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LOSS FACTOR AND DIELECTRIC CONSTANT CURVES FOR SOME PURE DIESTERS

by

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ABSTRACT

Diesters of the dibasic acids are finding increasing use as liquid dielectrics for audio and radio frequency capacitors. They have good chemical stability as a class, and, when properly selected have low losses and high dielectric constants over a wide range of temperatures and frequencies.

Loss factor and dielectric constant curves vs temperature at 10 Mc for a group of 36 miscellaneous pure diesters have been determined. A few of these showed favorable electrical properties for use at radio frequencies. Many more could be used at audio frequencies. Diesters of lower molecular weight than most of those in the group measured here would be found more suitable, in general, for use at the higher radio frequencies.

One of the materials measured was interesting theoretically in that it showed considerably more internal molecular rotation in the solid than it did in the liquid state.

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INTRODUCTION

A. Authorization

1. This work was done in connection with BuShips Project Order 385/46 dated 7-1-45 for the development of procedures for test on electrical insulating materials and BuOrd Project Order 50636-ORD dated 4-3-45 for the development of synthetic oils and greases.

B. Statement of Problem

2. During the course of work on synthetic lubricating fluids in this Laboratory a large number of diesters were prepared and purified. In this connection many of their physical and chemical properties were determined (1,2). Since some materials of this type are excellent dielectrics for liquid filled capacitors it was thought expedient also to measure their dielectric properties. Such information is of theoretical as well as practical interest.

METHODS

A. Apparatus and Procedure.

3. The equipment and methods for measuring the dielectric properties of the liquids used here are fully described in a previous report (3). The cell required a sample of only 0.2 to 0.3 ml. volume. The temperature of the cell could be varied readily over a range of -70 to 100°C. The diesters measured were the same materials as described in the previous reports on synthetic lubricating fluids (1,2). Most of them were synthesized in this Laboratory.

During the last stage of their purification the materials studied here were dried by being percolated one or more times through a column containing layers of fuller's earth, alumina, and silica gel, in the order named. No trouble was experienced by the samples picking up atmospheric moisture since the effect of the amount they picked up was within the experimental error of the method for 10 megacycle measurements. If measurements were made at audio frequencies then errors might be introduced into the loss factor data due to ionic conductivity, but at 10 Mc the impedance of the sample in the dielectric cell is only about 1000 ohms so that direct current leakage resistances as low as 1 megohm do not cause trouble. All dielectric constant and loss factor data are expressed to three significant figures in this work. This is sufficient since the electrical properties of these materials vary widely in the anomalous dispersion region.

DATA OBTAINED

A. Curves or Plots of Data.

4. Curves showing the dielectric constant (E^{1}) and loss factor (E^{11}) vs temperature for all materials studied are given on Plates 1 through 8. Because of the number of curves on most of the Plates experimental points are shown only on Plates 1, 2 and 3. A summary of this data is given in Table I.

5. The number and position of the points relative to the curves for these three Plates are typical for the whole series. At least two curves were made for every diester. If good checks were not obtained then additional curves were determined. The reproducibility was, in general, good. Limits of error were given

in a previous report (3).

B. Discussion of Data:

6. Unless otherwise stated all measurements were made under conditions of increasing temperature. The cell with the sample in it was cooled rapidly to the temperature desired and then allowed to warm slowly by itself as the measurements were being made. When it was necessary to apply external heat to the cell the heater was turned on for a period (pulse) of 15 seconds and then one to two minutes allowed for temperature equilibrium to be reached before each measurement was made. In the few instances where measurements were made with temperature decreasing a correction was applied to the thermometer readings to take care of the temperature gradient in the cell.

7. The lower dielectric constants shown on Plates 2 and 3 at temperatures above the transition point for the increasing temperature curve as compared to the decreasing temperature curve are not real. This difference is caused by voids introduced in the sample because of volume changes occuring during the phase transitions.

CONCLUSIONS

A. Facts Established.

8. Most of the diesters of the group measured here have loss factor peaks at too high a temperature to be useful as capacitor dielectrics for 10 Mc use. Di-(1-methyl-ethyl)sebacate is good down to its freezing point at +4°C. Di-(3-methyl-butyl)adipate and Di-(3-methyl-butyl)azelate can be taken down to about -15°C before the losses start becoming appreciable. In general, however, for low temperature work at the high radio frequencies, materials of lower molecular weight than the ones given here must be used since the smaller molecules will have shorter times of relaxation and so have their loss factor peaks at lower temperatures.

9. If a frequency of 1 Mc rather than 10 Mc is used then temperatures 10° to 20° lower are permitted before the equivalent losses appear in most of these diesters. Conversely, at frequencies above 10 Mc the peak temperature is shifted upward. At audio frequencies the loss factor peaks are pushed down to very low temperatures. Ionic conductivity, due to water and other impurities, however, becomes a much more serious factor in regard to increasing losses at the lower frequencies than it is at radio frequencies. Since ionic conductivity increases rapidly with increase in temperature, special care must be used in purifying materials for use as dielectrics in the upper temperature ranges.

B. Discussion.

10. Nearly all the materials measured gave the usual anomalous dispersion curves for the dielectric constant. Most of them that had freezing points in the temperature range covered showed considerable supercooling. One, for example, di-(2-ethyl-butyl)adipate, did not freeze when rapidly taken down to -70°C. On being warmed at a rate of about 2° per minute, however, it started freezing at -58°C and was nearly completely frozen by the time it reached -40°C. It started melting at about -30°C and was fluid again by the time it reached -25°C. This material might be thought of as a supercooled glass that slowly crystallized and then remelted as it was being warmed (4).

