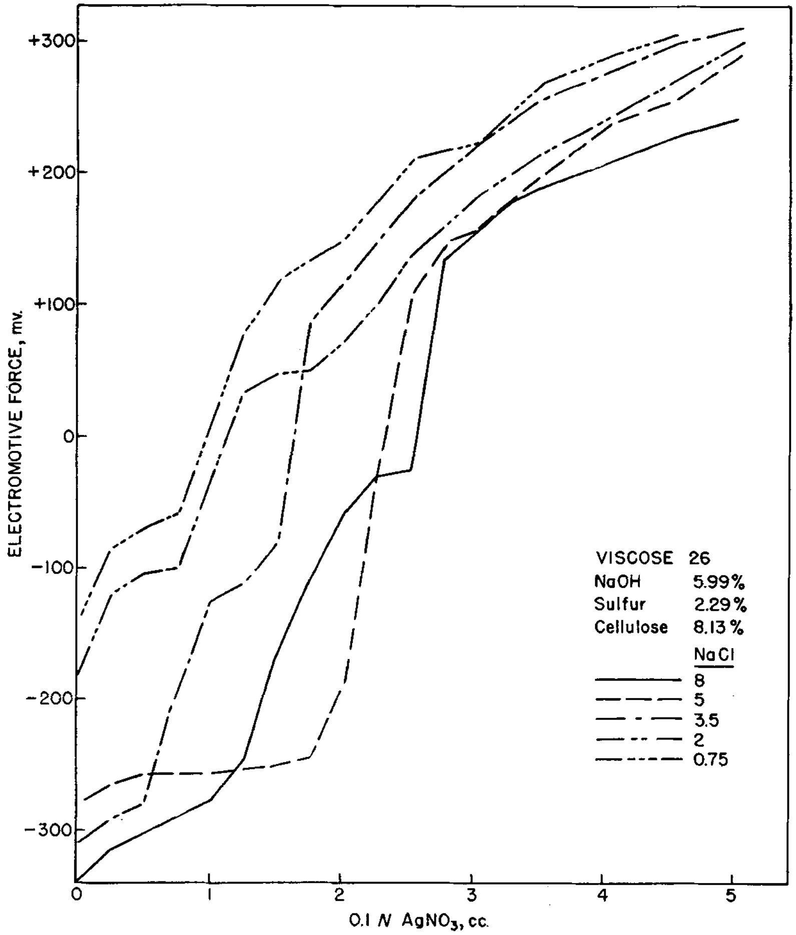


Fig. 7. Change in e.m.f. of a Ag–AgNO$_3$ concentration cell in a viscose neutralized during ripening.

Figure 6 represents the same stage of the titration of an altogether different viscose, the proportions of all of its components having been changed. Here again, we obtain the same general curve, with a sharp minimum in the plot of e.m.f. as a function of the degree of ripening. The numerical values which show the presence of a minimum in the curve relating the position of the silver xanthate plateau and the degree of ripening are given in Table II.

Potentiometric Titration of a Neutralized Viscose with Silver Nitrate

The same viscose used in most of the preceding experiments was neutralized with 0.5 *N* acetic acid to a *p*H of 6.2 (bromothymol blue indicator). After neutralization, the viscose was titrated as before with 0.1 *N* silver nitrate, and the titration curve during ripening recorded. This was more delicate, however, for the conditions of ripening were changed by the hydrogen sulfide formed as a by-product of the neutralization of the sulfur compounds; it was difficult to remove the hydrogen sulfide completely. Figure 7 reproduces the results obtained.

As expected, the sodium sulfide and the sodium thiocarbonate plateaus have disappeared. The position of the xanthate plateau is not changed, except the upper limit, which is somewhat higher, so that this stage of the titration now includes the region between −300 and +75 mv.

A new phenomenon was observed in this region, which can now be mentioned, but with reservations as it has still to be confirmed and explained; *i.e.*, the fact that the xanthate level seems to subdivide into two smaller plateaus. This fact, however, requires further investigation.

We find again the same change, and the same sharp minimum, in the position of the xanthate plateau as a function of the degree of ripening. The observation of e.m.f. oscillations between the xanthate and the silver ion concentration cell plateaus in the neutralized viscose also demonstrates the fact that sodium dithiocarbonate is not decomposed by acetic acid in the presence of silver xanthate.

Since a great portion of the salts are eliminated in the neutralized viscose, only 4 or 5 cc. of silver nitrate are needed for the titration. It would be simpler, therefore, to work with it were it not for the difficulties due to the hydrogen sulfide, which we soon hope to resolve.

