Journal of Thermal Analysis, Vol. 6 (1974) 67–77

THE EFFECT OF ZONE REFINING AND RECRYSTALLIZATION ON ORGANIC MATERIALS EXHIBITING ALLOTROPIC PHASE TRANSITIONS

A. W. NEUMANN and L. J. KLEMENTOWSKI

Department of Mechanical Engineering, University of Toronto, Toronto, Canada;
Department of Chemical Engineering, State University of New York at Buffalo
Buffalo, N. Y., USA

(Received April 24, 1972)

This paper assesses the effectiveness of zone refining and recrystallization from solution of three materials exhibiting allotropic phase changes, *n*-hexatriacontane cholesteryl stearate and *p*-azoxyanisole. Purity determinations are performed by means of a quantitative interpretation of the shape of DTA peaks following the procedure of Davis and Porter. It is concluded that zone refining of *n*-hexatriacontane is far more effective than recrystallization from solution. The results for cholesteryl stearate and *p*-azoxyanisole are more complex: Zone refining alone is in both cases somewhat more effective than recrystallization from solution. Evidence is presented which demonstrates in both substances the presence of at least one impurity component which increases the solid/smectic and solid/nematic transition temperatures, respectively. Such impurities are removed only very slowly by zone refining, but apparently even much slower, if at all, by recrystallization.

Allotropic phase transitions have found increasing attention in recent years. Porter et al. [1–5] investigated extensively liquid/liquid phase transitions in liquid crystal materials, mainly the class of the cholesteryl esters. The bulk of their work employs differential thermal analysis (DTA) or differential scanning calorimetry (DSC) and aims at a fundamental understanding of these phase transitions. Because of the important question of the change of surface free energies of a system undergoing a liquid/solid phase transition, Neumann et al. [6–10] investigated the effect of solid/solid phase transition on the surface free energy of several solids by means of measuring the temperature dependence of contact angles, as well as the effect of liquid/liquid phase transitions in liquid crystals on their surface free energy. For one liquid crystal not investigated by Neumann et al., cholesteryl myristate, Churchill and Bailey [11] reported the temperature dependence of the surface free energy. Their results show the same general features as Neumann et al. had found for other cholesteryl esters of long chain fatty acids [9]. In all of these investigations, the low molecular weight organic materials were recrystallized from solution, following the recipes given by Porter et al. Therefore it could be hoped that the results obtained by the different investigators were, at least to some degree, comparable. On the other hand, there remained in the minds of presumably all investigators involved reservations as to the adequacy of the purification by recrystallization from solution. These doubts were reinforced by a paper by Robinder and Poirier [12] who had purified *p*-azoxyanisole by vacuum sublimation at 100° and 0.07 torr after three recrystallizations from ethanol. They subsequently found in addition to the liquid (nematic)/ /solid phase transition two additional solid/solid phase transitions. These additional phases had not been observed by either Porter et al. nor Neumann et al., who had performed DTA runs on *p*-azoxyanisole samples which had been purified only by recrystallizations from ethanol. We therefore felt a definite need to investigate the effect of a different purification technique on effects previously observed with samples which had been purified by recrystallization from solution, and to determine the effect of different purifications quantitatively.

In this paper, we want to discuss the effectiveness of zone refining as compared to recrystallization from solution and describe some of the effects of purity on several previously described phenomena for three materials:

I. *n*-hexatriacontane
II. cholesteryl stearate
III. *p*-azoxyanisole

Quantitative purity determinations using the method of Davis and Porter [13] are used to judge the effectiveness of the purification processes. This technique is based on a quantitative interpretation of the shape of DTA peaks. In this investigation, the peak areas needed in the purity determination were determined by xeroxing the chart output of the DSC apparatus, cutting the peaks out of the Xerox paper and weighing them on a microbalance. The Xerox paper was found to be of sufficient quality, i.e. the weight of equal areas obtained from different pieces of Xerox paper was sufficiently constant.