11. Another peculiar performance was given by di-(3-methyl-butyl)azelate. This substance was unusual in that the dielectric constant showed a large <u>increase</u> when the material went from the liquid to the solid state rather than the <u>normal</u> decrease. Instead of the molecular rotation being reduced by the solidification there was apparently a large increase in the freedom for rotation.

12. It might be thought that the large increase in dielectric constant which occurs when this material freezes is caused by the presence of impurities or is due to the disorder in molecular arrangement which accompanies the change from the liquid to the solid state. In order to check this more carefully curves for the material were also determined at 1 and at 30 Mc (Plate 3) to compare with those at 10 Mc (Plate 2). It is apparent from the shift of these curves with frequency that the freezing point occurs in the midst of the anomalous dispersion region for both the solid and liquid states. The time of relaxation of the molecules and the amount of polarization are both greater in the solid state than in the liquid. The only place where molecular disorders or the presence of impurities appears to enter is the high dielectric constant peak marked "A" in the decending dielectric constant curve for 1 Mc (Plate 3). The ascending curve at this point, however, appears to be the normal one expected for a material having internal molecular rotation. The melting point of the substance happens to occur at about the same place that the

true peak (solid state) in the 1 Mc dielectric constant curve appears. The peak in the 1 Mc loss factor curve, "B", is far enough below the melting point of the substance to show up unmistakably. The dielectric constant and loss factor data at 30 Mc (Plate 3) is consistently a little low over the whole temperature range because of errors due to the inductance of leads in the cell and bridge.

13. From the shapes and positions of the parts of the curves shown on Plate 2 it is estimated that the loss factor peak for the super cooled liquid at 10 Mc would be rather low in height (under 1.0) and occur at about -65 to -70°C. A guess as to the value of the theoretical peak in loss factor curve for the solid state is given as about 3.0 in height and around -45°C in temperature. Other instances have been reported of materials having higher polarizations in the solid than in the liquid states (5,6). The polarization changes shown on Plates 2 and 3 are unusual in that they are so large. A study of volume changes, thermal properties and crystal structure of this substance at its transition temperature should be interesting.

SUMMARY

14. Plots of loss factor and dielectric constant vs temperature are given for 36 pure diesters. These measurements were made at a frequency of 10 megacycles and, except where freezing points were too high, over a range of temperatures that included the anomalous dispersion region for each substance. The dielectric properties of most of these materials were normal. Some of them having freezing points in the temperature range covered, showed an unusual degree of supercooling. One material was unusual in that it showed a marked increase in polarization on going from the liquid to the solid phase. This indicates an appreciable increase in molecular rotation as this substance freezes.

15. Many of the diesters are suitable for use as relatively high dielectric constant liquids for radio and audio frequency capacitors. Care must be exercised to choose materials whose loss factor peaks occur at temperatures well below those expected in service. It should be noted that all polar liquids show appreciable temperature coefficients of the dielectric constant.

REFERENCES

1. NRL Report No. P-2573 dated June 1945.
2. NRL Report No. P-2576 dated July 1945.
3. NRL Report No. P-2292 dated April 1944.
4. Baker, W. O., and Smyth, C. P., Annals of the New York Academy of Sciences, Vol. XL, Art. 5, pp 447-81 (1940).
5. White, A. H. and Bishop, W. S., J. Am. Chem. Soc. 62, 8-16 (1940).
6. Morgan, S. O., Annals of the New York Academy of Sciences, Vol. XL, Art. 5, pp. 357-69 (1940).

ACKNOWLEDGMENT

The authors are greatly indebted to the Lubrication Section for making available all the purified diesters used in this work.

TABLE I

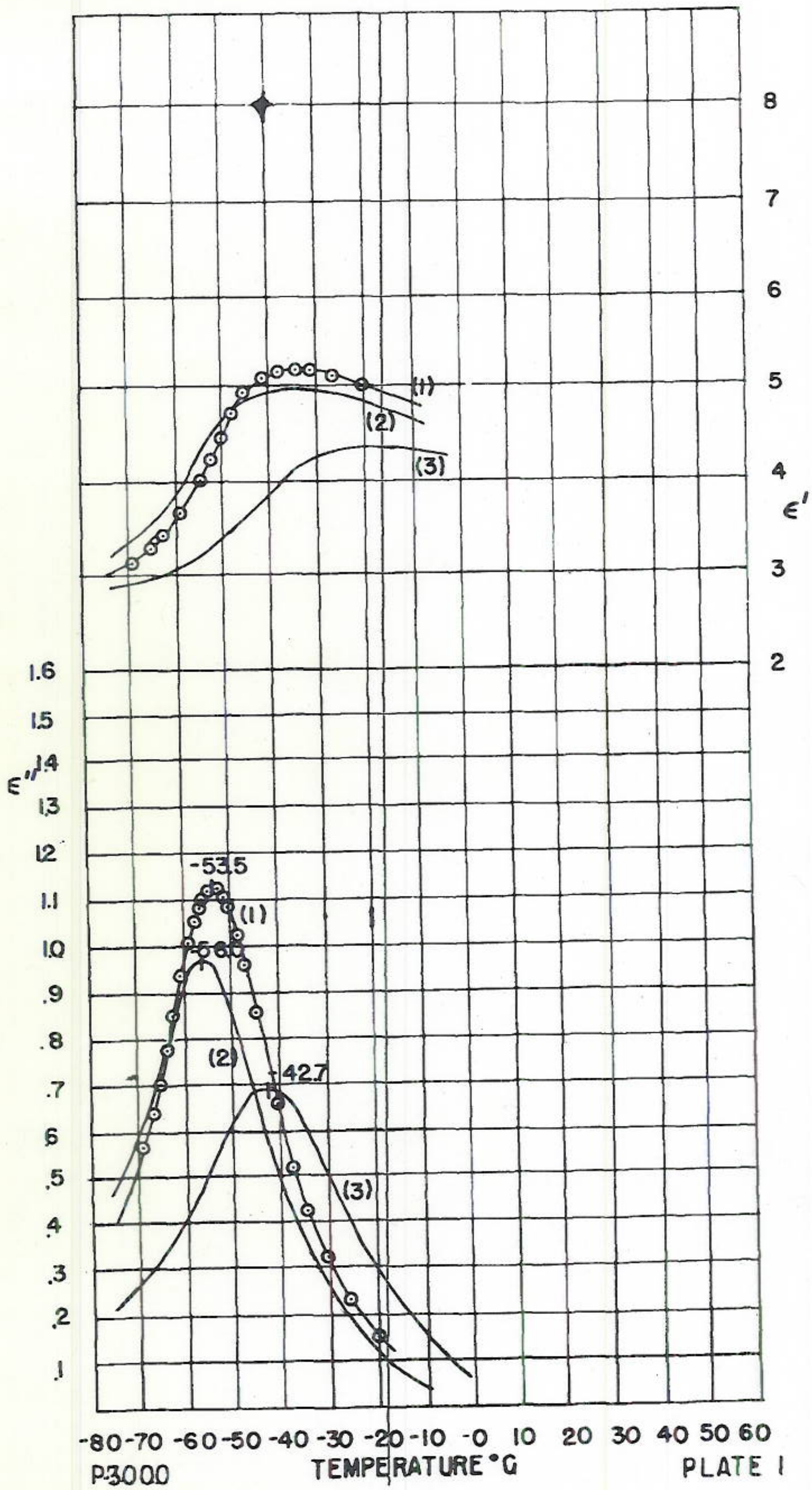
Dielectric Constant and Loss Factor Peaks for Some Diesters at a Frequency of 10 Mc.

