

ANALYSIS OF WAX/OIL MIXTURES USING DSC

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ABSTRACT

It is shown that DSC analysis can be used to quantify ingredient levels in three-component microcrystalline wax/paraffin wax/mineral oil mixtures. The method presented utilizes both enthalpy of crystallization data as well as a comparison of peak shapes with reference DSC scans. These two pieces of data are shown to give wax/oil ratios and wax/wax ratios respectively. This information is then used to derive specific ingredient levels. It is also shown that the percentage of each component in microcrystalline/paraffin blends can be obtained from enthalpy of crystallization data.

INTRODUCTION

Microcrystalline and paraffin waxes have a variety of industrial applications including paper, cosmetics and explosives. Both are distillation products of crude oil. Paraffins, obtained from the petroleum distillates, contain C18 to C40 hydrocarbon chains, have little branching, and are mainly saturated normal isomers. Microcrystalline waxes are highly branched C28 to C68 chains which are recovered from the residue.

These waxes are used in some cases in mixtures with mineral oils. Significant differences can occur in the properties of products containing these mixtures which are related to the relative levels of each of the three ingredients. It is, therefore, quite important to be able to quantitatively determine the various levels. The use of thermal methods of analysis appears to be one of the first to consider in this area. Recent advances in Differential Scanning Calorimetry (DSC) technology makes this particular method an attractive choice.

A review of the literature, however, gave no useful method nor even an indication as to whether this goal could be achieved. Previous work to qualitatively characterize paraffin and microcrystalline waxes have been reported by Lange and Jochinke [1] using a DTA in the range of 20 to 140°C. Currell and Robinson [2] also employed DTA but in the range of 20 to 600°C and used a high temperature endotherm to estimate the micro wax content. Data was obtained on a variety of wax mixtures composed of

various percentages of microcrystalline. DSC was employed by Flaherty [3] to qualitatively study hydrocarbon and natural waxes in the range 40 to 100°C. Heats of transition were calculated for over 70 waxes but mixtures were not evaluated. Giavarini and Pochetti [4] also used the DSC but in the range -30 to 90°C. In their study of petroleum products, microcrystalline and paraffin waxes were analyzed separately as well as a two-component mixture of paraffin wax and oil. It was found that a quantitative analysis of oil could be done. Miller and Dawson [5] supported the development of DSC "fingerprints" for waxes and compared this method to others including IR and RI.

The present paper attempts to characterize both qualitatively and quantitatively two-component mixtures of microcrystalline and paraffin waxes and three-component mixtures of these two waxes with oil. It is shown that by examining the peak shape and enthalpy of crystallization the percentage of microcrystalline and paraffin can be determined in binary mixtures and the percentage of oil in three-component mixtures estimated.

EXPERIMENTAL

DSC analysis were conducted on a Perkin-Elmer DSC-2C with nitrogen as the purge gas. Volatile sample pans were used, and each sample (~5-10 mg) was heated, cooled, and reheated. Initial melting curves were not typical due to sample configuration and served only as thermal conditioning. Cooling curves were recorded because current industrial specifications normally use the congealing point which is easily detected. Samples were scanned at 20°C min⁻¹ and analyzed using Perkin-Elmer TADS.

The waxes and oil are commercially available. Mixtures were made in the lab. and kept in an oven overnight to insure complete melting and homogeneous mixing.

RESULTS AND DISCUSSION

In the typical case a sample of the three-component mixture is obtained with only a rough guideline as to approximate percentages of the ingredients. The types of waxes and oil are usually known. What is normally required is an estimate (within about 5%) of the percentage of each ingredient.

The method presented here uses two steps to obtain this information: first, an estimate of microcrystalline to paraffin wax ratio is obtained based on DSC peak shapes and second, an estimate of ingredient levels is obtained based on the enthalpy of transition for the mixture.