A Fisher Zone Refiner was used to perform the zone refining operations described below. The rates of the moving molten zones were kept as low as the apparatus allowed, at about 3 mm per hour; the motion of the liquid zones was from the top to the bottom of the vertical column, so that impurities which lower the melting point of the main component were swept with the moving zone towards the bottom of the column. The molten zones were adjusted to a length of about 20 cm and the lengths of the ingots were about 20 cm. The adherence to these conditions could be expected to insure relatively high efficiency of our zone refining operations [14].

The DTA data reported in this paper were obtained with a Perkin – Elmer differential scanning calorimeter 1B. The temperature scanning rate was generally 2.5°C/min, the sample size usually approximately 3 mg. Care was taken, however, to make samples to be compared, e.g. those yielding Fig. 3a and 3b, respectively, exactly the same size.

I. *n-Hexatriacontane*

n-Hexatriacontane exhibits a solid/solid phase transition several degrees below its melting point, which is ascribed to rotational premelting of the long hydrocarbon chains. The effect of this phase transition on the temperature dependence of the contact angle against water was investigated in a previous paper [7]. The effectiveness of recrystallization from ethanol in that investigation was not very satisfactory; however, it was felt that the production of the actual samples which were used in the contact angle measurements by a condensation process in high vacuum effected a further purification. The results of Robinder and Poirier in fact make it appear to be likely that the actual contact angles were measured on a material which was purer than the recrystallized material. In Figure 1, the DTA curves of an unpurified sample (obtained from Eastman Organic Chemicals), the DTA curve of the sample used in the previous investigation [7] after two recrystallizations from ethanol and the DTA curve of a sample which originated from the same batch as the material whose DTA curve is shown in Figure 1a, but after extensive zone refining, are shown.

The DTA curve shown in Figure 1c, obtained from a sample after very extensive zone refining for several weeks (approximately 50 zone passes) exhibits very narrow peaks for the solid/solid as well as for the solid/liquid transition, indicating

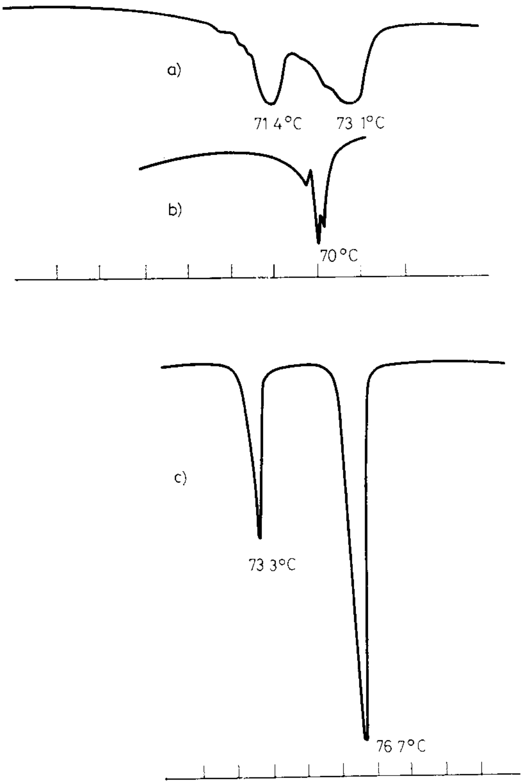

Fig. 1. DTA curves demonstrating the effect of different purification procedures on the purity of *n*-hexatriacontane: a) Unpurified material; b) After two recrystallizations from ethanol; c) After extensive zone refining

high purity. In Figure 1b, on the other hand, these two transitions are not even completely resolved; the third peak in Figure 1b was presumably due to an impurity which was not, or at least not completely, removed by the recrystallization processes. Although there is no assurance that the unpurified materials in this investigation and the previous one [7] were similarly impure, the conclusion seems inevitable that zone refining of *n*-hexatriacontane is by far more effective than recrystallization from alcohol.