Diester	Temp. of loss factor peak °C	Height of loss factor peak	Temp. of max. dielec. const. °C	Dielec. Const. at max.	Plate & Curve No.
Di-(1-ethyl-propyl) azelate	-53.5	1.12	-33	5.20	1(1)
Di-(3-methyl-butyl) azelate	Froze	---	-43*	5.25*	2 & 3
Di-(2-ethylbutyl) azelate	-56.0	0.965	-33	5.03	1(2)
Di-(2-ethyl-hexyl) azelate	-42.7	0.700	-20	4.37	1(3)
Di-(1-methyl-ethyl) adipate	Froze	---	---	---	4(1)
Di-(1-ethyl-propyl) adipate	-55.0	1.23	-33	5.62	4(2)
Di-(3-methyl-butyl) adipate	Froze	---	---	---	4(3)
Di-(2-ethyl-butyl) adipate	-54.0	0.990	-38*	5.19	4(4)
Di-(2-ethyl-hexyl) adipate	-43.0	0.753	-22	4.52	4(5)
Di-(1-methyl-4-ethyloctyl)adipate	-19.0	0.550	+2	3.72	4(6)
Di-(1-(2-methyl-propyl) -4-ethyl)adipate	+5.0	0.520	+25	3.40	4(7)
Di-(1-(3-ethyl-amyl)-4-ethyl-octyl)adipate	+11.0	0.415	+33	3.15	4(8)
Di-(1-methyl-ethyl) sebacate	Froze	---	---	---	5(1)
Di-(1-ethyl-propyl) sebacate	-49.5	1.00	-25	4.90	5(2)
Di-(3-methyl-butyl) sebacate	Froze	---	---	---	5(3)
Di-(1,3-dimethyl-butyl)sebacate	-42.5	0.900	-23	4.65	5(4)
Di-(2-ethyl-butyl) sebacate	Froze	---	---	---	5(5)
Di-(2-ethyl-hexyl) sebacate	-41.0	0.668	-20	4.20	5(6)
Di-(2-(2-ethyl-butoxy) ethyl)sebacate	-41.0	0.975	-15	5.32	5(7)
Di(1-methyl-4-ethyl octyl)sebacate	-18.0	0.493	+3	3.62	5(8)