The microcrystalline and paraffin waxes were first studied separately in

an attempt to characterize and compare them. Consistent with previous work [3] the microcrystalline cooling curve is broad, has an enthalpy of recrystallization (ΔH) of 35.65 cal g^{-1} and a congealing point of 72.5°C . The paraffin wax reveals a sharp, double peak with ΔH equal to 48.34 cal g^{-1} and a congealing point of 61.0°C . The curves are different because paraffin wax is composed of long chain hydrocarbons with mainly saturated normal isomers having minimal branching. Paraffins are in a C18 to C40 range while microcrystallines are highly branched C28 to C68 chains. The double paraffin peak is due to a solid–solid transition that occurs after the liquid–solid transition.

When the two waxes were blended in different proportions and scanned, peak shapes changed noticeably. As the microcrystalline content increases, the peak broadens (Fig. 1 A–E). The notch on the left side of the curve in Fig. 1 A, B, and C is due to the presence of paraffin wax. This disappears as the microcrystalline content increases and overshadows the paraffin peak. Enthalpy of recrystallization decreased as the percentage of microcrystalline wax (M) increases. This can be seen in Fig. 2. The relation between ΔH and M is

$$M = -7.97 \Delta H + 382 \quad (1)$$

This has a correlation coefficient of 0.995 with a standard deviation of 3.0%. Thus, ingredient levels in this two-wax system can be obtained directly from heats of crystallization data to within 6% at the 95% confidence level.

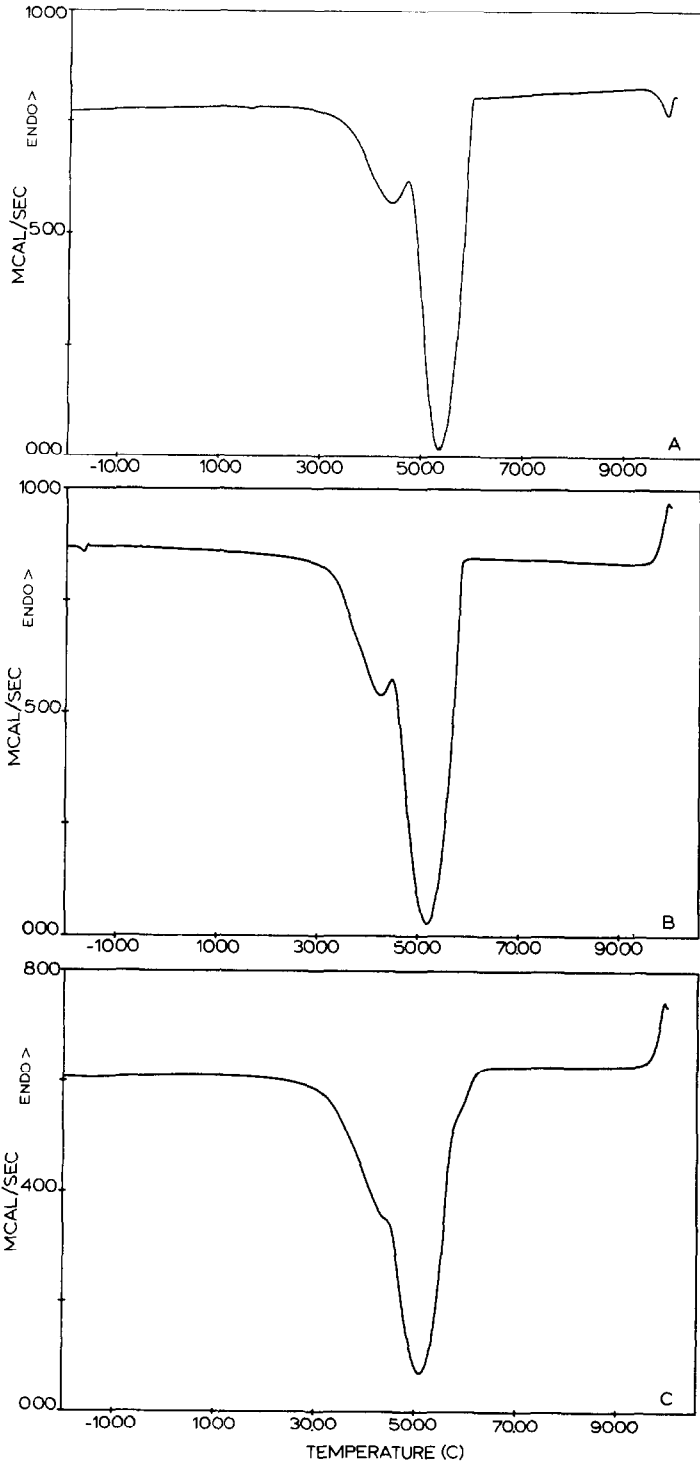
The effect of oil on various wax blends is shown in Fig. 3. It is readily apparent from this data that the oil is acting mainly as a diluent. Within the limits of precision required for the present application, it does not appear to affect the results in any other significant manner. It can also be seen from the data that a straight line can be drawn for each of the various wax combinations. For the three cases illustrated the following relations hold,