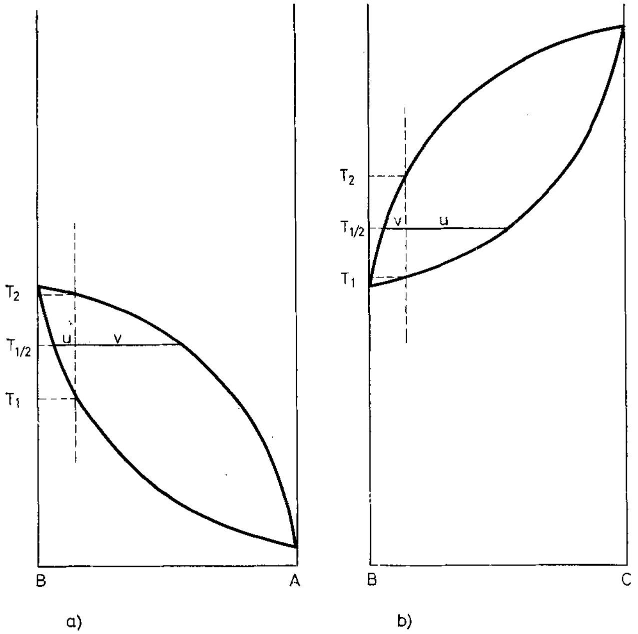

Fig. 2. Schematic phase diagrams: a) the impurity A lowers the melting point of B; b) the impurity C raises the melting point of B

Figure 1c was obtained from a sample from the very top of the column of hexatriacontane obtained by zone refining. The purity of this sample was determined using the technique of Davis and Porter as explained above. Two determinations were made on the same DTA peak, giving the purity of the sample as 98.9 and 99.0 percent, respectively. Thus, the reproducibility is very good; however, the purity of the sample as predicted by this technique appears to be very low. We, as well as Porter [15], actually feel that the purity of our sample may be higher, or, in other words, that the method overestimates the amount of impurities [15]. This suspicion is due to the fact that the half-width of the DTA peak of our zone refined hexatriacontane and the half-width of a Fisher triple point sample of naphthalene of presumably very high purity were very similar, suggesting similar purity for the two substances. However, the slope of the low temperature side of the naphthalene peak was steeper and the slope of the high temperature side less steep than the corresponding slopes for the hexatriacontane peak. Since the method of Davis and Porter utilizes only the slope of the low temperature side of the DTA peak, their method predicts a substantially smaller purity for our hexatriacontane than for the triple point naphthalene. Observations of this type may be explained by considerations of phase diagrams. Consider the following thought experiment: Let us produce two solid solutions of three substances A, B and C. In both solid solutions let B be the main component (say 98%). Let us in one case add 2% of substance A, which has a lower melting point than B, and in the other 2% of substance C, whose melting point is just as much higher than the melting point of B as A is lower than the melting point of B. Assuming, for the sake of simplicity, complete solubility of A and C, respectively, in B, we have, schematically, the two cases sketched in Figure 2.

The shape of the DTA peak is essentially determined by the amount of material transformed during the passage of the system through successive temperature intervals of the melting range T_1 to T_2 (Fig. 2). It will therefore suffice for our purposes to compare the amounts of material molten at $T_{1/2}$, the mid point of the melting temperature interval in the two cases shown in Figure 2a and 2b. Looking at the melting process, we have for the particular choice of phase diagram at the temperature $T_{1/2} = (T_2 - T_1)/2$ in

