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Direct Observation of Time-Temperature-Transformation Curves  
for Crystallization of Ice from Solutions  
by a Homogeneous Mechanism

by  
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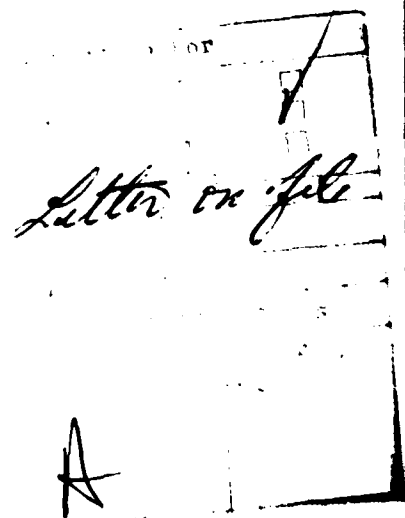
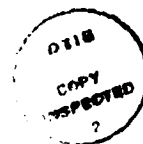
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Emulsified samples of aqueous solutions of lithium chloride have been rapidly cooled to temperatures in the vicinity of the "homogeneous nucleation temperature" $T_g$ and observed isothermally in a differential calorimeter to identify the time delay before the maximum crystallization rate (detected by the release of the heat of crystallization) is achieved. The locus of the time $t_p$ to reach the maximum rate at different temperatures has the classic form of the time-temperature-transformation TTT curve described in theories of homogeneous |                                     |                                                                  |

20. continued

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## TABLE OF CONTENTS

|                            |   |
|----------------------------|---|
| Abstract . . . . .         | 1 |
| Introduction . . . . .     | 1 |
| Experiments. . . . .       | 2 |
| Concluding Remark. . . . . | 5 |
| Acknowledgments. . . . .   | 5 |
| References . . . . .       | 6 |
| Figure Captions. . . . .   | 7 |



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**DIRECT OBSERVATION OF TIME-TEMPERATURE-TRANSFORMATION CURVES  
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BY A HOMOGENEOUS MECHANISM**

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**ABSTRACT**

Emulsified samples of aqueous solutions of lithium chloride have been rapidly cooled to temperatures in the vicinity of the 'homogeneous nucleation temperature'  $T_g$  and observed isothermally in a differential calorimeter to identify the time delay before the maximum crystallization rate (detected by the release of the heat of crystallization) is achieved. The locus of the times  $t_p$  to reach the maximum rate at different temperatures has the classic form of the time-temperature-transformation TTT curve described in theories of homogeneous nucleation and growth. The displacement of this TTT curve to longer times and lower temperatures can be observed by increasing solution concentration. The results correlate well with much longer time observations made recently using electrical conductivity studies of thin bulk samples near their glass transition temperatures.

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The system  $H_2O + LiCl$  has been used in a number of recent investigations as a model system in which the study of the homogeneous nucleation and crystallization phenomenon for ice can conveniently be pursued.<sup>(1-6)</sup> A composition range has been identified in which crystallization of bulk samples occurs with a crystallite density as high as  $2,500 \text{ centers}/\mu m^3$ <sup>(2)</sup>, leaving no doubt that the phenomenon under study is homogeneous in character. In more dilute solutions, in which the nucleation and growth rates are considerably higher, the study of the homogeneous phenomenon can be extended by using emulsion samples to segregate the heterogeneous nucleation sites into a small fraction of the total sample.<sup>(1,7)</sup> Using this technique we have now been able to study the isothermal nucleation process using a differential calorimetry technique to monitor the crystallization through the release of the heat of crystallization and report here the results of this study.

With appropriate choice of composition range for study, the emulsion isothermal calorimetry technique allows us to observe the conditions under which the crystallization rate has a maximum value for a given composition, and to determine the manner in which this maximum rate changes with composition. Essentially we are determining directly, (surprisingly for the first

time, <sup>(8)</sup> the classical time-temperature-transformation (TTT) curve <sup>(9)</sup> for each of a series of solutions of different concentration. These results can in turn be connected with much longer time scale observations about the glass transition temperature recently obtained using a conductimetric technique. <sup>(3)</sup>

## EXPERIMENTS

Solutions of dry LiCl in triply distilled water, in the composition range 8.50-9.89% LiCl were prepared by weighing and confirmed by subsequent vacuum dehydration to constant weight. Samples were emulsified using the surfactant Span 65 (sorbitran tristearate) dissolved in a 1:1 methyl cyclohexane-methyl cyclopentane mixture which is itself noncrystallizing in the temperature range under study. Approximately 20 mg of the emulsion was hermetically sealed in an aluminum DSC pan and introduced to a Perkin-Elmer DSC-2 sample head, held initially at ambient temperature. The sample was then quenched at the maximum rate attainable in the DSC-2 (approximately 140 K/min) to a preselected temperature in the range 150-185 K, and held while its thermal evolution at constant temperature was recorded on a chart.