$$O(30) = -2.23 \Delta H + 96.0 \quad (2)$$

$$O(50) = -2.42 \Delta H + 96.5 \quad (3)$$

$$O(70) = -2.47 \Delta H + 94.3 \quad (4)$$

Where e.g. O(50) represents the oil content for various oil/wax blends whose wax portion is composed of equal parts of microcrystalline and paraffin. Likewise, O(30) refers to the percentage of oil in an oil/wax blend whose wax portion contains 30% microcrystalline and 70% paraffin. Each of these relations has a correlation coefficient equal to or greater than 0.999. The standard deviation for the three curves are 0.98, 0.92, and 1.38 respectively. Thus, at the 95% confidence level, the oil concentration can be estimated to within 2.8%. However, before these relations can be used it is necessary to be able to identify which one is appropriate for the situation being investigated.



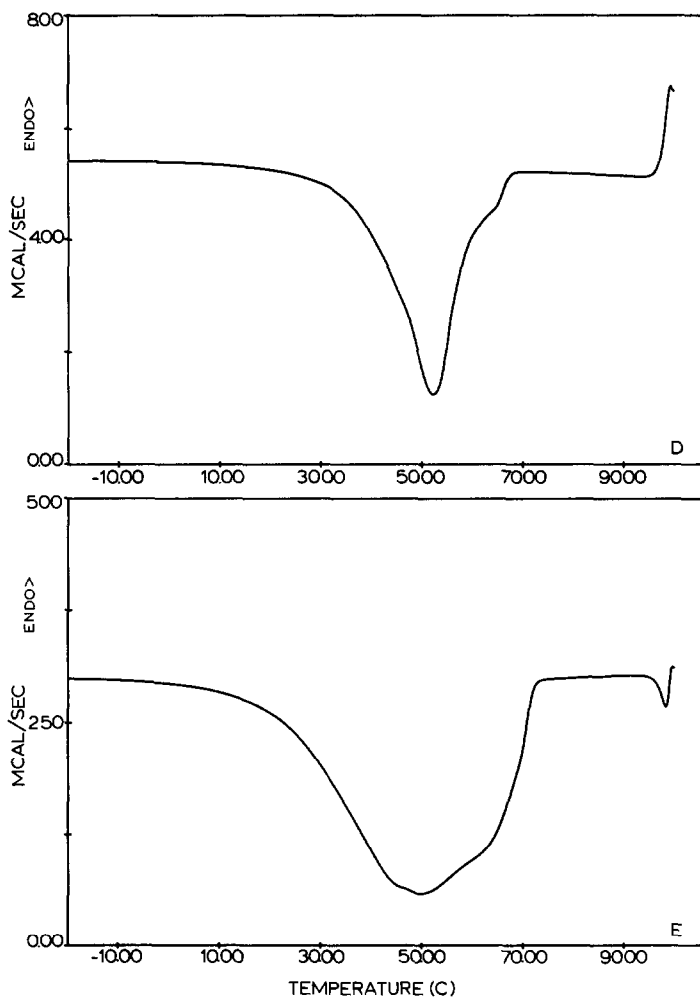


Fig. 1. DSC scans of microcrystalline and/or paraffin waxes. A through E are respectively 100, 70, 50, 30, and 0% paraffin and 0, 30, 50, 70, and 100% microcrystalline.