Case a: Solid solution AB

Amount of liquid at $T_{1/2}$: $\frac{u}{u+v} \approx 18\%$

Case b: Solid solution BC

Amount of liquid at $T_{1/2}$: $\frac{u}{u+v} \approx 82\%$

These two simple calculations show that the amount of material transformed per unit of temperature change ΔT is drastically different in the two cases. In our particular example over 80% melts over the first half of the melting range in the case of the solid solution BC, whereas over 80% remains solid over the corresponding temperature interval in the case of the solid solution AB. Obviously, these differences will have drastic effects on the shape of the DTA peaks. We may expect the leading edge to be considerably less steep for AB than for BC. For the latter substantial amounts of solid will melt just above T_1; the behaviour of the solid solution BC at the low temperature side of the DTA peak will be similar to that of pure B. The high temperature side of the DTA peak of BC will be fairly drawn out, since there will, as the temperature increases, remain small amounts of solid left which will melt, thus preventing the recorder from returning to the base line. The solid solution AB on the other hand may be expected to exhibit a shallow leading edge and a relatively steep high temperature edge. The peak area for the two solid solutions may be expected to be quite similar, and the amounts of impurities in the two cases are equal, due to the way in which we have set up our thought experiment. The purities determined by the method of Davis and Porter would however appear to be different, since the use of the slope of the leading edge is one of the main features of their technique. From this discussion it would appear that the technique of Davis and Porter would apply strictly only to a description of the removal of impurities which lower the melting point of the substance.

There is one further point which should also be given attention in the discussion of purity determinations from the shape of DTA peaks. Following the procedure of Davis and Porter, we used the DTA scan of an ultrapure sample of indium (99.9999 percent pure) as reference. The onset of the DTA peak (not shown in this paper) is considerably sharper than the onset of the peak of any organic material we ever investigated, including Fisher triple point substances. We feel that the onset of the DTA peak of a metal may always be sharper than the onset of the peak of an organic material of the same purity, due to the different thermal conductivities of the two different types of materials. In other words, it may be expected that the shape of the DTA peak may to some extent be a function of the thermal conductivity also. Until a complete answer to the above questions can be given, some caution in the use of this method may be indicated. On the other hand, it should be pointed out that the technique of Davis and Porter is a fast and convenient way of performing purity determinations and is moreover extremely sensitive to small changes in purity.

With these reservations in mind, the technique will be used throughout the remainder of this paper.

II. *Cholesteryl stearate*

Cholesteryl stearate, as supplied by Aldrich Chemical Co. with a nominal purity of 96% was found to have a purity* of less than 95%. Three purification procedures were used

a) recrystallization twice from pentanol
b) zone refining
c) recrystallization twice from pentanol, followed by zone refining.

Table 1

Purity of cholesteryl stearate

As supplied	less than 95%
Recrystallized 2 times from pentanol	97.7%
Zone refined (14 zone passes)	97.9%
Zone refined after recrystallization (44 zone passes)	98.2%

---

* Purity in the remainder of this paper will mean the purity as determined by the technique of Davis and Porter.

The results are given in Table 1, from which we infer that even a small number of zone passes in the zone refining process is somewhat more effective than recrystallization from solution. Extensive zone refining of the previously recrystallized cholesteryl stearate brings about a marked improvement of the purity. However, it has to be remembered that the purity of the zone refined material will vary along the ingot. In Table 2, the purity of zone refined material is given at three locations along the ingot. We see that the purity is highest in the lower central part of the column and lower both at the top and the bottom. This indicates that at least two impurities were present in the material supplied by Aldrich Chemical Co., one raising and one lowering the transition temperature solid/smectic of cholesteryl stearate. Considerations of phase diagrams show that impurities which lower the melting point of the main component are rejected by the solidification front and hence tend to be swept along the column with the pass of a single zone. Impurities which raise the melting point are, on the other hand, preferentially included in the newly formed solid, i.e. they travel opposite to the direction of the moving zone, in our case to the top of the column. Therefore, such an impurity molecule can, at the most, travel through a distance equal to the zone length during one zone pass. The removal of impurities which raise the melting point of the main component is therefore at best a very slow and inefficient process.

