

A ROUTINE METHOD FOR MEASURING MOLASSES VISCOSITY

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Abstract

Viscosity of molasses is determined under standard conditions (50°C, 80% Karl Fischer solids) using a Hoesppler viscosimeter. Samples are pretreated by dilution and concentration under vacuum to dissolve crystal and remove air. Measurements are made at two different concentrations, preferably slightly below and slightly above 80% solids and the required value obtained by extrapolation using the straight line relationship of log viscosity to concentration between 78% and 84% solids. The importance of the slope of this straight line is discussed.

Centrifuging of molasses reduces viscosity substantially.

Introduction

Part of the service offered to Group factories by the Hulett's Central Laboratory has been measurement of the viscosity of final molasses. The techniques used have been changed during the past four years in an attempt to obtain more and more meaningful data on this important physical property of molasses. It has been the policy to express viscosity at two concentrations; firstly at the actual brix at which the sample was received and secondly at a reference concentration. The 'factory brix' viscosity was originally determined at the saturation temperature of the molasses, which varied from 50°C to 55°C, but this was changed to a standard temperature of 50°C. The reference concentration used was initially 80° refractometer brix (1 to 1) but this has been changed to 80% total solids, determined by the Karl Fischer method. The 'reference' viscosity has always been measured at 50°C.

The 'factory brix' data were recorded to try to compare the viscosities of molasses handled by the centrifugal stations of the different factories. This has been only partially successful because of the difficulty in obtaining an undiluted sample. At the high concentrations handled in the factories, even a small amount of dilution can have a considerable effect on the viscosity, and it was possible to obtain completely undiluted molasses at only one of our factories. Alternative methods have been tried for collecting the sample for viscosity measurement. Probably the only satisfactory solution is to use a Nutsch molasses prepared from massecuite as fed to the centrifugal.

A more reliable basis for comparison between factories is the viscosity measured at standard concentration and standard temperature. Under standard conditions the figure obtained for viscosity is a measure of a physical property of the molasses rather than a round-about expression of the concentration. This paper deals with the measurement of viscosity under standard conditions, not at 'factory brix'.

Viscosity is affected by small changes in temperature and it is necessary to control the temperature of the molasses at the time of measurement. This can be accomplished without much difficulty using a thermostatically controlled water bath. Far more of a problem is the control of concentration. It is almost impossible to obtain molasses at an exact, set concentration. When the target was 80° brix it was not quite so difficult, but the target of 80% total solids is unobtainable. This problem has been overcome by measuring viscosity at two known concentrations near to the required standard concentration and using graphical and algebraic means to obtain the desired figure.

Recent meetings of ICUMSA^{5, 6, 7, 8, 9} have included a subject on viscosity and surface tension. Unfortunately most of the reports and discussions deal with theoretical formulae for the relationship between viscosity, concentration, and temperature, and little information is given on methods for viscosity measurement.

More extensive discussions on viscosity are given by Brown and Zerban³, and Bates¹. These include details of methods of measurement by various means, including the Hoesppler Viscosimeter, the instrument used in our laboratories. A more detailed account of the operation of this instrument is given in the manufacturer's handbook⁴. Most of the laboratory manuals prepared for various sugar industries do not discuss the measurement of viscosity. An exception is the Hawaiian manual¹¹ which gives details of the method using the HSPA rotating cylinder viscosimeter.

Some details of the pretreatment of molasses samples for viscosity measurement are given by Beesly². Pretreatment is necessary to remove air from the molasses and to dissolve crystal, though De Whalley⁵ found the Hoesppler viscosimeter more useful than the rotating cylinder type instrument for molasses samples which contained crystal.

Many workers^{1, 2, 3, 6, 7, 8, 9} have investigated the relationship between viscosity and concentration. The

Koganov formula⁶ has been used for predicting viscosity at any concentration from data measured at known concentrations. Beesly², among others, found a straight line relationship between the logarithm of the viscosity and the dry solids content.

