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DIFFERENTIAL SCANNING CALORIMETRY OF
CELLULOSE ACETATES

B. Kokta, et al

State University of New York

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United States Department of the Interior



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DIFFERENTIAL SCANNING CALORIMETRY OF CELLULOSE ACETATE

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17a. Descriptors

*Desalination, *Reverse Osmosis, *Membranes, *Cellulose Acetate, *Heats of Fusion
*Melting Points, *Crystallinity

17b. Identifiers

*Differential Scanning Calorimetry, *Asymmetric Membranes, *Dense Films

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CELLULOSE ACETATE

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Applied Science Division

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UNITED STATES DEPARTMENT OF THE INTERIOR . Rogers C. B. Morton, Secretary
James R. Smith, Assistant Secretary for Water and Power Resources

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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DIFFERENTIAL SCANNING CALORIMETRY OF CELLULOSE ACETATE*

B. Kokta, P. Luner, and R. Suen

SUMMARY AND CONCLUSIONS

The melting temperatures and heats of fusion have been determined for cellulose acetate (2.5) in the form of a powder, dense film, ultra-thin film, and reverse osmosis membrane. The main melting temperatures were in the range of $230^{\circ}\text{C} + 2^{\circ}\text{C}$ although often a secondary peak was located at $217 + 2^{\circ}\text{C}$. Powdered samples showed broad melting peaks with low heats of fusion. Higher heats of fusion and sharper peaks were obtained from films prepared by the "dipping" technique. Varying the sample techniques did not change the values for the heats of fusion. Still higher heats of fusion were obtained when the cellulose acetate (2.5) was cast from acetone. Some increase in the heats of fusion resulted when the latter samples were heat treated at 85°C . The heats of fusion of commercial membranes were independent of the reverse osmosis properties. It is suggested that the rejection layer of Loeb-type membranes has the same degree of crystallinity as the porous substrate.

INTRODUCTION

Reid and Breton showed that cellulose acetate acts as highly selective membrane in the separation of water from salt solutions by reverse osmosis (1). The possibility of using these membranes in larger scale operations was realized when Loeb and Sourirajan (2) introduced suitable casting techniques which resulted in increased flux. Since then, a number of different methods to produce asymmetric membranes have been published (3). Electron microscopy has shown that cellulose acetate Loeb-type membranes have a dense layer approximately 0.25μ thick on the air-dried surface (4), and it has been suggested that it is this "skin" which provides essentially all the resistance to salt and water flow through the membrane (5). Recently Riley et al. (6) have prepared ultra-thin cellulose acetate films on porous supports which in reverse osmosis gave close to the theoretical salt rejections calculated from the solution diffusion model of membrane transport.

While considerable data have accumulated regarding the transport behavior of these membranes, as well as the physical and chemical variables effecting their preparation, the problem regarding their crystallinity remains largely unknown. The question of crystallinity in "modified" cellulose acetate membranes has been considered by Kesting et al. (7) who postulated that the

*Advances in Chemistry Series, American Chemical Society, Applied Polymer Symposia 13, 169-179 (1970).

active layer consists of a large number of small crystallites. However, Lonsdale (8) is doubtful of the presence of highly ordered regions, since the transport properties are not altered under conditions of membrane preparation which would be expected to affect the crystallinity. X-ray diffraction spectra of the cellulose acetate membranes showed that the latter had poor local order while thin films had only a somewhat more ordered structure (7). Deuteration experiments have also been unsuccessful in resolving the question of crystallinity of the membranes (7).

Differential scanning calorimetry (DSC) offers a convenient way to locate transitions and measure the heats of fusion of polymers (9-11). This technique has now been applied to cellulose acetate films and membranes prepared under a number of different conditions, in an attempt to establish possible relationships between the method of sample preparation and the melting behavior of the sample.

EXPERIMENTAL

Materials

The following three samples of cellulose acetate were obtained from Eastman Organic Chemicals, Distillation Products Industries: (1) acetyl content 39.4%, ASTM viscosity 45; (2) acetyl content 39.8%, ASTM viscosity 3; (3) acetyl content 40.0%, ASTM viscosity 25. Another sample, cellulose acetate E 398-3 and commercial membranes HT-00, MF-10, RO-89, and RO-97, were obtained from Eastman Chemical Products, Inc., Tenn. The solvents used were all reagent grade.

Sample Preparation

The samples were used in the form of pressed powder, dense film, asymmetric membrane and "dipped" films. The dense films were prepared by casting automatically or manually using a Gardner knife. The membrane fabrication procedure can be briefly described as follows (3). Cellulose acetate was dissolved in a mixture of acetone and formamide. Membranes were cast on glass plates, evaporated for a predetermined time and then immersed in distilled water at 0-3°C. The thin "dipped" films were prepared as follows (6). The cleaned and conditioned glass slides were dipped into the polymer solution (E 398-3 in acetone) manually, equilibrated for 20 min in the solution and then withdrawn at a rate of 30 cm/min. The polymer films were dried for 2 hr in air at ambient temperature. The polymer films were recovered by floating them off into water. The film thickness was either measured with a precision gauge or calculated by weighing a dried rectangular section 2 x 4 cm, and using a bulk density of 1.3 g/cm³.

Procedure

The samples were studied by means of a Perkin-Elmer scanning calorimeter, model DSC-1B. Standard pans were used and the scanning speed was usually 10 or 20°C/min with a sensitivity range of 1-8 mcal/sec, full scale. Dried helium or nitrogen was used as the inert carrier.

RESULTS AND DISCUSSION

Calorimetric Characteristics of Cellulose Acetates

Powder. Secondary cellulose esters show very diffuse x-ray patterns indicating a low ordered crystalline structure. In addition, these derivatives are not readily crystallizable. The main objective of this study is to show how the sample history affects the melting characteristics of secondary cellulose acetate.

Figure 1 shows the thermal behavior of cellulose acetate E-398-3 in powder form. Rather broad melting peaks with maxima at 232°C, with heats of fusion of 0.4 ± 0.2 cal/g, are characteristic for the powdered samples. Often a second peak at 213°C (Fig. 1C) is observed. No pronounced difference in the melting behavior was observed when the powdered sample was heat treated in water at 85°C for 60 min. Thermal values for a number of cellulose acetate powders are summarized in Table I. It is quite evident from these results that the heats of fusion of the powders is low with values near 0.6 ± 0.2 cal/g, except for the CA 39.4% Vis 45, which has a heat of fusion of 1.3 cal/g. A higher degree of crystallinity for this sample is apparent from the sharper melting peak. The maximum melting temperature was $235 \pm 2^\circ\text{C}$ for all the samples except E-398-3 which gave a maximum melting temperature of $232 \pm 2^\circ\text{C}$.

TABLE I

Heats of Fusion and Maximum Melting
Temperatures of Cellulose Acetate Powders

Sample	ΔH (cal/g)	Peak melting temperatures ($^\circ\text{C}$)
Eastman CA 39.4% - Vis 45	1.3	236
Eastman CA 40.0% - Vis 25	0.2	234
Celanese Sec. CA	0.8	237
Du Pont CA - 39.8%	0.8	235
Du Pont CA - 37.7%	0.8	237
Eastman CA E-398-3	0.6	232

Ultra-thin films. Since ultra-thin films of cellulose acetate have transport properties similar to the rejection layer in a Loeb-type membrane (6), their melting behavior was investigated. Figure 2 shows several typical calorimetric curves for these "dipped" films. The maximum melting peak at $229 \pm 2^\circ\text{C}$ are very similar to the powdered samples. The heats of fusion are 1.2 cal/g for the thin films, independent of sample thickness (0.6-4.5 μ).