Typically there is a slow rise with increasing time of the heat evolution per unit time reaching a maximum value at  $t_p$  which is followed by a asymptotic decline. Examples for the case of the composition 9.5% LiCl at a series of temperatures are shown in Fig. 1(a). The values of  $t_p$  are plotted in the same diagram, part (b).

In the temperature range 150-170 K the values of  $t_p$  show a well-defined minimum which is described as the 'nose' of the time-temperature-transformation (TTT) curve. <sup>(9)</sup> At temperatures above 170 K a new phenomenon, to be discussed briefly below, enters. This presumably has to do with the heterogeneous

nucleation and growth phenomenon in these emulsions recently described by Clausse and coworkers.<sup>(10)</sup>

Results for a series of compositions ranging from 8.50-9.89% LiCl are shown in Fig. 2. At the highest concentrations, where the crystallization process is very sluggish, the crystallization peaks are rather poorly defined and considerable uncertainty in fixing the maximum value,  $t_p$ , is encountered. Nevertheless, the trend for the TTT curve to be displaced to longer times, with the 'nose' falling at lower temperatures as concentration of LiCl increases, seems clear enough.

It is interesting to mark on each curve the value of the 'homogeneous nucleation temperature,'  $T_h$  obtained by a continuous cooling experiment and described in recent publications.<sup>(1,5)</sup> This quantity is defined by the relatively sudden release of the heat of crystallization during cooling at a continuous rate in the range 1-40 K/min. The values plotted are for the cooling rate  $10 \text{ K min}^{-1}$ . It appears that with increasing LiCl concentration, the temperature  $T_h$  is displaced continuously to points lower on the TTT curve. This reflects the increasing importance of crystal growth rate as opposed to nucleation per se, in determining the value of  $T_h$  in this higher concentration range.<sup>(5)</sup>

Finally, it is of importance to connect these relatively short time observations with the much longer time scale determinations of homogeneously nucleated crystallization rate reported recently using conductimetric observations on thin bulk samples of these solutions.<sup>(3)</sup> The latter measurements were restricted in composition range to concentrations above 9.3% because of the need to avoid nucleation during quenching in the bulk samples. For purposes of comparison, we adopt the point of inflection in the conductivity-

time curve<sup>(5)</sup> as the point of maximum crystallization velocity, though there is some uncertainty in this assignment because of the possibility of nonlinear conductance-concentration relations in this system near  $T_g$ . Using error bars on the time axis to recognize this uncertainty, we plot the values of  $t_p$  for both DSC and conductivity experiments on the same diagram in Fig. 3.

Finally, we comment on the crystallization curves observed in Fig. 1 at temperatures above 172.5 K. On quenching these samples to  $T < 140$  K and rewarming, a glass transition followed by a sharp crystallization was observed. Samples quenched after  $t_p$  from lower temperature runs show only the glass transition which is itself expected from the glass-forming residual solution of composition ~15% LiCl formed by concentration as the crystallization of ice desaturates the solution with respect to ice. This behavior indicates that for  $T > 172.5$  K only a fraction of the droplets present have been nucleated even at times well beyond the observed peak time. This is consistent with an analysis of the TTT curves<sup>(10)</sup> which indicates that in this temperature regime  $T > 172.5$  K the probability of a single nucleus developing in each droplet is very small, it may be supposed that the phenomenon responsible for the partial crystallization has a heterogeneous origin. This is probably related to the phenomenon which leads, unexpectedly, to the crystallization of pure water in these emulsions in the temperature regime  $-30$  to  $-15^\circ\text{C}$  studied recently by Clausse and Broto.<sup>(10)</sup>

#### CONCLUDING REMARK

Although this phenomenology has been described for the specific case of aqueous solutions of LiCl, there is no reason to believe that the results are atypical of the general case of nucleation of crystals from solution. In subsequent studies we will use low temperature stable emulsions of hydrocarbons

in aqueous dispersant phases<sup>(11)</sup> to show the similarity. Amongst the liquid metal systems, it seems that the Cu + Tc alloys studied in emulsion form by Perepezko and Smith<sup>(12)</sup> have the right range of nucleation and growth rates for successful experiments of this type.