Experimental

The molasses samples received from the factories are heated to $\pm 70^{\circ}\text{C}$ in a large water bath and thoroughly mixed. A portion of the mixed sample is diluted to 60 to 65° brix to dissolve any grain. The diluted molasses is transferred to the round bottomed flask of a Buchi Rotavapor and the molasses is re-concentrated under vacuum.

During the concentration, samples of the molasses are removed from time to time and the brix measured using a Jena food refractometer. With experience it is possible to gauge when the concentration of the molasses nears 80% total solids. Samples of the molasses are withdrawn from the Rotavapor for the measurement of viscosity. At least two samples are needed, preferably one at a slightly lower concentration and one at a slightly higher concentration than the target of 80% total solids, though two samples at different concentrations both below or both above 80% total solids will suffice, provided they are both within the range 78 to 84% total solids.

The molasses samples, from which all air has been removed during re-concentration under vacuum, are used to fill the cylinder of the Hoesppler falling ball viscosimeter. The temperature of the apparatus and molasses is controlled at 50°C , $\pm 0,1^{\circ}\text{C}$, by means of a Colora Ultra-thermostat, and the viscosity of the molasses is measured following the instructions in the manufacture's handbook⁴.

After completion of the viscosity measurement, the molasses is drained from the cylinder into a dry beaker. This molasses is used for the determination of solids by the Karl Fischer method, using the same apparatus and essentially the same techniques described by Oosthuizen for raw sugars¹⁰. The solvent used is methanol.

The procedure of viscosity and solids measurement is repeated for the molasses at the second concentration.

The two viscosities are plotted on the logarithmic axis of semi log graph paper against total solids and the viscosity at 80% total solids found by interpolation.

Alternatively, the viscosity at 80% total solids may be calculated using the formula:

$$\log \eta_{80} = \log \eta_A - (S_A - 80) \left(\frac{\log \eta_A - \log \eta_B}{S_A - S_B} \right)$$

where: η_{80} = Viscosity in centipoises at 80% solids
 η_A = Viscosity in centipoises at concentration S_A
 η_B = Viscosity in centipoises at concentration S_B

Results

The straight line relationship between the logarithm of viscosity and the total solids content was confirmed using nine samples of Refinery final molasses. The viscosities of these samples at 50°C were measured at several different concentrations, following the method described in this paper.

The results and the statistics of the correlations are shown in Table I and Figs. 1 to 3.

It can be concluded that within the range 78 to 84% solids, the relationship between the logarithm of the viscosity and the solids content is a straight line with a correlation having significance at more than the 99% level. Any two measurements in this range, preferably more than 1% different in total solids content and preferably bracketing the 80% solids 'target', may be used with confidence to calculate the viscosity under the chosen standard conditions.

Because of the problem of preparing two samples of the same total solids content, an assessment of the reproducibility of the method is difficult. The figures in Table II, taken from the series of tests described above, indicate that the reproducibility of the method is more than adequate.

TABLE I
Data for the relationship : log viscosity v solids content

Sample	Number of Measurements	Statistical Regression	Coefficients Correlation	Significance of Correlation	Solids Content %	
					Max.	Min.
1	6	0,190	0,999	99,9%	84,25	80,48
2	10	0,183	0,987	99,9%	83,68	79,67
3	6	0,189	0,994	99,9%	82,80	80,87
4	5	0,283	0,997	99,9%	83,74	82,11
5	5	0,244	0,998	99,9%	84,50	78,63
6	10	0,187	0,978	99,9%	84,01	78,93
7	5	0,247	0,952	98%	83,11	77,88
8	5	0,205	0,985	99%	86,36	76,78
9	5	0,178	0,963	99%	83,86	78,58

TABLE II
Reproducibility of viscosity measurement

Sample	Determination One		Determination Two	
	Solids %	Viscosity cp	Solids %	Viscosity cp
1	80,70	2840	80,75	2910
4	83,68	13230	83,74	13330
9	78,68	1700	78,76	1740

Beesly² reported that the figure obtained for viscosity using the Hoeppler viscosimeter could be affected by the ball used, though the differences were not really significant. In the tests carried out in Huletts Central Laboratory, two balls were used, ball 5 for less viscous and ball 6 for more viscous molasses.