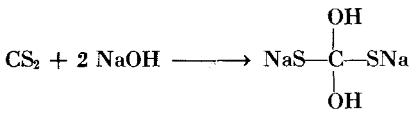
THE REACTION OF CARBON DISULFIDE AND SODIUM HYDROXIDE

The entire potentiometric curve obtained cannot be explained sufficiently by the general classic reaction of carbon disulfide and sodium hydroxide:

$$6\ NAOH + 3\ CS_2 \longrightarrow 2\ Na_2CS_3 + Na_2CO_3 + 3\ H_2O$$

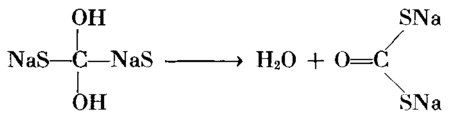
The definite, though transient existence of the sodium dithiocarbonate seems to have been established. The following work represents a further attempt to account for all the reactions occurring during the ripening of the viscose, the products of which were revealed in the potentiometric curve.

First, in the presence of sodium hydroxide, the double bond in carbon disulfide becomes saturated, with the formation of a dithio-ortho-carbonic derivative:



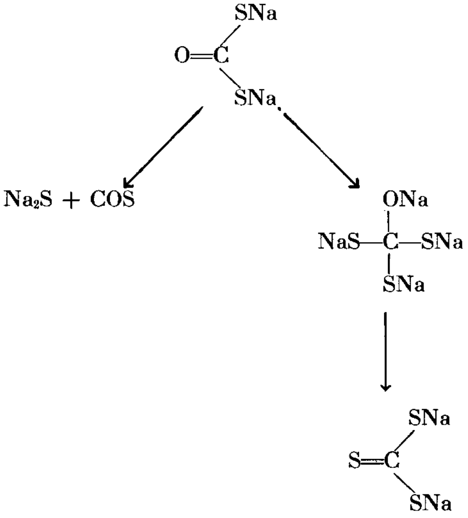
$$CS_2 + 2\ NaOH \longrightarrow NaS{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}{-}SNa$$

Upon loss of a molecule of water, sodium dithiocarbonate is obtained:



$$NaS{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}{-}NaS \longrightarrow H_2O + O{=}C\begin{matrix}\diagup SNa\\ \diagdown SNa\end{matrix}$$

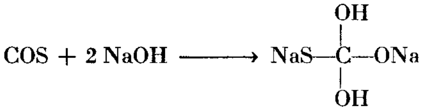
This dithiocarbonate is, as we have seen, rather unstable and can react in two well-known ways: it may either lose a molecule of sodium sulfide to give carbon oxysulfide, or it may react with a molecule of sodium sulfide in the basic medium thereby being converted into trithiocarbonate by way of an orthocarbonic intermediate. However, as we have established in the first part of this paper, this conversion is not complete and does not use up all the sodium sulfide at its disposal:



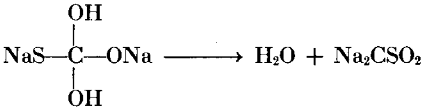
The excess sodium sulfide reacts with the carbon disulfide to give sodium trithiocarbonate:

$$Na_2S + CS_2 \longrightarrow Na_2CS_3$$

The carbon oxysulfide, reacting with two molecules of sodium hydroxide, yields a monothio-ortho-carbonate which, upon losing a molecule of water, gives a monothio-carbonate. This latter compound, in turn, is converted to the carbonate:



$$COS + 2\,NaOH \longrightarrow NaS\text{—}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}\text{—}ONa$$