Dense films. Two different means of film casting were followed. One method involved the motorized movement of a glass plate under a coating blade, while another consisted of the conventional use of a Gardner coating knife. The melting curves in Figure 3 for films obtained by automatic casting all showed sharper melting peaks than those obtained with powders or dipped films. A second peak is also observed at $217 \pm 2^\circ\text{C}$. The heats of fusion for these samples were 2 ± 0.5 cal/g. The intensity of the peak at 217°C is much greater than that observed for the powdered samples (Fig. 1C) as well as for the dipped films (Fig. 2). Heat treating these films (Fig. 4) in water for 60 min at 85°C increased the heat of fusion to 2.6 ± 0.5 cal/g but did not alter the peak melting temperature.

The thermal behavior of cellulose acetate (E-398-3), film cast manually from acetone is seen in Figs. 5 and 6. Fig. 5A shows three melting peaks, at 201, 214, and 228.5°C , the latter temperature being the most reproducible. The heat of fusion of $2.4 \pm$ cal/g was slightly higher than that obtained by automatic casting. Heat treatment in water of these films resulted in an increase in the heat of fusion to 2.9 ± 0.5 cal/g with only small changes in the peak melting temperatures (Fig. 6). Attempts to trace which casting variables were responsible for the increase in crystallinity were not successful and these are unknown at this time. However, it can be concluded that the casting technique could induce crystallization as a result of orientation. This conclusion is consistent with experiments which showed that when these films were exposed to acetone vapors, subsequent heats of fusion were lower.

The melting temperature of $229 \pm 2^\circ\text{C}$ for E 398-3 is in good agreement with the values given by Boy et al. (12) for cellulose acetate with comparable acetyl content. The magnitude of the heat of fusion for E 398-3 (1-3 cal/g) is in the range of values given for cellulose trinitrate ($\Delta H = 3-5$ cal/g), cellulose tributyrate ($\Delta H = 8$ cal/g), and cellulose tricaprilate ($\Delta H = 5.2$ cal/g) (13).

Asymmetric membranes. Manjikian (3) showed that membranes cast at room temperature from the ternary system, cellulose acetate-acetone-formamide, produced membranes with good flux rates and salt rejection. The performance of these membranes depends on the coating solution composition, evaporation period after casting, and curing temperature. These facts raise the question whether and how the conditions of sample preparation influence sample crystallinity.

Figure 7A-C shows the calorimetric curves for laboratory cast, unannealed membranes and Fig. 7D curves for membranes annealed by heating in water at 85°C for 60 min. The maximum melting temperature was 229°C for both samples, while the heats of fusion of the heat treated sample increased only slightly. Variation in casting composition and drying time prior to water immersion did not have any significant influence on the peak melting temperature or the heat of fusion.

Calorimetric curves for commercial membranes with very low salt rejection (HT-00) and a 97% salt rejection (RO-97) are shown in Figs. 8 and 9 and the results summarized in Table II. The melting temperatures of all these samples are in the 230°C range. A second melting temperature was observed at 217°C for all the samples except the RO-97 membrane. The heats of fusion were ~1 cal/g, irrespective of reverse osmosis properties, with only slightly higher values after the samples had been heated in water (85°C, 1 hr).

Table II

Calorimetric Characteristics of Commercial Membranes

Sample	Treatment	Heat of fusion [ΔH (cal/g)]	Peak melting temperatures (°C)
HT-00	None	1.2 \pm 0.3	230 \pm 1°C 204, 217
HT-00	85°C, Water, 60 min	1.3 \pm 0.1	230 \pm 1°C 219 \pm 2°C
UF-10	None	0.5 \pm 0.1	228 \pm 2°C
UF-10	85°C, Water, 60 min	1.2 \pm 0.3	230 \pm 1°C 218
RO-89	None	1.1 \pm 0.1	228 \pm 2°C 217
RO-89	85°C, Water, 60 min	1.6 \pm 0.5	230 \pm 3°C
RO-97	None	0.7 \pm 0.2	229 \pm 2°C
RO-97	85°C, Water, 60 min	1.8 \pm 0.6	230 \pm 2°C
E-398-3 ^a	None	1.3 \pm 0.2	229 \pm 2°C
E-398-3 ^a	85°C, Water, 60 min	1.7 \pm 0.5	229 \pm 2°C

^aLaboratory cast from 25% CA, 20% formamide, and 55% acetone.

Concluding remarks. Among the noteworthy features of the melting behavior of the cellulose acetate samples studied here are the multiple melting peaks observed. This behavior has previously been noted in the DTA work of Boy et al. (12) who suggested that these multiple peaks are a result of the melting of molecular regions differing in the degree of substitution, since a similar melting behavior was observed with mixed acetate derivatives. As the multiple melting peaks become more pronounced when

the samples are cast from a good solvent, i.e., acetone, the peaks may also be a result of the melting of crystallites of different sizes. It is clear that further work with well fractionated and characterized samples is necessary to resolve this question.

The heats of fusion of cellulose acetate "dipped" films and dense films were not very different, even when the sample thickness was varied. In addition, membranes over a large range of salt rejection values showed no appreciable differences in their heats of fusion. From these results, it seems clear that the thin rejection layers of Loeb-type membranes do not differ significantly in crystallinity from the porous substrate. However, the rejection layer may still show a difference in organization from that of the substrate, a difference not affecting the heats of fusion.