A few comparisons were made which confirmed Beesly's findings. These are summarised in Table III.

TABLE III
Viscosity measurement with different balls

Sample Source	Refinery		DL		Refinery	
	EM	DL	Refinery	DL	Refinery	
viscosity, cp, ball 5	3044	3143	3355	4103	4597	7250
viscosity, cp, ball 6	3072	3160	3367	4131	4610	7280

Discussion

Although the results reported in this paper were obtained with refinery molasses, a similar straight line relationship between the logarithm of viscosity and solids content of mill molasses has been found both by Beesly² and by Huletts Research and Development. In addition, Smith¹² has found the same relationship for high test molasses in the range 76 to 86% total solids.

The principal aim of this paper has been to give details of a routine method for measuring molasses viscosity in order to compare factory with factory. Because the suggested standard conditions are 50°C and 80% solids, the relationships between viscosity, temperature and concentration far away from these conditions have not been investigated. The ease of practical control in the laboratory led to the decision to ignore variations in temperature away from 50°C while practical considerations also contributed to setting the concentration limits from 78% to 84% total solids. There is considerable discussion on the variation of viscosity in a wide range of temperatures and concentrations in the proceedings of I.C.U.M.S.A.^{5,6,7,8,9}

50°C was chosen as standard temperature because it is a few degrees below the saturation temperature of normal mill molasses and is therefore a satisfactory temperature at which to process C-masseccuite.

The standard condition of 80% total solids is somewhat lower than the normal concentration of mill final molasses but is close enough to be mean-

ingful for comparison purposes and is a practicable concentration from the point of view of the laboratory.

The pretreatment of the molasses samples is essential if comparative viscosity figures are to be obtained. A good case can probably be put forward for additional pretreatment through removal of suspended matter by centrifuging. There is no doubt that 'desludging' reduces viscosity appreciably. Table III summarises the results of viscosity measurements on various molasses samples which were analysed in 1962. In each case the samples were divided into two portions, one of which was diluted to 50° brix and centrifuged. The amount of insoluble sludge removed by this treatment was often as much as 15 to 20% by volume. Both samples were de-aerated by a procedure similar to that described in this paper. Viscosity measurements were made at 80° brix.

TABLE IV
Effect of desludging on molasses viscosity

Sample Source	Viscosity at 80° Brix in centipoises					
	Untreated			Centrifuged		
	40°C	60°C	80°C	40°C	60°C	80°C
EM	4900	1170	500	3380	850	350
FX	4960	1230	510	3690	920	370
AK	3790	940	350	2760	690	250
DL	6360	1480	590	4610	1070	420

The results of viscosity measurement at 80% total solids and 50°C on molasses samples from Huletts mills are given elsewhere in these Proceedings¹³. An interesting feature which emerged from these measurements concerns the slope of the straight line plot of log viscosity against solids. The value of this slope for the four mills, Empangeni, Felixton, Amatikulu, and Darnall throughout the season is given in Table V.

TABLE V
Variations through the season 1970 in the slope of the curve:- log viscosity v solids content %.

	EM	FX	AK	DL
May	0,1901	0,1999	0,1992	0,2202
June	0,1933	0,2044	0,2051	0,2323
July	0,2372	0,2113	0,2231	0,2107
August	0,2592	0,2554	0,1943	0,2067
September	0,2380	0,2212	0,1879	0,2193
October	0,2185	0,2228	0,1920	0,1885
November	0,2039	0,2170	0,1956	0,1843
December	—	0,2267	0,2077	0,1902

The seasonal variations in the value for the increase of viscosity with concentration are considerable, particularly for Empangeni and Felixton. For these two mills there is a negative correlation (95% significance) between the slope and the viscosity at 80% solids, 50°C. This correlation is absent at Amatikulu and Darnall.