Table 2

Zone refining of cholesteryl stearate; purity along the column

Location	Purity
Top	96.3%
2nd quarter from bottom	97.9%
Bottom	95.9%

Unfortunately, recrystallization from solution did not remove the impurity or impurities which raise the melting point, at least not completely. In Figure 3, we have the DTA endotherms for the solid/smectic transition of a cholesteryl stearate sample after recrystallization and of a sample from the top of the column after zone refining the previously recrystallized cholesteryl stearate. The peak for the material from the top of the column is considerably wider than the peak for the recrystallized substance. This means that the zone refining process increased the concentration at the top of the column of those impurities, which raise the transition temperature. This interpretation is consistent with the fact that the peak temperature of the zone refined sample in Figure 3 is higher than the peak temperature of the sample which had only been recrystallized from pentanol.

We conclude that, although the removal of impurities which raise the melting point by zone refining is slow and inefficient, it may in certain cases still be preferable to recrystallization from solution. Concluding the section on cholesteryl stearate, we would like to point out that the surface properties of the liquid phases of zone refined cholesteryl stearate do not differ drastically from those of a material which had been recrystallized from alcohol: The general features of the surface tension vs. temperature curves for heating and cooling runs are the same for the zone refined material [10] as we reported in our previous work on cholesteryl stearate which had been recrystallized from ethanol [9].

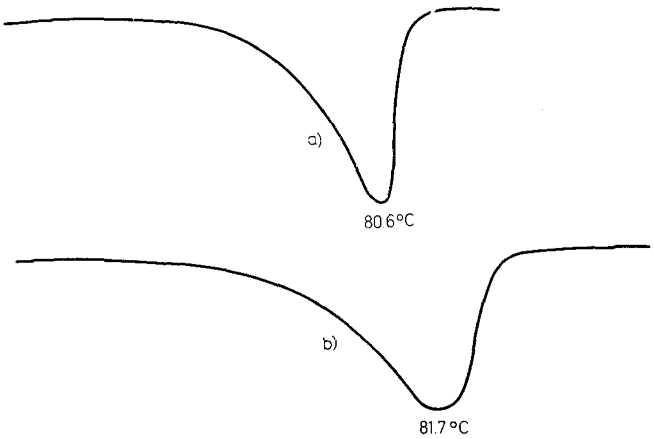

Fig. 3. DTA peaks of cholesteryl stearate: a) After recrystallization from pentanol; b) Material from the top of the column after zone refining the previously recrystallized cholesteryl stearate

III. *p-Azoxyanisole*

p-Azoxyanisole was obtained from Eastman Organic Chemicals. It was purified just as the cholesteryl stearate in three different ways by

a) recrystallizing it twice from pentanol
b) zone refining
c) zone refining the doubly recrystallized material

The purities obtained by the different purification processes are summarized in Table 3. The reason that the purities obtained are altogether greater than those obtained for cholesteryl stearate may be due to the fact that the purity of the azoxyanisole as obtained was considerably higher than that of the cholesteryl

Table 3

As supplied	97.7%
Recrystallized 2 times from pentanol	98.4%
Zone refined	98.6%
Zone refined after recrystallization	98.9%

stearate. Apart from this fact, the results are very similar to those obtained with cholesteryl stearate: Zone refining alone is somewhat more effective than recrystallization from solution, and zone refining of a previously recrystallized material brings a significant improvement in purity. Just as in the case of the cholesteryl stearate, the recrystallization from pentanol did not remove at least one impurity which increases the solid/nematic transition temperature. The purity at the top of the column of the material had been zone refined after recrystallization from