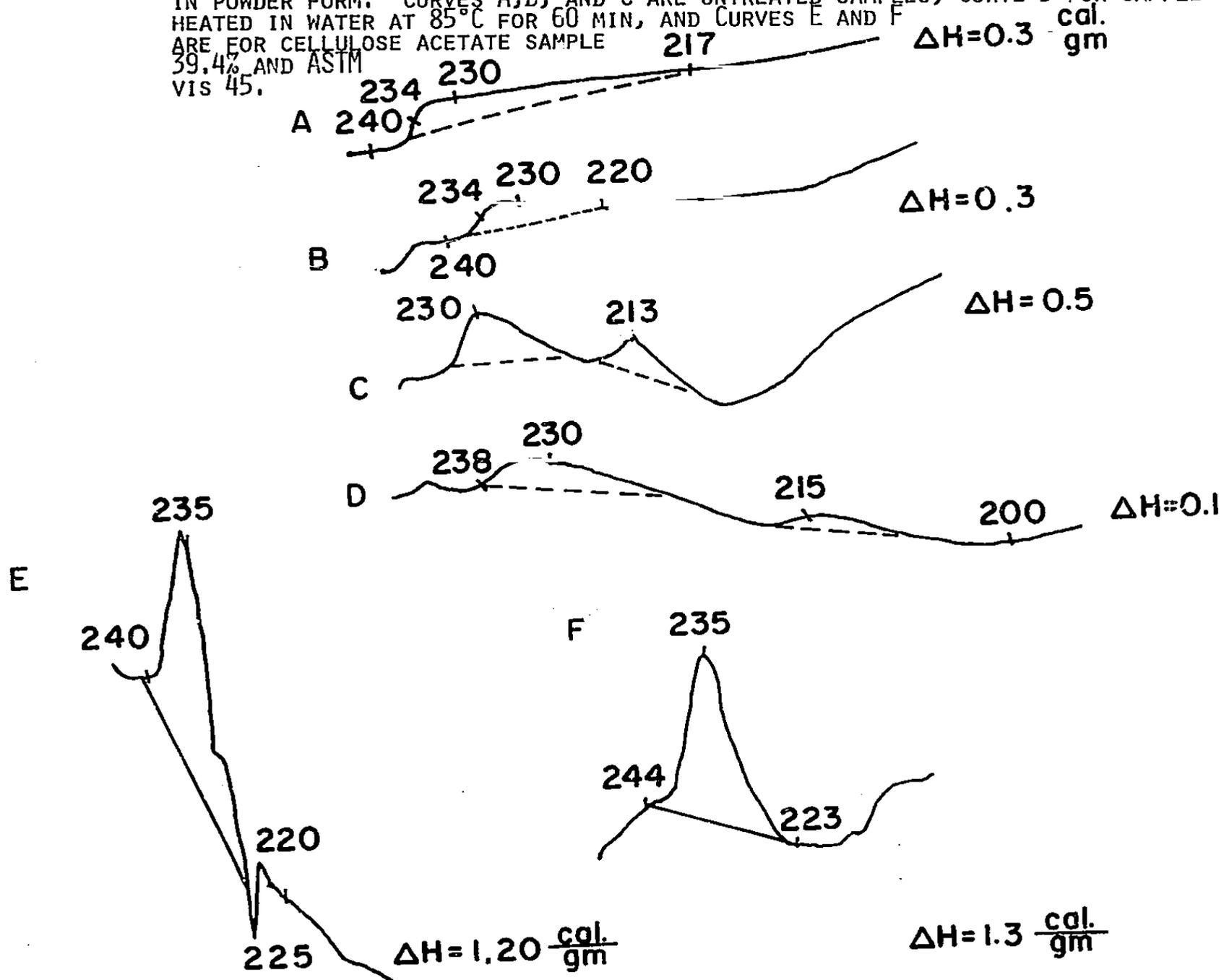
To convert the values for heats of fusion to "crystallinity," a heat of fusion value for the repeating unit is necessary. If the heat of fusion of cellulose octaacetate is used, then the cellulose acetate films can be calculated to be 10% crystalline (14). This value is much too low to be detected using x-ray methods.

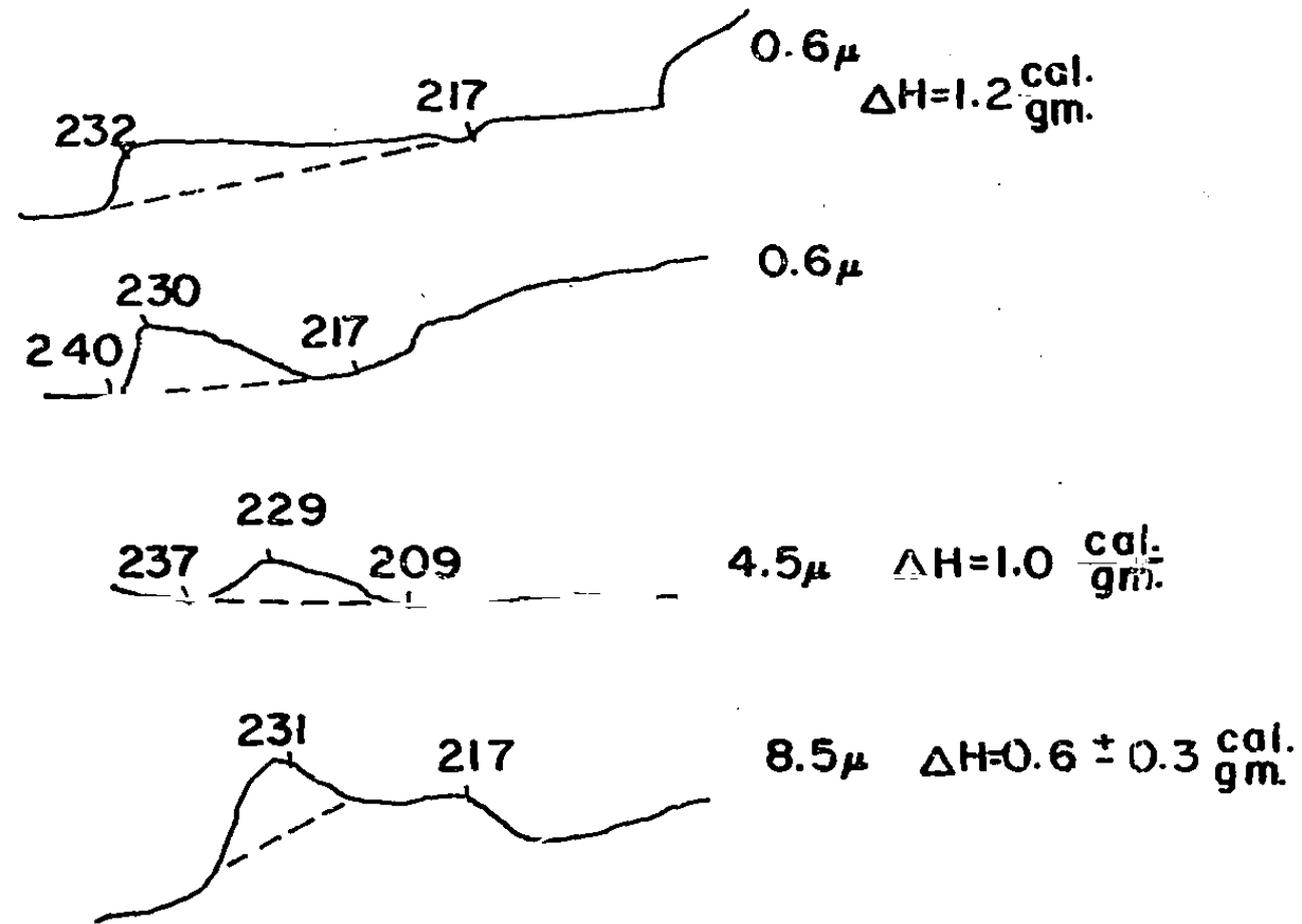
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FIG. 1. DIFFERENTIAL SCANNING CALORIMETRY (DSC) CURVES FOR CELLULOSE ACETATE E-398-3 IN POWDER FORM. CURVES A, B, AND C ARE UNTREATED SAMPLES, CURVE D FOR SAMPLE HEATED IN WATER AT 85°C FOR 60 MIN, AND CURVES E AND F ARE FOR CELLULOSE ACETATE SAMPLE 39.4% AND ASTM VIS 45.





6

FIG. 2. DSC CURVES FOR "DIPPED" FILM OF VARYING THICKNESS MADE FROM CELLULOSE ACETATE E-398-3.