It is also interesting to note the differences in the regression coefficients (slopes) for the curves of the refinery molasses samples summarised in Table I. Some of these samples were molasses from C-masseccutes which had been boiled using a chemical pan boiling aid.

In view of the important influence that the increase of viscosity with concentration has on the optimum brix for handling C-masseccutes, the reasons for the seasonal variations both in the slope of the concentration/viscosity curve and in the viscosity itself, could profitably form the subject of a future investigation.

Acknowledgements

The authors wish to thank those members of Hulets Research and Development who carried out viscosity measurements mentioned in this paper.

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Discussion

Mr. Smith: Mr. Jennings has mentioned the effect of concentration on viscosity determination. Would this effect be as great if a different type of viscosimeter, e.g. a torsion type, was used?

Mr. Jennings: It depends if the molasses, containing suspended matter, acts as a Newtonian or non-Newtonian liquid. If as non-Newtonian, then the Hoeppler viscosimeter is not a good method for

determining viscosity over a wide concentration range but nor is the rotating cylinder Brookfield viscosimeter. Other methods would have to be used.

Dr. Matic (in the chair): Work on molasses is being carried on in Berlin and Braunschweig and in their experience cane molasses behave as a non-Newtonian liquid.

Mr. Jennings: Even if it is considered non-Newtonian, in the range we are working in the errors are not likely to be very great.

Mr. Lenferna: A research worker named Rolando in the Trianon factory in Mauritius added milk of lime to molasses in order to remove sludge, and ended up with aconitate of lime.

I have done this in the laboratory by adding milk of lime at 60°C to B molasses and a considerable amount of sludge was deposited.

However, this is apparently not considered a practical method to use in a raw sugar factory.

Mr. Alexander: Many years ago we carried out tests at the S.M.R.I. on molasses from Tongaat and were able to remove by centrifuging over 1.5% of suspended solids by weight, mainly in the form of calcium sulphate.

If sludge is removed the final masseccute can be concentrated to a much higher degree and will still centrifuge satisfactorily. This has been demonstrated in Australia and Mauritius. The purity of the sludge must be determined before it is disposed of in case it is higher than that of the final molasses.

Dr. Matic: Mention is made of the variation in viscosity throughout the season. Is there any explanation for this?

Mr. Jennings: I cannot explain this, it must be due to variations in the chemical composition of the molasses.

Mr. Cox: Regarding measurement of viscosity, I read an article on viscosity of asphalt compositions and it was found that if 30% of stone was included, the viscosity corresponded to the liquid portion of the asphalt, but as the solids increased the viscosity reached a plateau level.

If the solids fraction influences the molasses viscosity it would have to be about 30%, which seems high.

Mr. Jennings: I do not think that example is analogous. If you look at Table IV you will see that up to 20% by volume of sludge was removed and the influence on the viscosity was considerable.

Mr. Cox: I think the analogy would apply if the solids were present in the form of crystals.

Mr. Francis: Were the figures in Table III taken throughout the season or were they from random samples? They seem to reflect a marked increase in viscosity over a period.

Mr. Jennings: The refinery figures may not all have been measured this year and they may not be on 80% total solids but on 80° Brix.

FIGURE I. GRAPH OF LOG VISCOSITY v SOLIDS % ; SAMPLES 1,4,9.