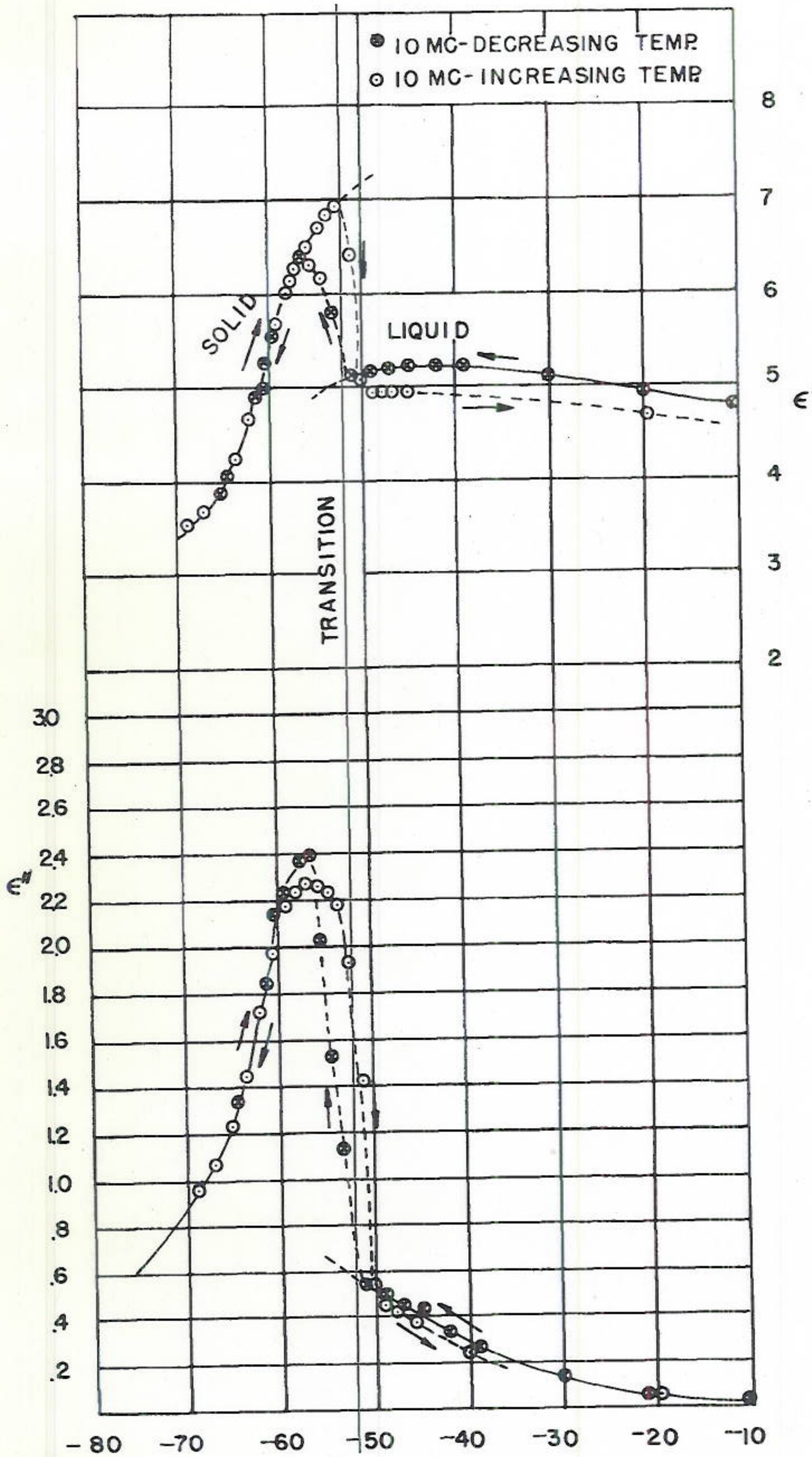
TABLE I (Cont.)

Diester	Temp. of loss factor peak °C	Height of loss factor peak	Temp. of max. dielec. const. °C	Dielec. Const. at max.	Plate & Curve No.
Di-(1-(2-methyl-propyl) -4-ethyl-octyl)sebacate	+5.0	0.490	+22	3.25	5(9)
Di[1-(3-ethyl amyl)-4-ethyl octyl] sebacate	+12.5	0.395	+37	3.15	5(10)
1,6 hexane di-2-ethyl hexanoate	-42.0	0.798	-21	4.45	6(1)
Decamethylene glycol-di-2 ethyl hexanoate	-39.5	0.695	-18	4.20	6(2)
Tri ethylene glycol di-2-ethylhexanoate	-33.0	1.39	-14	6.05	6(3)
Polyethyleneglycol di-2-ethylhexanoate	-31.0	1.23	-9	6.31	6(4)
Di-(ethyl)phthalate	-37.5	2.16	-22	8.55	7(1)
Di-(butyl)phthalate	-31.5	1.89	-12	7.01	7(2)
Butyl phthalyl butyl glycolate	-11.5	1.69	+12	7.99	7(3)
Ethyl phthalyl ethyl glycolate	-7.0	1.96	+12	6.87	7(4)
Methyl phthalyl ethyl glycolate	-1.8	1.92	+19	8.29	7(5)
Di(2-ethyl hexyl) azelate-suberate	-43.0	0.720	-18	4.41	8(1)
Di(2-ethyl hexyl) glutarate	-42.3	0.840	-22	4.65	8(2)
Di(1-methyl-4-ethyl octyl)glutarate	-18.8	0.610	+1	3.82	8(3)
Tri(2-ethyl hexyl) tricarballylate	-11.5	0.740	+16	4.28	8(4)
Di[1-(2-methyl propyl) -4-ethyl octyl]glutarate	+3.0	0.544	+21	3.46	8(5)

* For liquid state at 10 Mc.



DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR



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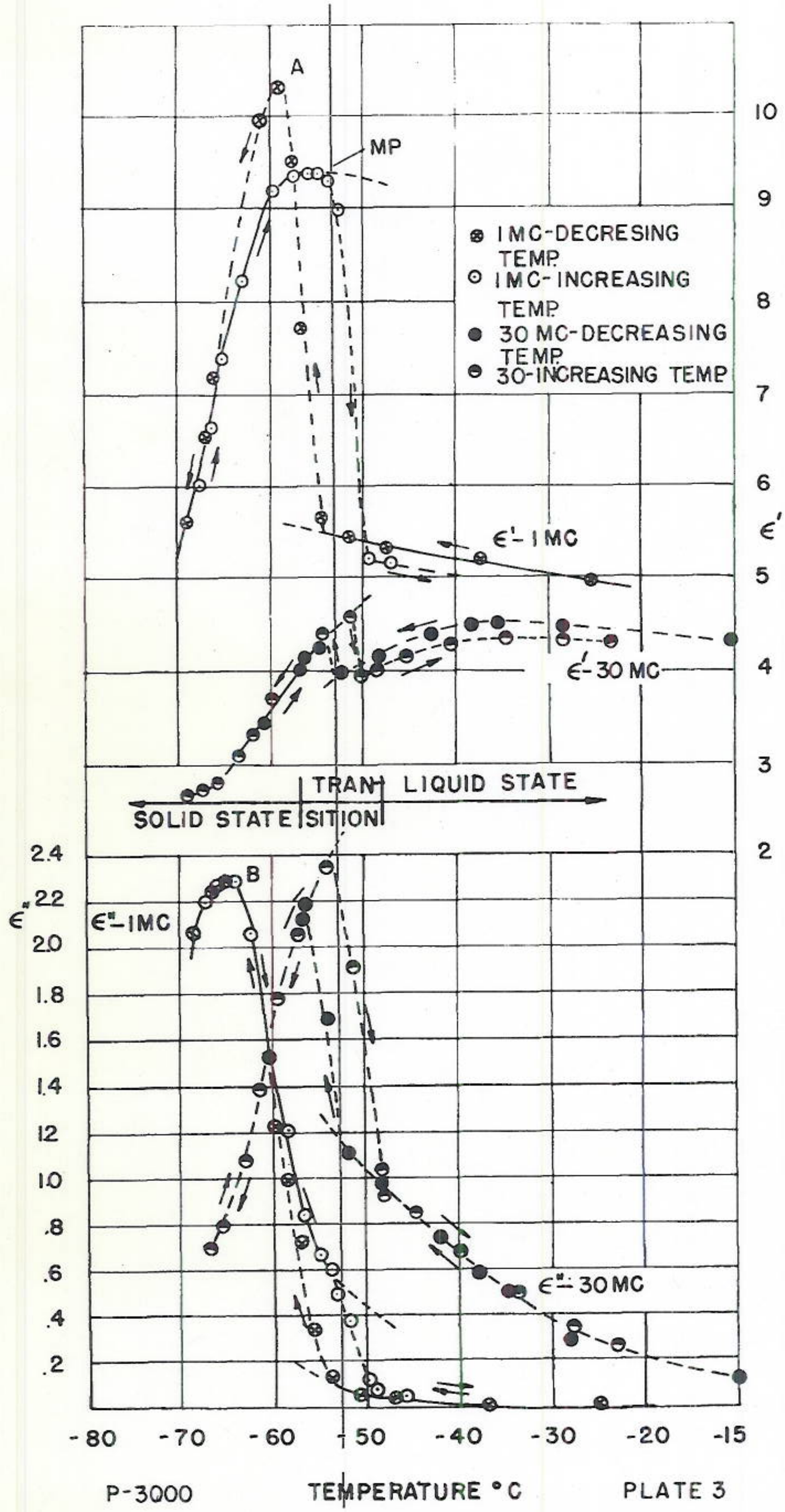
TEMPERATURE °C

PLATE 2

DIELECTRIC CONSTANT AND LOSS FACTOR CURVES FOR
DI-(3-METHYLBUTYL) AZELATE AT 10 MC



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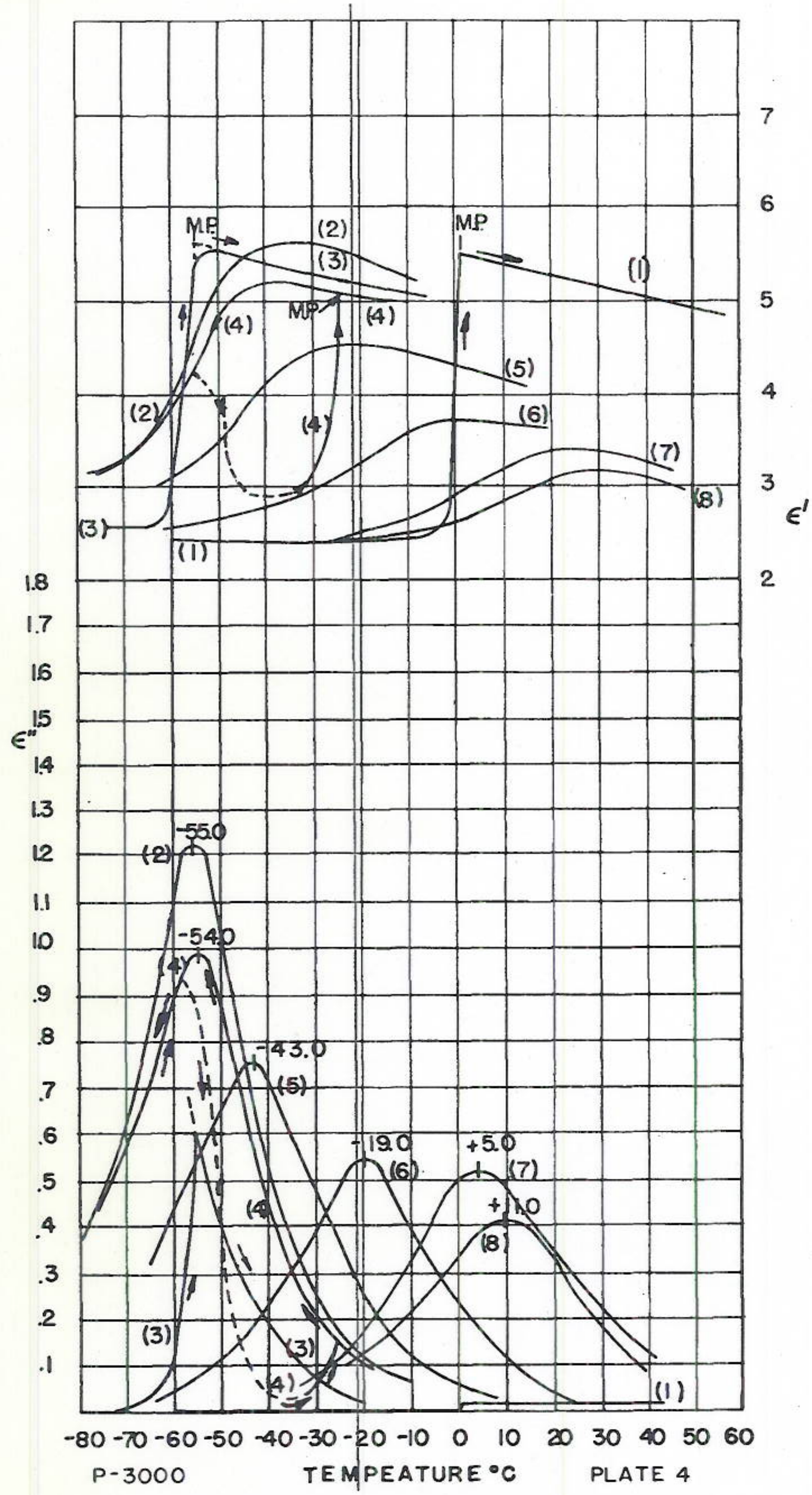
DIELECTRIC CONSTANT AND LOSS FACTOR CURVES FOR DI-(3-METHYBUTYL) AZELATE AT 1 MC AND 30 MC



DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR SOME DIESTERS OF ADIPIC ACID. SEE TABLE I FOR IDENTIFICATIONS

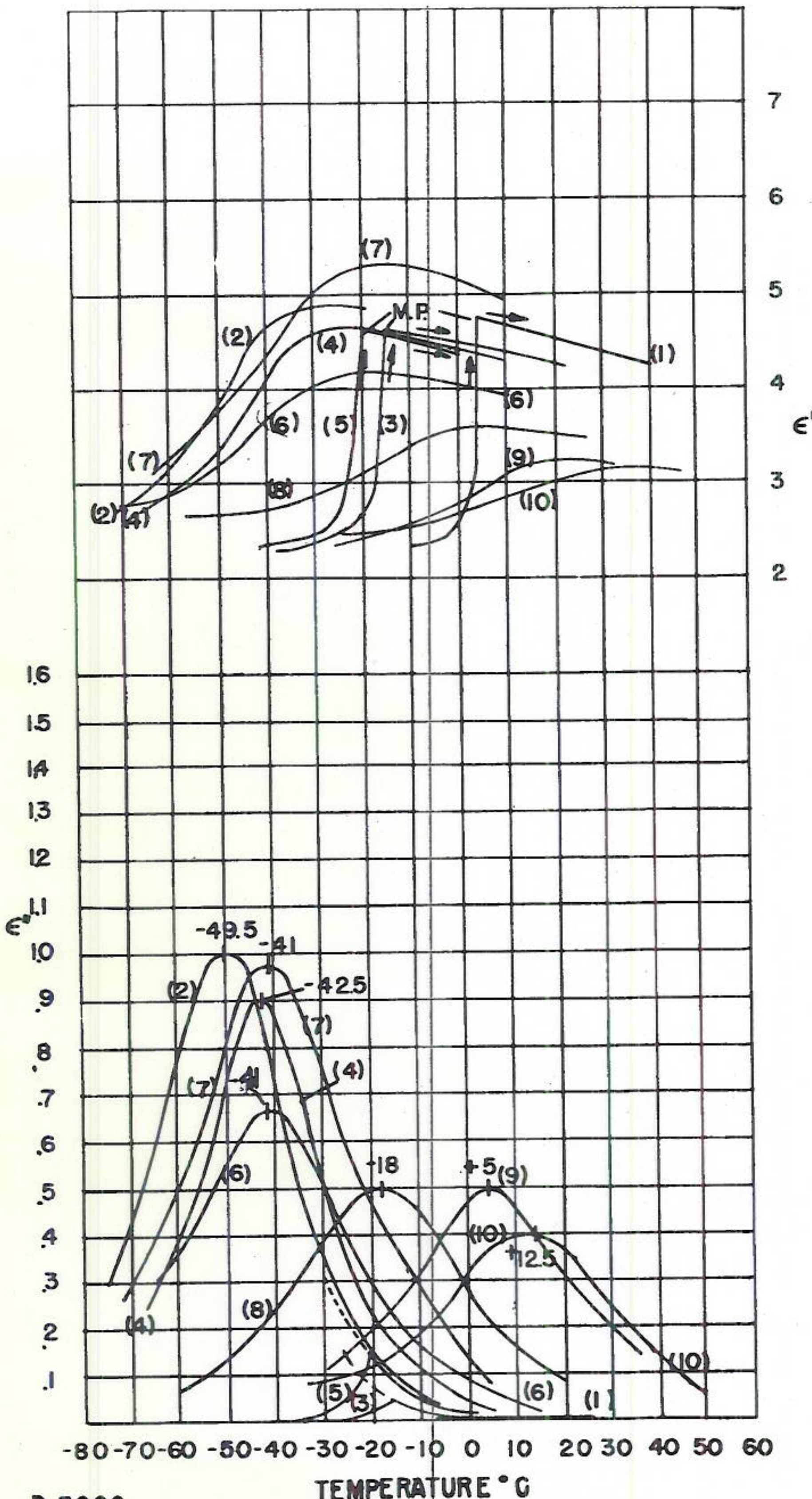