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# **FIGURE CAPTIONS**

**Figure 1(a)** Isothermal crystallization curves for 9.5% LiCl aqueous solution observed by differential calorimetry at different temperatures.

(b) Plot of the time to reach maximum crystallization rate  $t_p$ , as a function of temperature of observation. The curves at temperatures above 175 K correspond to a state of partial crystallization only, and appear to be linked to a heterogeneous nucleation phenomenon the details of which are as yet imperfectly understood.

**Figure 2** Maximum crystallization rate times  $t_p$  vs. temperature of observation for a series of LiCl aqueous solutions of differing composition. Note the position on the TTT curve of the previously determined homogeneous nucleation temperature  $T_h$  (obtained from continuous cooling at fixed scan rate of  $10^\circ\text{min}^{-1}$ ).

**Figure 3** Combination of present DSC-determined maximum crystallization rate times  $t_p$ , with those determined at lower temperatures from isothermal conductimetry studies on bulk samples.

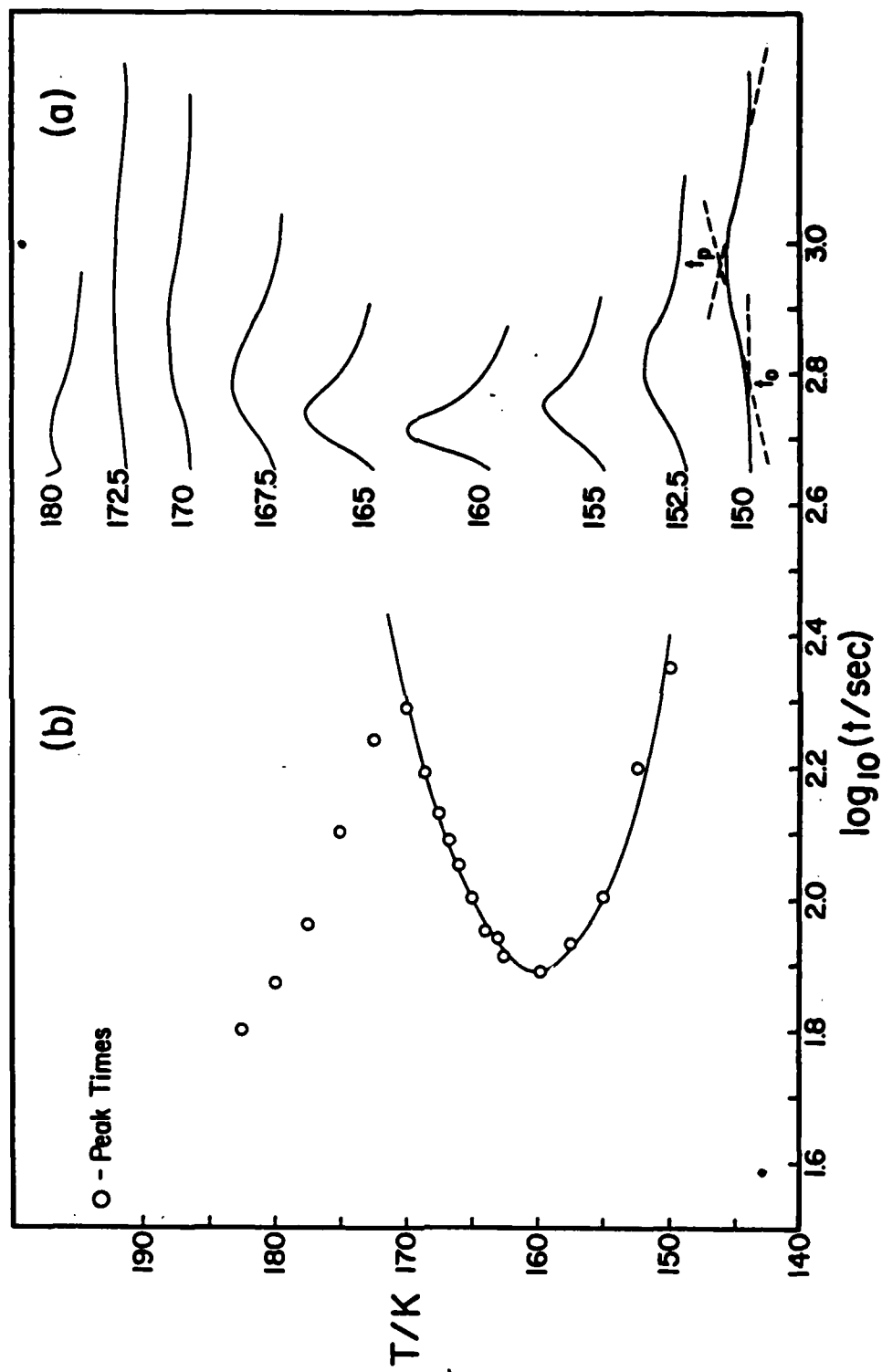


Fig. 1

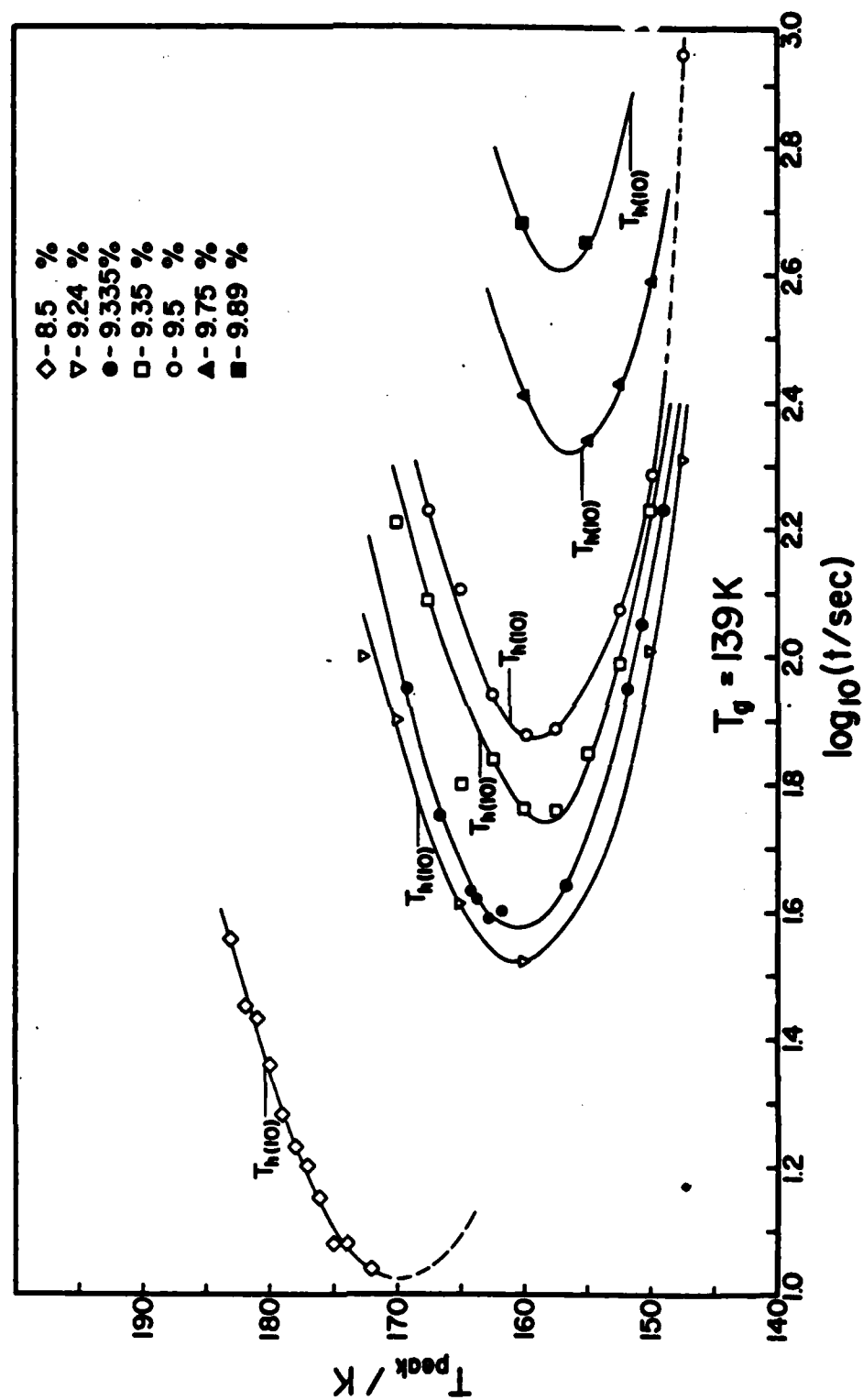


Fig. 2

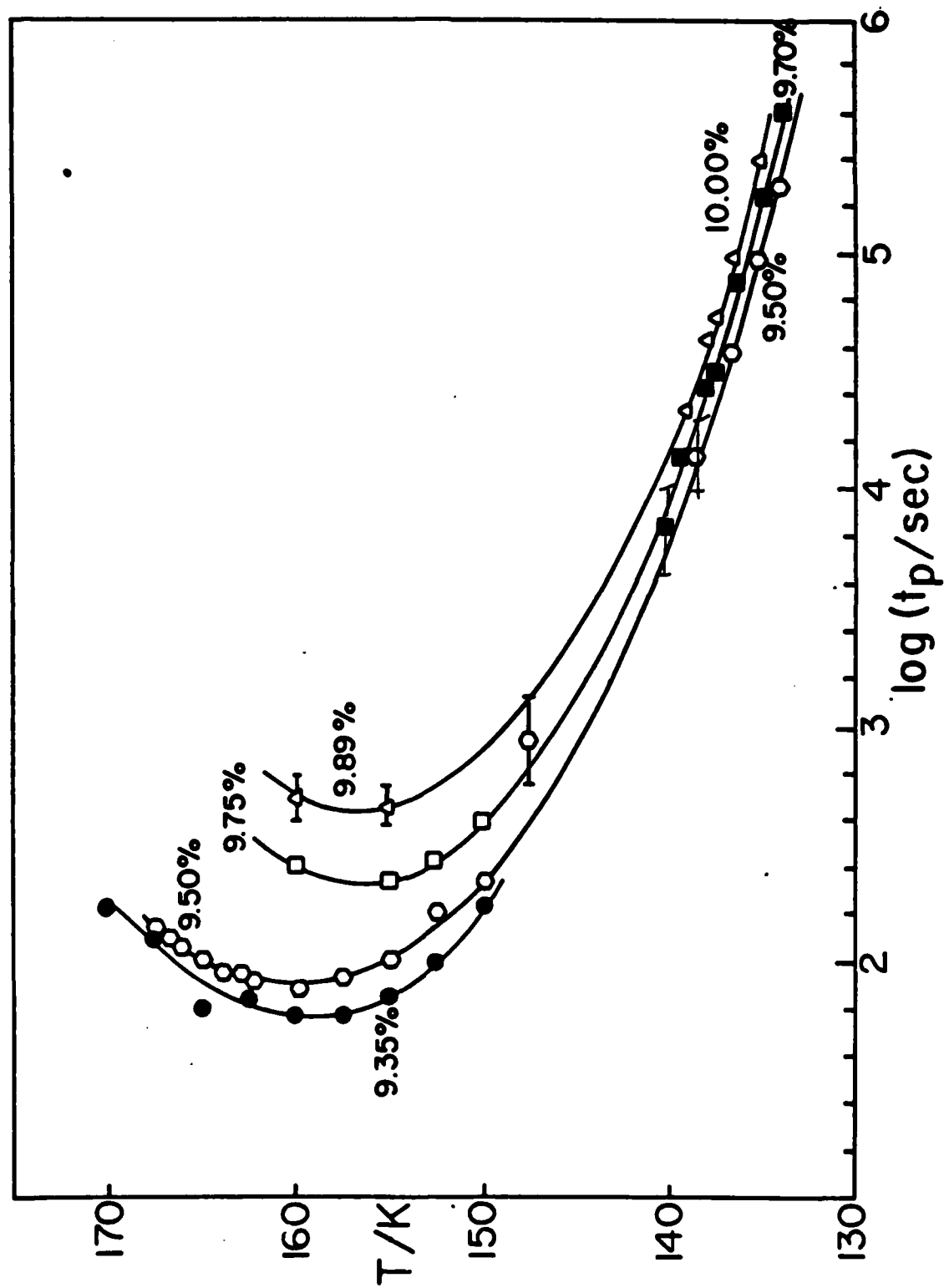


Fig 3