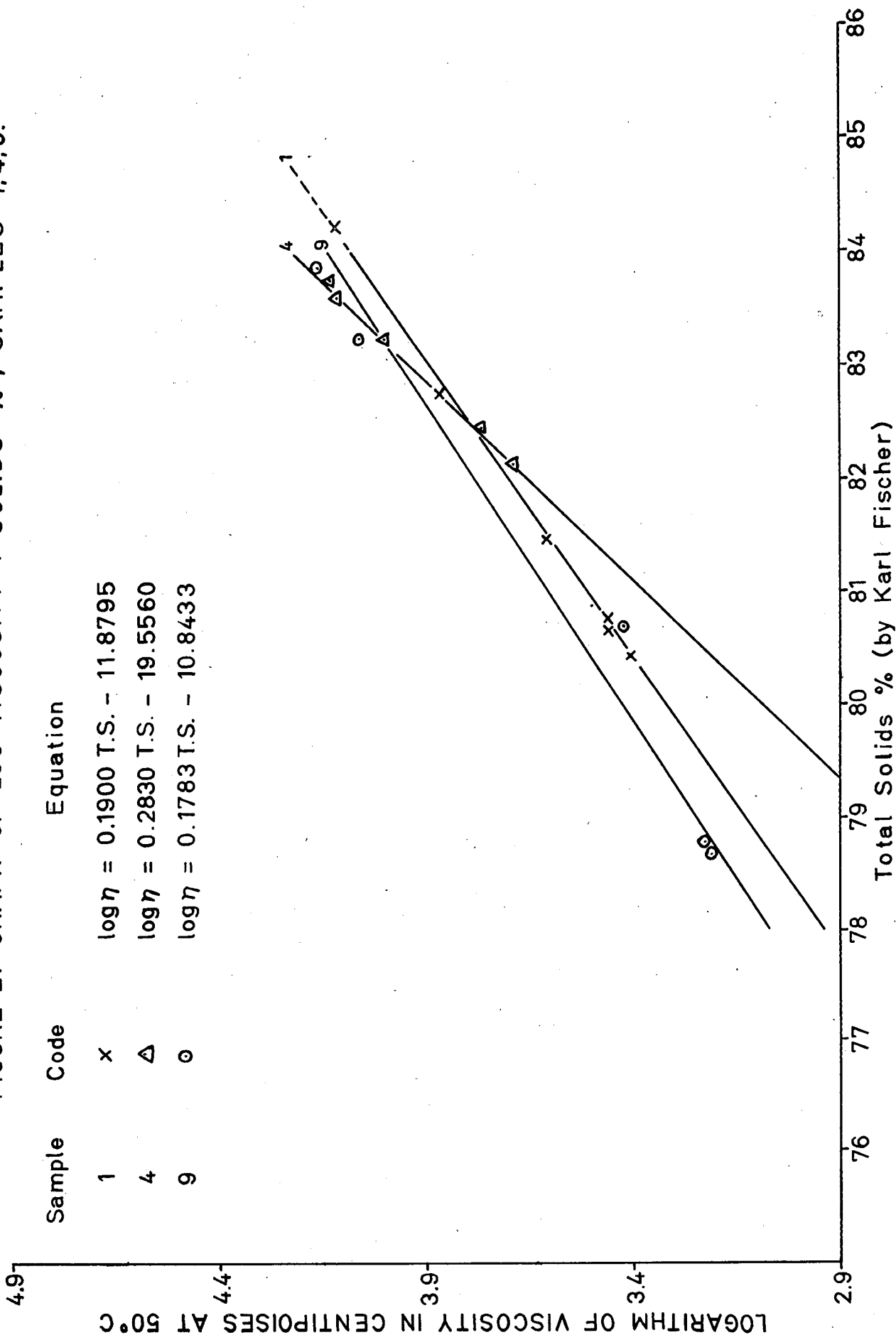


FIGURE II. GRAPH OF LOG VISCOSITY v SOLIDS % ; SAMPLES 2, 5, 8.