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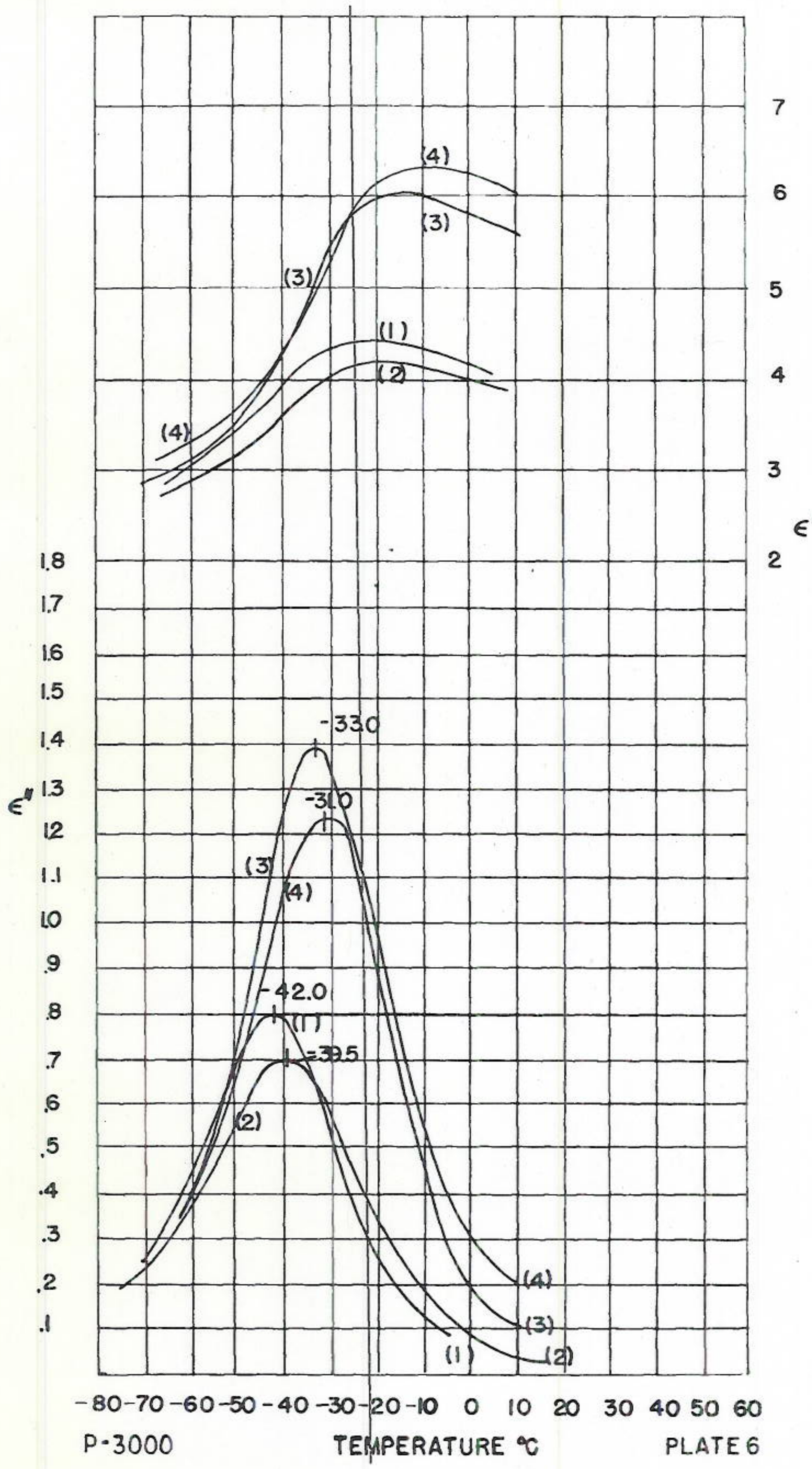
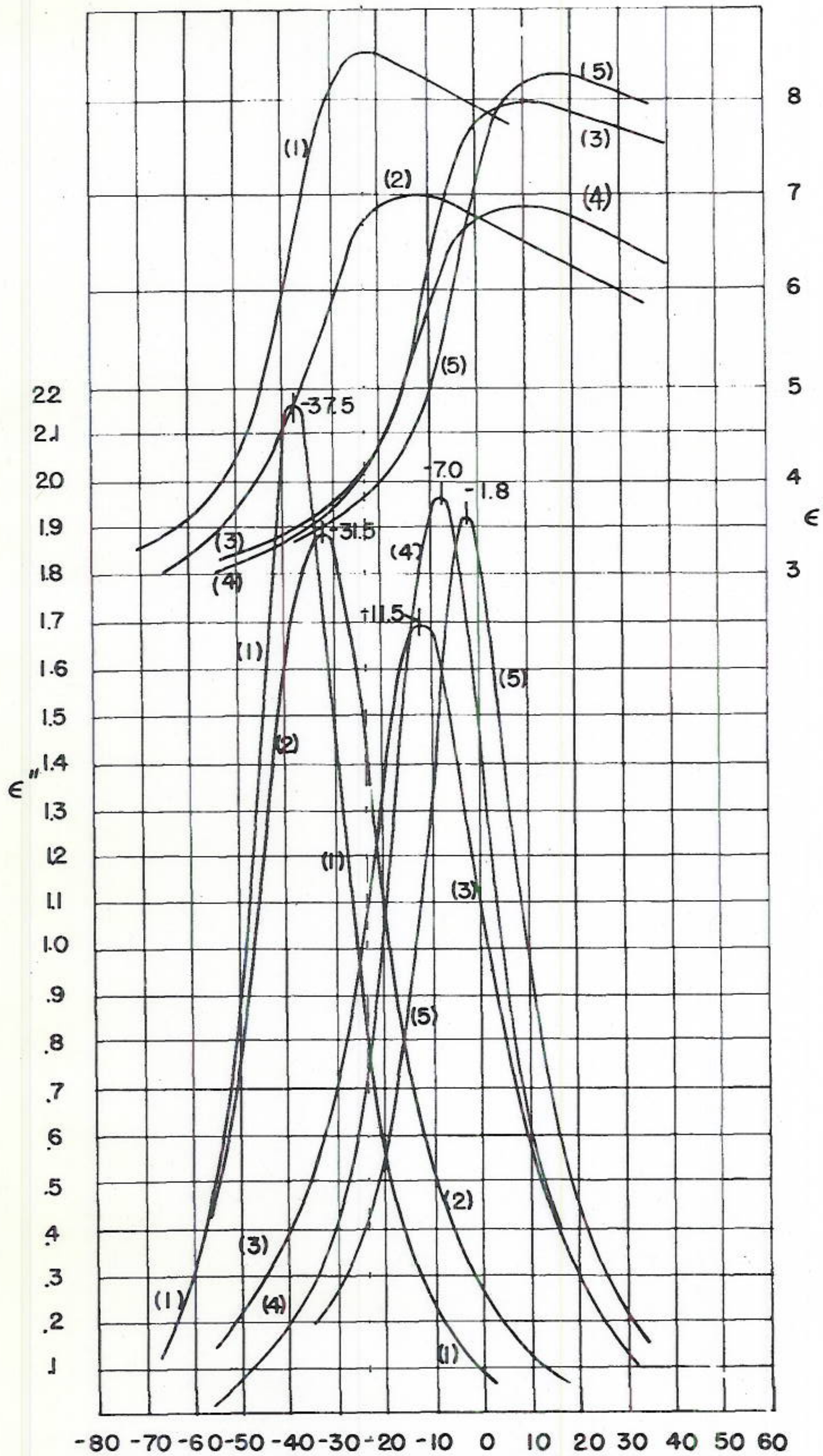
PLATE 5

DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR SOME



DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR SOME ESTERS OF HEXANOIC ACID. SEE TABLE ...



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DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR SOME

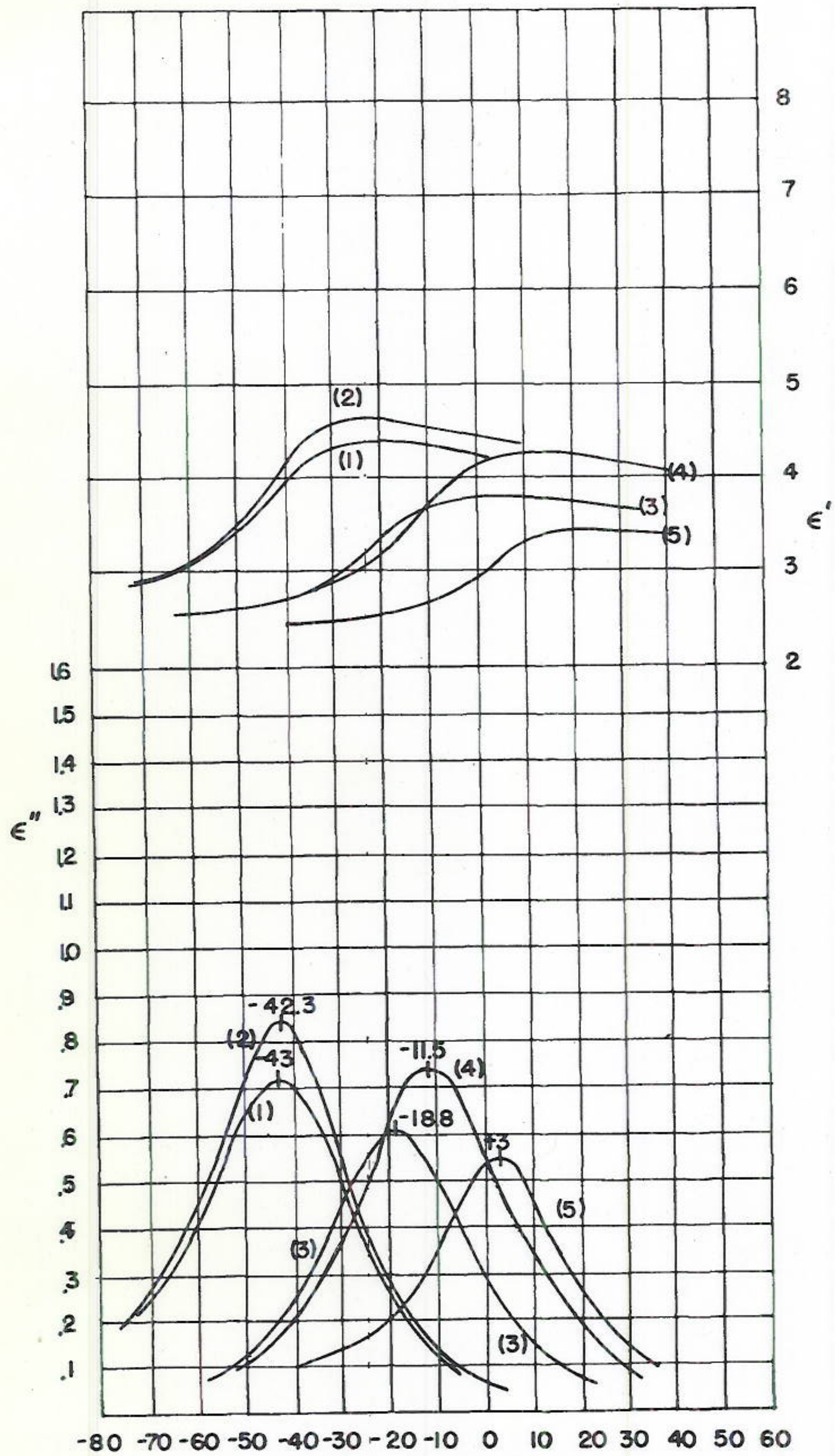

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PLATE 8

DIELECTRIC CONSTANT AND LOSS FACTOR CURVES AT 10 MC FOR SOME RSTERS OF MISCELLANEOUS POLYBASIC ACIDS. SEE TABLE I FOR