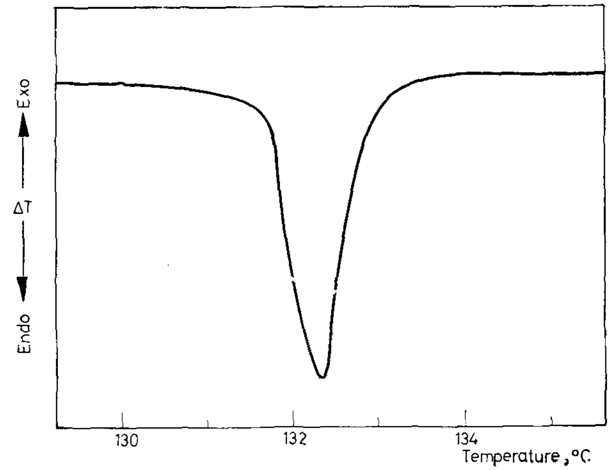

Fig. 4. DTA peak for the nematic/isotropic transition of *p*-azoxyanisole

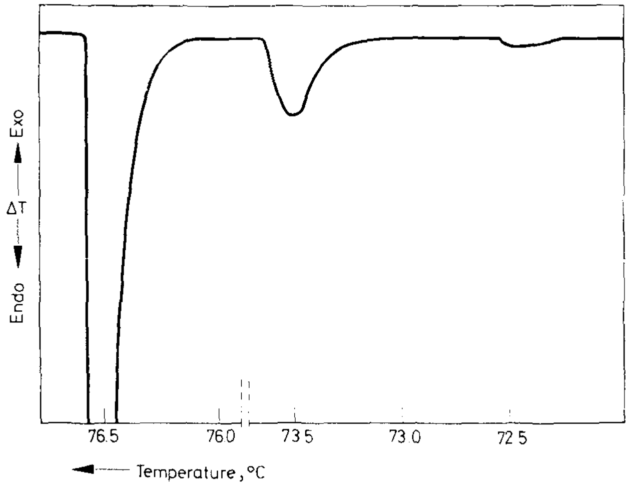

Fig. 5. DTA peaks indicating the existence of three different solid phases of *p*-azoxyanisole

solution turned out to be 98.6% then increased half way down the column to 98.9% and decreased again towards the bottom of the column. Thus again zone refining removes impurities which raise the melting point of *p*-azoxyanisole, although the process is inefficient, whereas recrystallization from solution does not.

Unlike zone refined cholesteryl stearate, zone refined *p*-azoxyanisole shows properties markedly different from those of material which has been recrystallized from solution only: The surface tension of recrystallized *p*-azoxyanisole was reported to show a step downwards of about 0.1 dynes/cm upon heating through the nematic-isotropic phase change [9]. The zone refined material shows a step upwards of about 0.4 dynes/cm [16]. Porter et al. [2] reported that the DTA peak due to the nematic/isotropic transformation was split. This result was confirmed by unpublished observations made in connection to previously reported surface tension measurements [9]. The DTA peak obtained for the zone refined material [16] is reproduced in Figure 4, which suggests that the previously reported split peak may be due to an impurity. The two solid/solid phase transitions reported by Robinder and Poirier [12] for the *p*-azoxyanisole which had been purified by recrystallization from solution [2, 9] and subsequent vacuum sublimation appear to be real (Fig. 5, reproduced from [16]). The considerable changes of the behaviour of *p*-azoxyanisole with increasing purity suggest that more attention should be given to the purity in future investigations of liquid crystals.

*

We gratefully acknowledge the contributions of Professor R. W. Springer, Mr. E. J. Rabenda, Jr. and Mr. R. T. Bruce to this paper. This work was partially supported by NRC Grant Nr. NRC–A–8278.

References

1. R. S. Porter and J. F. Johnson, J. Appl. Phys., 34 (1963) 55.
2. E. M. Barrall II, R. S. Porter and J. F. Johnson, J. Phys. Chem., 68 (1964) 2810; ibid. 70 (1966) 385; ibid. 71 (1967) 895; ibid. 71 (1967) 1224.
3. G. J. Davis, R. S. Porter and E. M. Barrall II, Molecular Crystals and Liquid Crystals, 10 (1970) 1.
4. G. J. Davis and R. S. Porter, Molecular Crystals and Liquid Crystals, 10 (1970) 13.
5. R. S. Porter, E. M. Barrall II and J. F. Johnson, Accounts of Chemical Research Febr., (1969) 53.
6. A. W. Neumann and W. Tanner, J. Colloid Interface Sci., 34 (1970) 1.
7. G. E. H. Hellwig and A. W. Neumann, Kolloid-Z. u. Z. Polymere, 229 (1969) 40; Fifth Internat. Congr. Surface Activity, Barcelona, 1968, Vol. 2, p. 687.
8. W. Funke, G. E. H. Hellwig and A. W. Neumann, Angew. Makromolekulare Chem., 8 (1969) 185.
9. A. W. Neumann and P.-J. Sell, Z. physik. Chem. Neue Folge 65 (1969) 19; 5th Internat. Congr. Surface Activity, Barcelona, 1968, Vol. 2, p. 125.
10. A. W. Neumann, L. J. Klementowski and R. W. Springer J. Colloid Interface Sci. 41 (1972) 538.
11. D. Churchill and L. W. Bailey, Molecular Crystals and Liquid Crystals, 7 (1969) 285.
12. R. C. Robinder and J. C. Poirier, J. Am. Chem. Soc., 90 : 17 (1968) 4760.