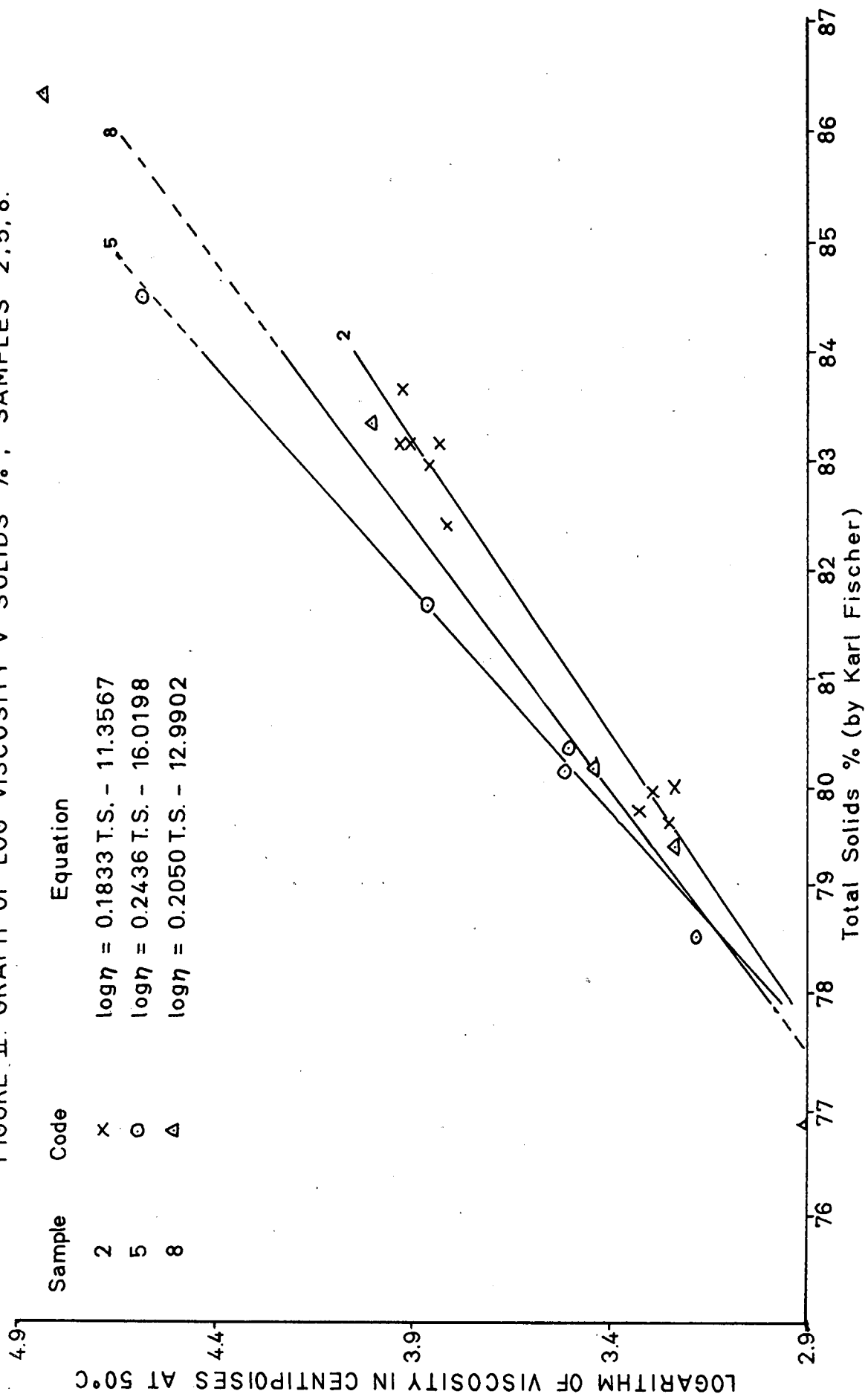


FIGURE III GRAPH OF LOG VISCOSITY v SOLIDS % ; SAMPLES 3,6,7.