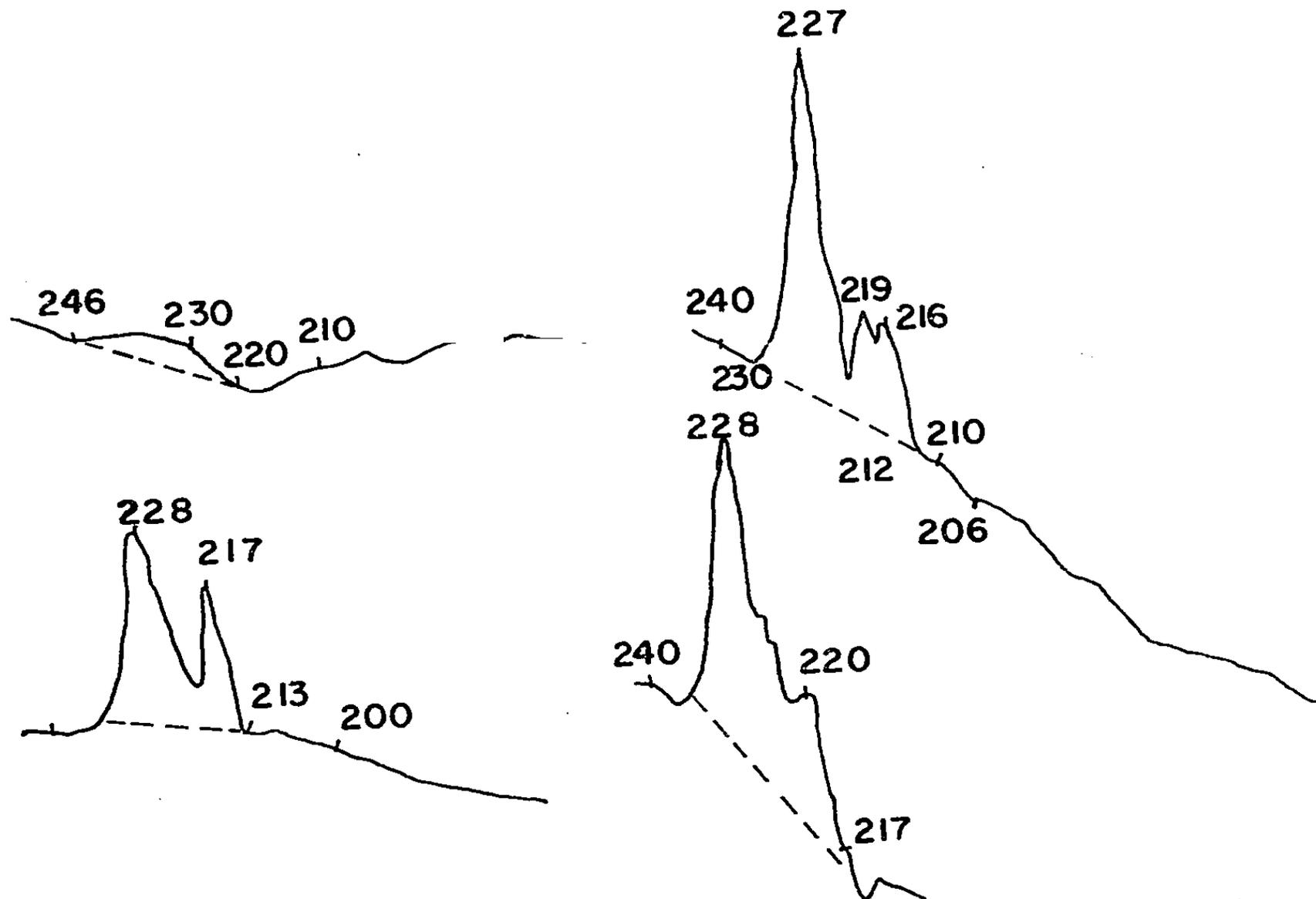
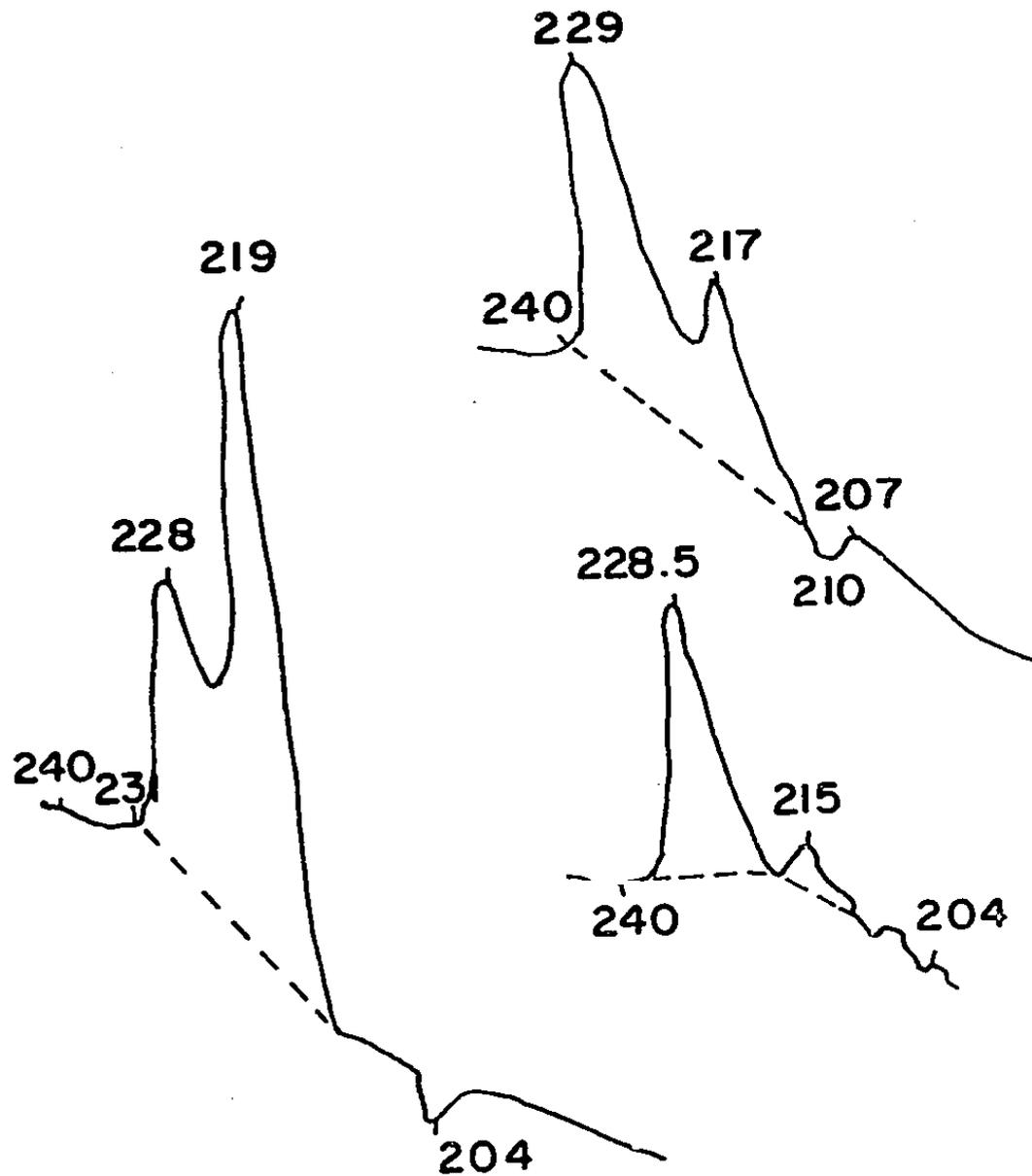