13. G. J. Davis and R. S. Porter, J. Thermal Anal. 1 (1969) 449.
14. E. F. Herrington, Zone Melting of Organic Compounds, New York, 1963.
15. R. S. Porter, Private communication.
16. A. W. Neumann, R. W. Springer and R. T. Bruce (in preparation).

Résumé — Comparaison des procédés de purification par fusion de zone et par recristallisation en solution dans le cas de trois composés présentant des changements de phase allotropiques, le *n*-hexatriacontane, le stéarate de cholestéryle et le *p*-azoxyanisol. Les déterminations de pureté s'effectuent en interprétant quantitativement la forme des pics ATD, selon la méthode de Davis et Porter. Les résultats montrent que dans le cas du *n*-hexatriacontane, la purification par fusion de zone est beaucoup plus efficace que le procédé par recristallisation en solution. Pour le stéarate de cholestéryle et le *p*-azoxyanisol, les résultats sont plus complexes: la purification par fusion de zone est un peu plus efficace que la recristallisation en solution. On montre que ces composés contiennent au moins un constituant à l'état d'impureté qui augmente les températures des transitions état solide/état smectique et état solide/état nématique.

Zusammenfassung — Es wird über die Wirksamkeit von Zonenschmelzen und Umkristallisierung aus Lösungen dreier Substanzen mit allotropen Phasenänderungen, und zwar *n*-Hexatriakontan, Cholesterylstearat und *p*-Azoxyanisol berichtet. Die Reinheitsbestimmungen werden nach dem Verfahren von Davis und Porter an Hand der quantitativen Interpretation der Form der DTA-Peaks durchgeführt. Es wird gefolgert, daß bei *n*-Hexatriakontan Zonenschmelzen viel wirksamer ist als die Umkristallisierung aus der Lösung. Die Ergebnisse sind bei Cholesterylstearat und *p*-Azoxyanisol viel komplexer. Die Zonenschmelzen allein ist in beiden Fällen etwas wirksamer als die Umkristallisierung aus der Lösung. Die Gegenwart mindestens einer Verunreinigungskomponente wird in beiden Substanzen nachgewiesen, welche die Temperaturen des fest-smektischen bzw. des fest-nematischen Überganges erhöht.

Резюме — Описана эффективность зоны рафинирования и рекристаллизации из раствора трех веществ, проявляющих аллотропные фазовые изменения, —*n*-гексатриаконтана, холестерилстеарата и р-азоксианизола. Определение чистоты проведено с помощью количественной интерпретации пиков DTA по методике Девиса и Портера. Сделан вывод, что зона очищения *n*-гексатриаконтана значительно более эффективна, чем рекристаллизация из раствора. Результаты для холестерил-стеарата и *p*-азоксианизола более сложны. Зона очищения несколько более эффективна в обоих случаях, чем рекристаллизация из раствора. Установлено, что в обоих веществах присутствует, по крайней мере, один примесный компонент, который увеличивает температуры переходов твердое/смектическое и твердое/нематическое, соответственно. Такие примеси удаляются очень медленно зоной очищения, и, очевидно, еще значительно медленнее, если вообще удаляются рекристаллизацией.