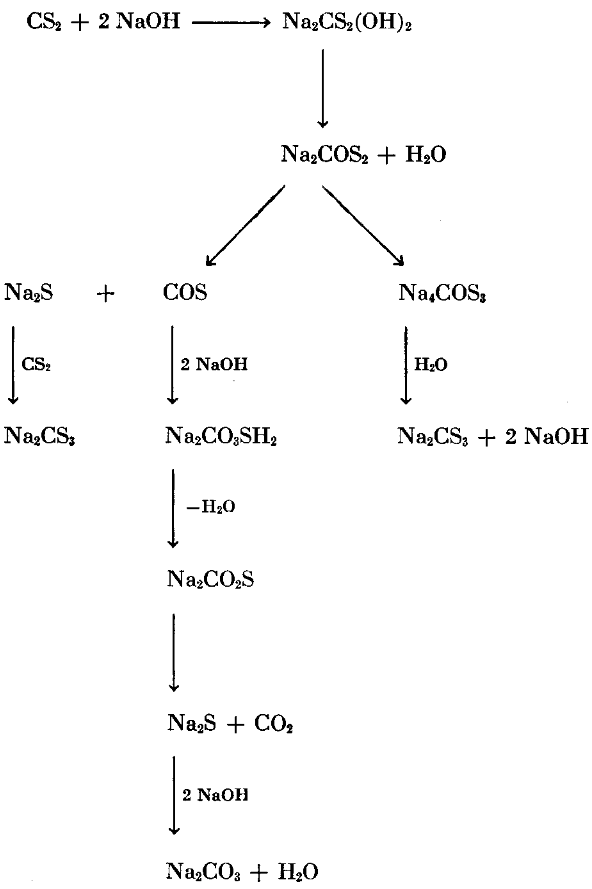
$$NaS\text{—}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}\text{—}ONa \longrightarrow H_2O + Na_2CSO_2$$

$$Na_2CSO_2 \longrightarrow Na_2S + CO_2$$

$$2\,NaOH + CO_2 \longrightarrow H_2O + Na_2CO_3$$

The formation and increase in content of sodium carbonate during the viscose ripening are thus explained.

The following schematic outline of the reaction of carbon disulfide and sodium hydroxide indicates all the intermediate products that influence the titration curve. Strictly stoichiometric considerations were disregarded since they are not of immediate interest and lead too far afield.



CONCLUSIONS

The following conclusions can be drawn from this first investigation:

(*1*) The *p*H changes occurring during titration of a viscose with 0.1 *N* hydrochloric acid are not sharp enough to determine its degree of ripening.

(*2*) The study of the electrochemical behavior exhibited by a silver–silver nitrate concentration cell in a ripening viscose has revealed two new facts, one very important for manufacturing purposes and the other for the scientific study of the process: (*a*) There exists a very sharp minimum in the plot of the e.m.f. of a characteristic inflection in the potentiometric titration curve of the xanthate against degree of ripening. This minimum, which may be due either to a radical change in the shape or state of molecular aggregation or association of the cellulose particle or to a change in the rate of removal of the xanthate radicals, coincides with the degree of ripening optimum for spinning. This new fact parallels a similar phenomenon recently observed in the study of the viscosity of viscose (unpublished). (*b*) The existence of sodium dithiocarbonate in viscose is indicated by transient fluctuations of e.m.f. at a certain stage of the titration.

(*3*) The same methods applied to a viscose neutralized with acetic acid showed, in addition to the expected results, a new fact which needs further confirmation and explanation.

(*4*) The complete scheme of reactions occurring in a ripening viscose was postulated from the indications given by the potentiometric titration with silver nitrate.

Synopsis

A new method is investigated to determine by means of potentiometric titration the degree of ripening of viscose. It is found that when the e.m.f. of a characteristic inflection in the potentiometric titration curve is plotted against a measure of the degree of viscose ripening a sharp minimum occurs at a point corresponding to the optimal degree of ripening. Moreover, evidence is offered to indicate the formation of sodium dithiocarbonate in viscose during ripening. This last fact leads to a reasonable postulation of the complete scheme of reactions taking place in a ripening viscose.

Résumé

Une nouvelle méthode de détermination du degré de mûrissement de la viscose est envisagée au moyen de titrations potentiométriques. Si on porte la force électromotrice, correspondant à l'inflection caractéristique de la courbe de titration potentiométrique, en fonction du degré de mûrissement, de la viscose, un minimum net s'avère au point de mûrissement, optimal au filage. En outre, la formation de dithiocarbonate sodique durant le mûrissement de la viscose est mise en évidence. Ceci permet d'établir un postulat raisonnable de schéma complet des réactions qui se passent durant le mûrissement de la viscose.

Zusammenfassung

Es wird eine neue Methode vòrgeschlagen, um den Reifungsgrad von Viskose mit Hilfe von potentiometrischer Titration zu bestimmen. Es wird gefunden, dass eine Kurve, in der die E.M.K. eines charakteristischen Umkehrpunktes in der potentiometrischen Titrationskurve gegen den Reifungsgrad von Viskose aufgetragen wird, ein scharfes Minimum für den optimalen Reifungsgrad zeigt. Ferner wird experimentelle Evidenz geliefert für die Bildung von Natriumdithiocarbonat während des Reifungsprozesses. Dies führt zur Entwicklung eines kompletten Reaktionsschemas für die Viskosereifung.

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