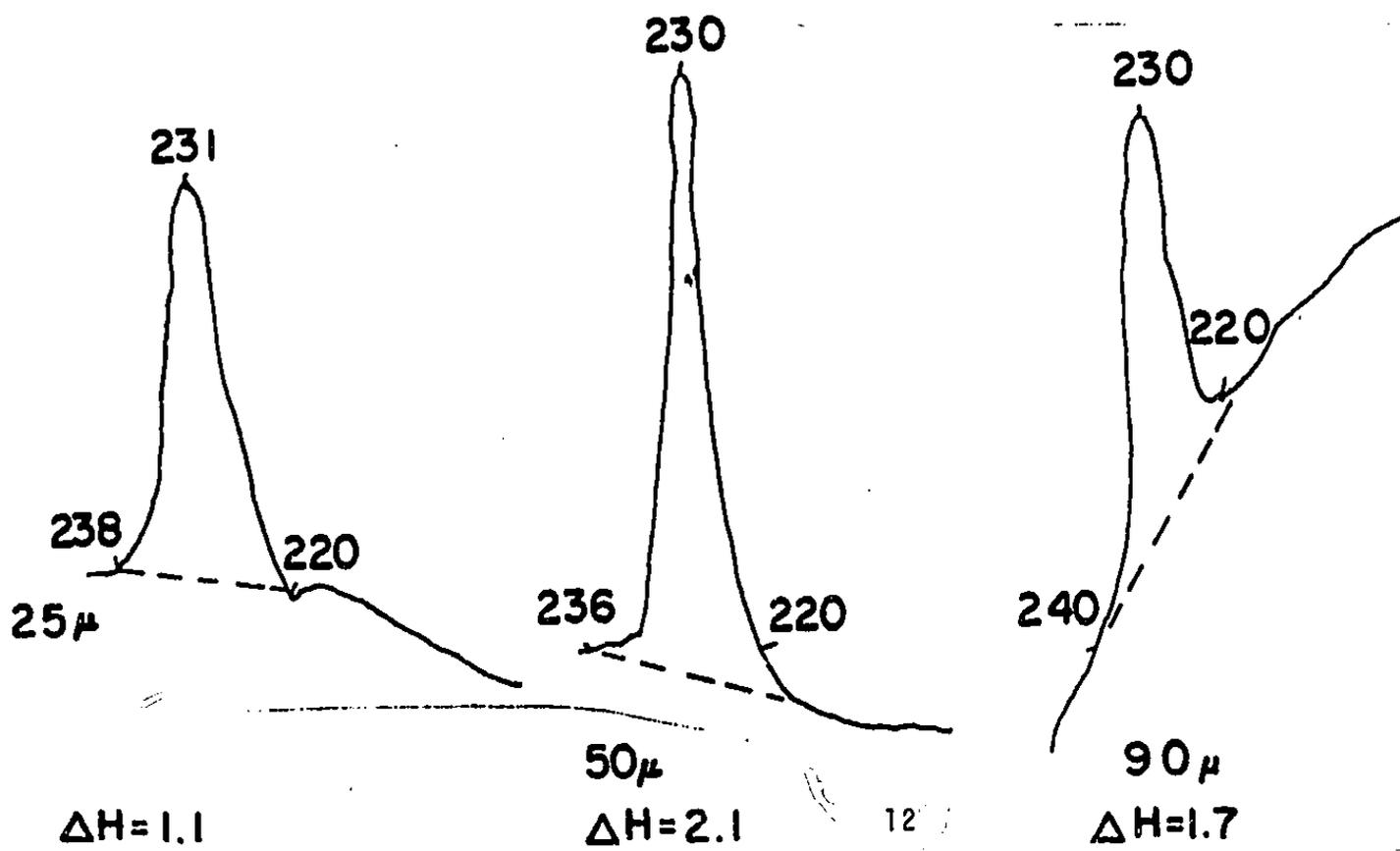
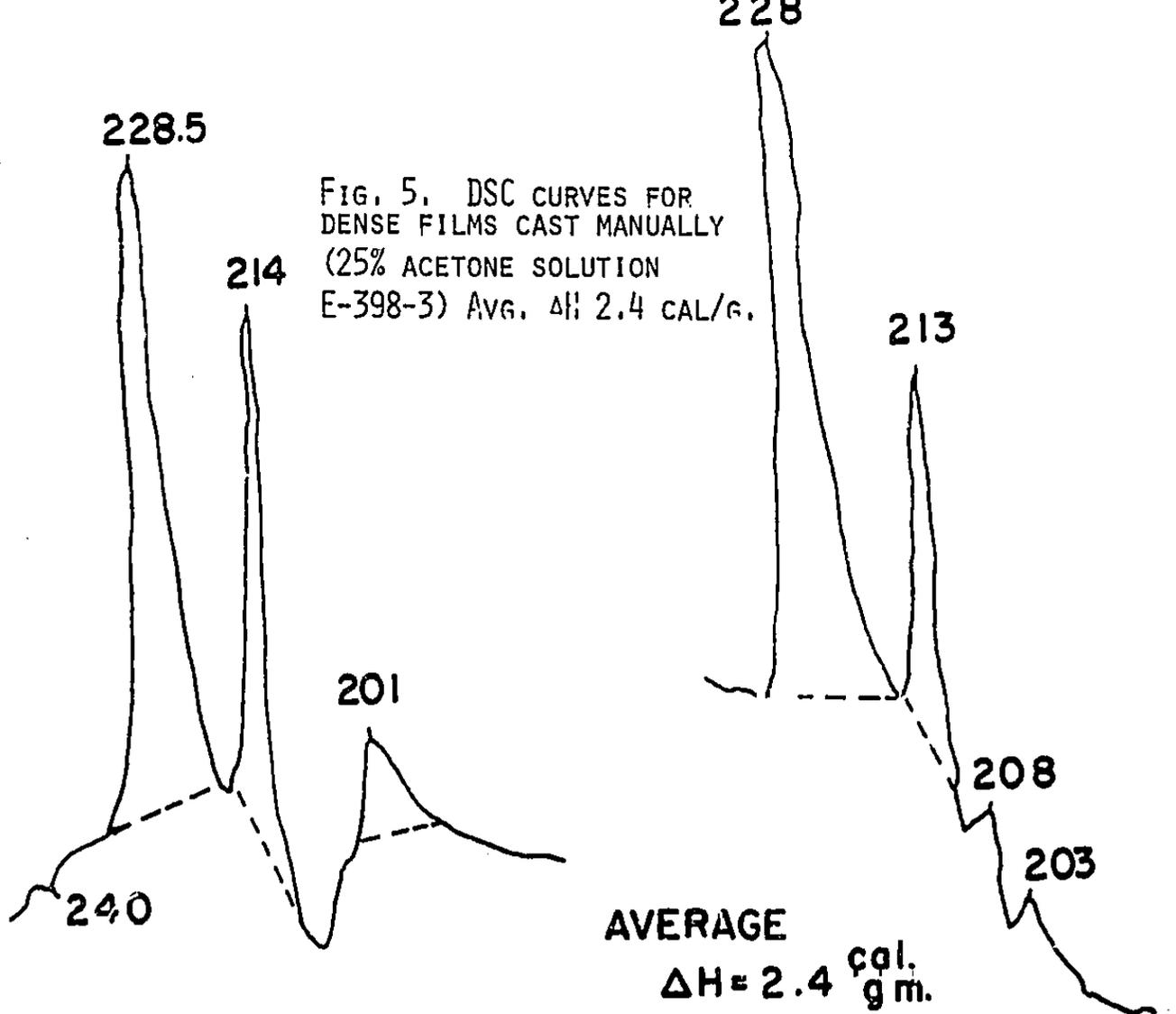
FIG. 3. DSC CURVES FOR AUTOMATICALLY CAST DENSE FILMS (25% ACETONE SOLUTION E-398-3).

AVERAGE $\Delta H = 2.0 \frac{\text{cal.}}{\text{gm.}}$



AVERAGE $\Delta H = 2.6 \frac{\text{cal.}}{\text{gm.}}$

FIG. 4. SAME AS FIG. 3 EXCEPT SAMPLES WERE HEATED IN WATER AT 85°C FOR 60 MIN.



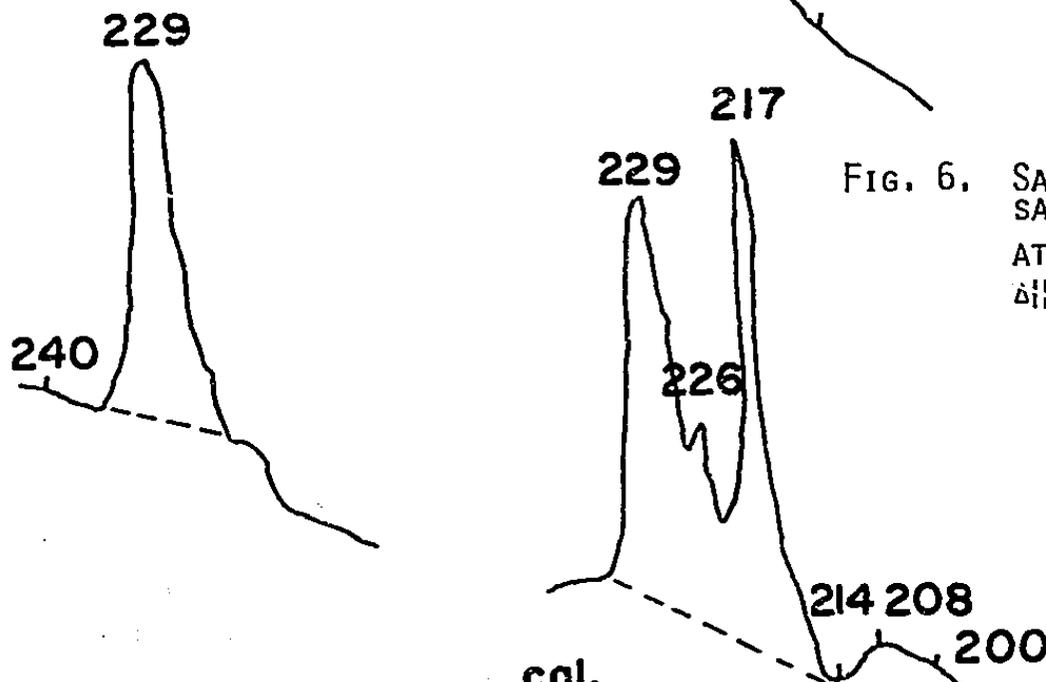
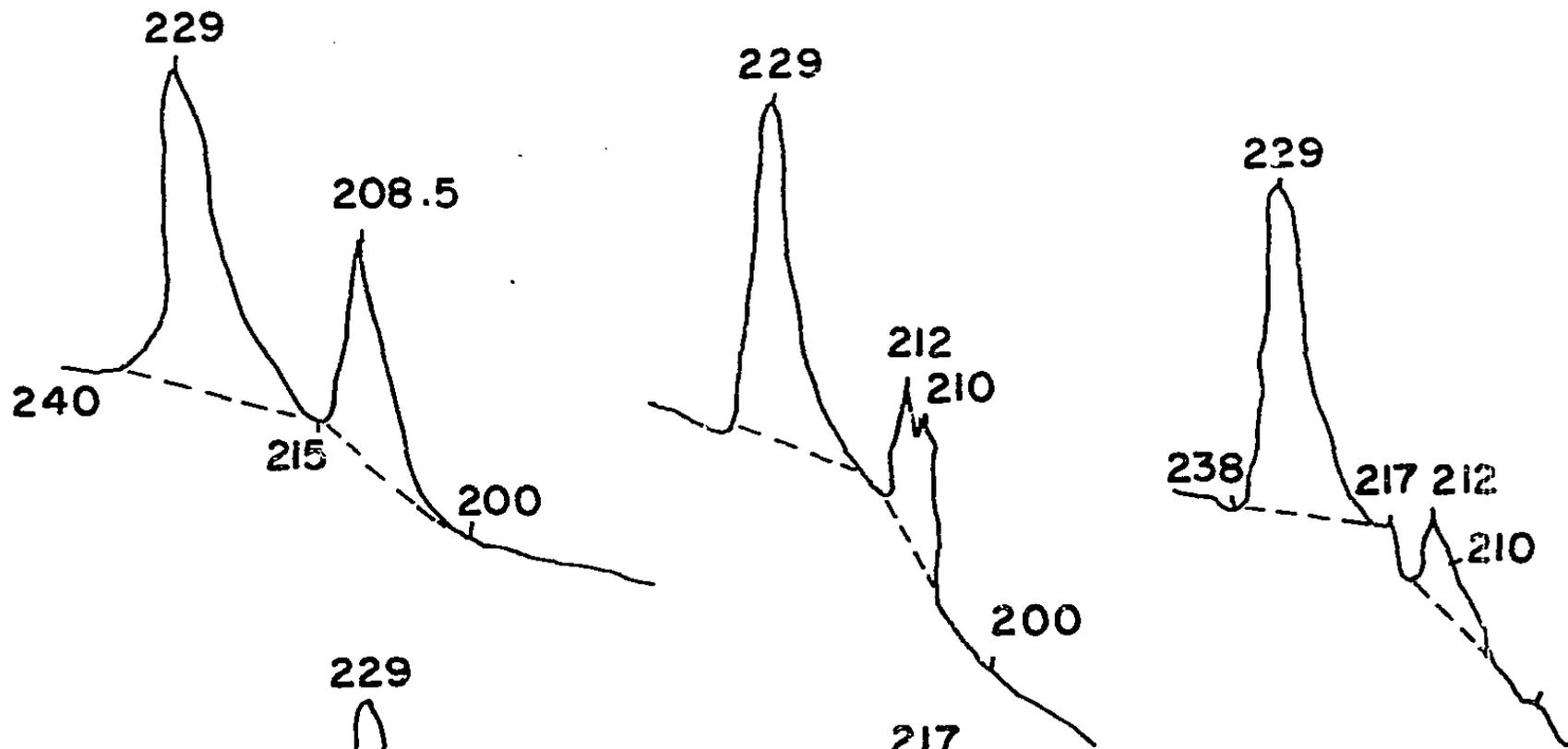


FIG. 6. SAME AS IN FIG. 5 EXCEPT SAMPLES WERE HEATED IN WATER AT 85°C FOR 60 MIN. AVG. $\Delta H = 2.9$ CAL/G.

AVERAGE $\Delta H = 2.9$ cal. gm.

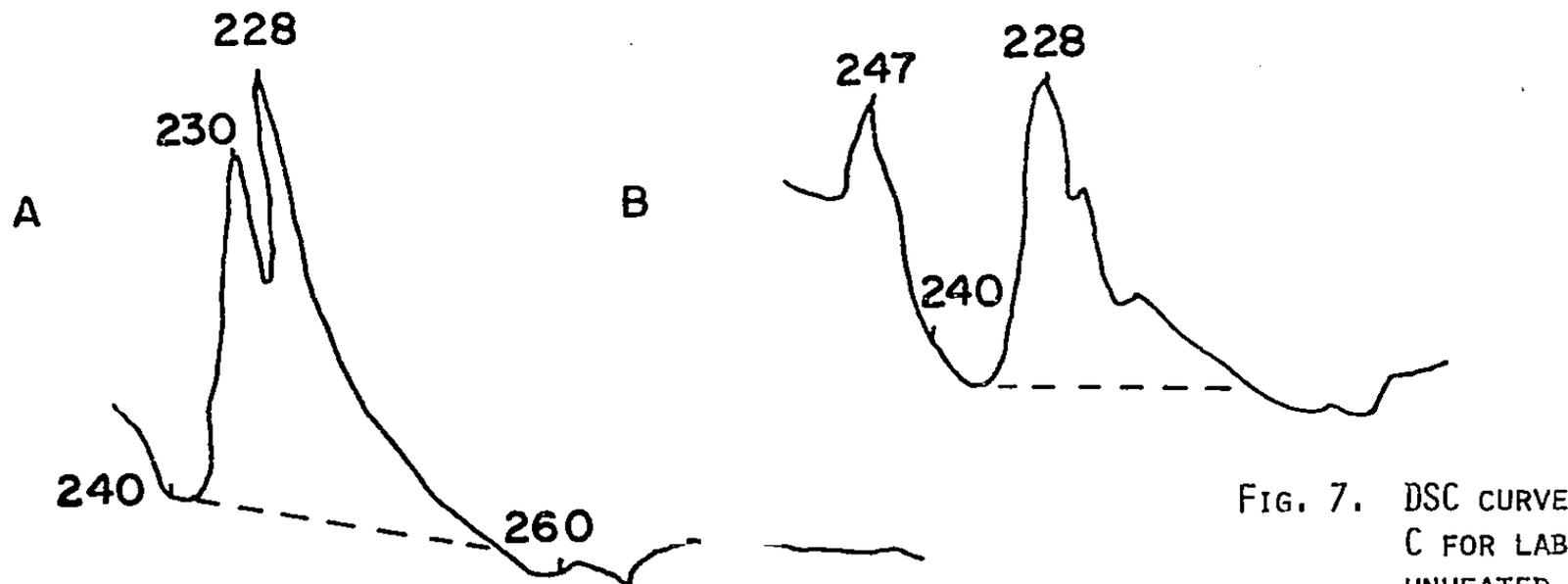
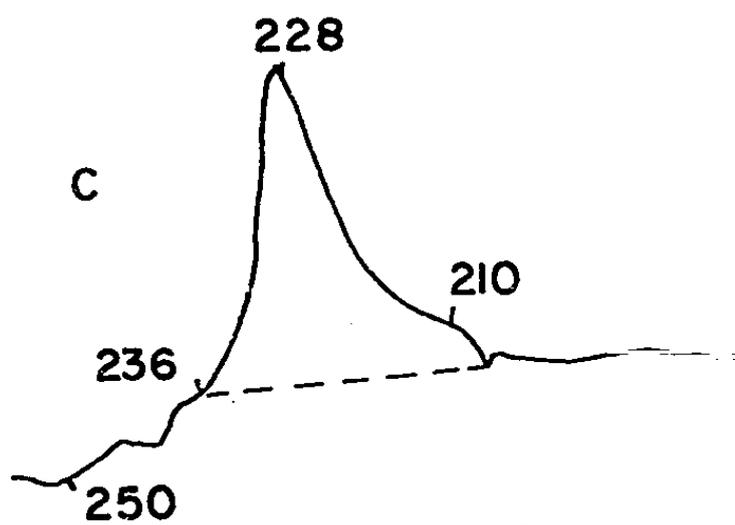
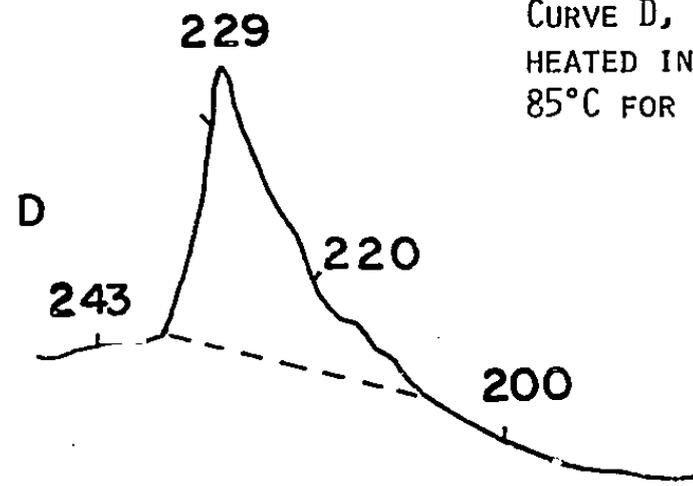


FIG. 7. DSC CURVES A, B, AND C FOR LABORATORY CAST UNHEATED MEMBRANES AND CURVE D, MEMBRANES HEATED IN WATER AT 85°C FOR 60 MIN.

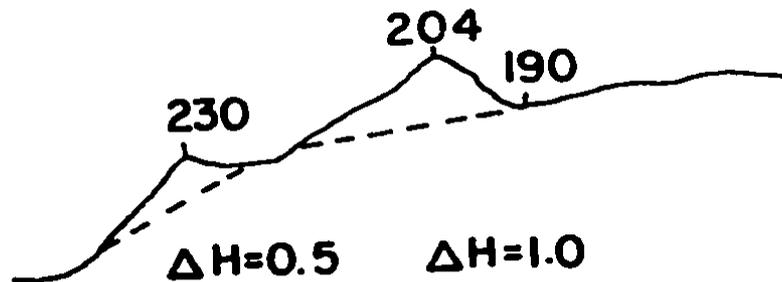
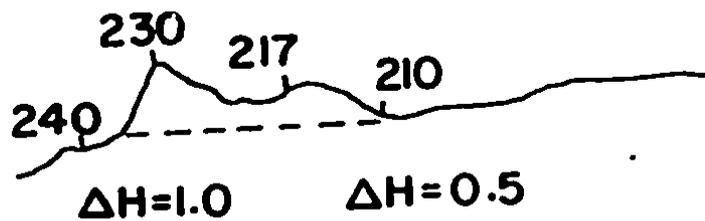
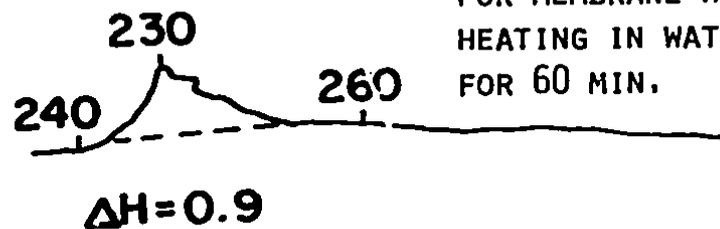
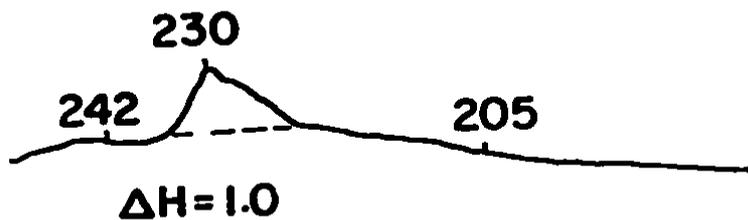


AVERAGE $\Delta H = 1.3 \frac{\text{cal.}}{\text{gm.}}$



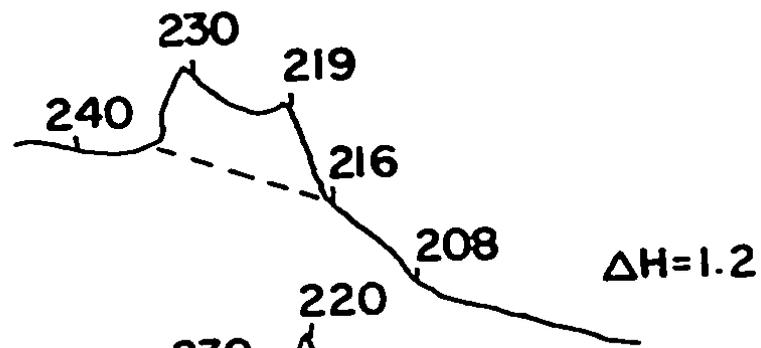
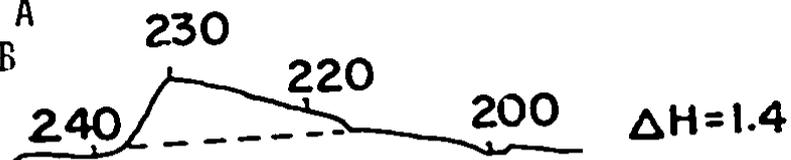
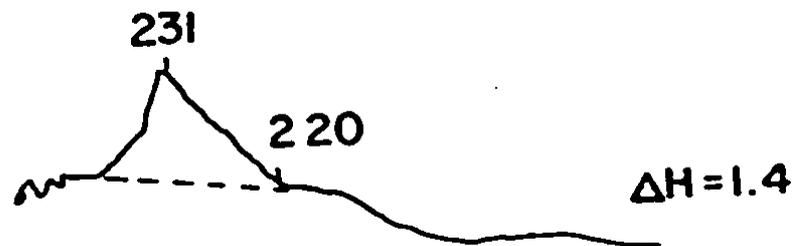
AVERAGE $\Delta H = 1.7 \frac{\text{cal.}}{\text{gm}}$ FOR HEATED SAMPLE

SERIES A



AVERAGE $\Delta H=1.2 \frac{\text{cal.}}{\text{gm.}}$

SERIES B



AVERAGE $\Delta H=1.4 \frac{\text{cal.}}{\text{gm}}$

FIG. 8. DSC CURVES; SERIES A FOR MEMBRANE HT-00; SERIES B FOR MEMBRANE HT-00 AFTER HEATING IN WATER AT 85°C FOR 60 MIN.

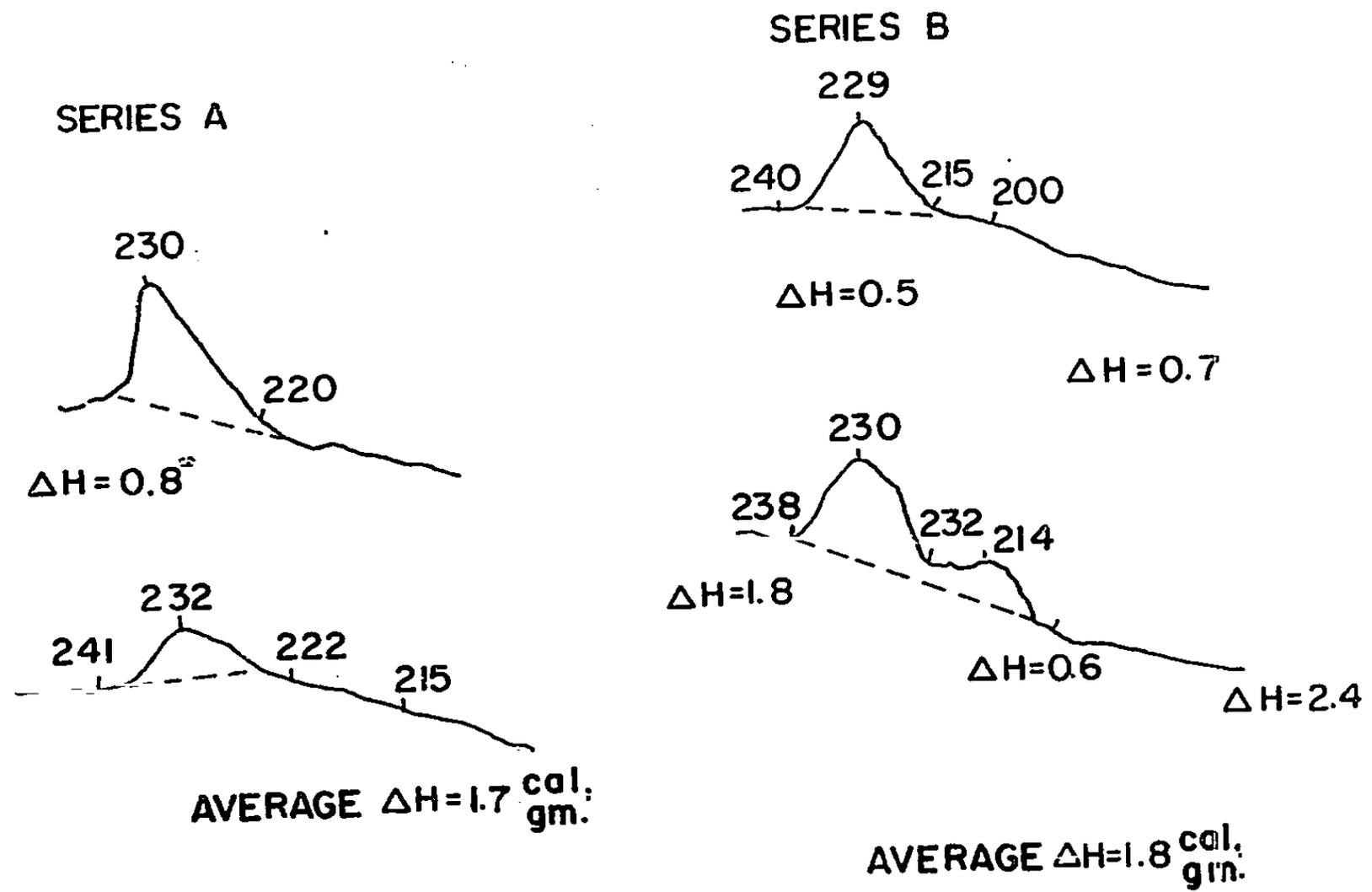


FIG. 9. DSC CURVES; SERIES A FOR RO 97 MEMBRANE; SERIES B FOR RO 97 MEMBRANE AFTER HEATING IN WATER AT 85°C FOR 60 MIN.