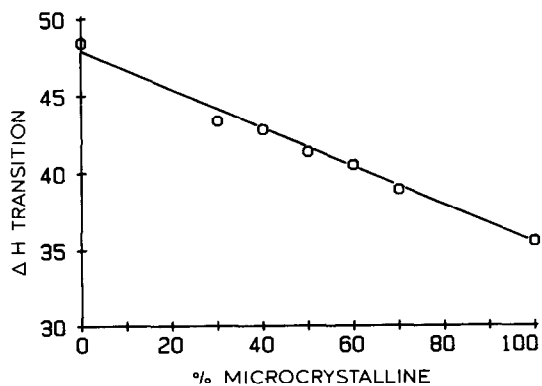


Fig. 2. Enthalpy of crystallization vs. percentage microcrystalline wax in microcrystalline/paraffin blends.

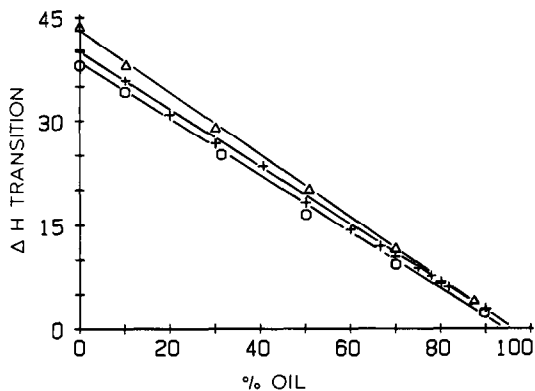


Fig. 3. Enthalpy of crystallization for various oil dilutions of three different microcrystalline-paraffin wax blends. These contain respectively 30% (O), 50% (+), and 70% (Δ) by weight of microcrystalline wax in the wax portion of the oil/wax mixture.

It will be shown that this can be done by comparing the DSC curves of the sample with standards. By way of illustration consider two examples. In the first case, assume that the measured ΔH of the sample is 28.5 cal g^{-1} . Equation (2) gives $O(30) = 32.4$ whereas eqn. (3) gives $O(50) = 27.5$. The difference in these two results gives an absolute uncertainty of 4.9% in the oil level. In order to illustrate the recommended procedures for determining the correct equation, consider Fig. 4. Both 4A and 4B are scans with ΔH values near 28.5 cal g^{-1} . It can be seen that there is a qualitative difference between them. Thus, if the scan of the sample has a shape similar to either of these or an intermediate shape, then either of these equations or an intermediate one can be used. Thus, a simple comparison of the DSC scans can give the equation to use. Note that Fig. 3 contains data for only three wax ratios. Theoretically, relations can be obtained for any ratio desired. This, of course, would allow for finer distinctions. It is impractical, however, to use wax/wax ratio increments below about 10%. This yields a maximum value of $\pm 5\%$ in the estimation of the wax/wax ratio. This is in approximate conformity with the 6% precision obtained above.

In practice it is normally sufficient to know the wax/wax ratio and oil %. However, it should be noted that this information also yields ingredient levels directly. For example, if visual inspection shows the 50% wax/wax curve to be appropriate in this example, then $O(50) = 27.5$ and it follows that both percentage microcrystalline and percentage paraffin is given by $0.5 \times (100 - 27.5)$ or 36.3.

As a second example, consider a ΔH value of 3 cal g^{-1} . The region of interest in this case is the lower right portion of Fig. 3. Once again using eqns. (2), (3), and (4) gives oil values of 89.3, 89.2, and 86.9% respectively. In this case the range is only 2.4%. Thus, the comparison of DSC scan shapes is

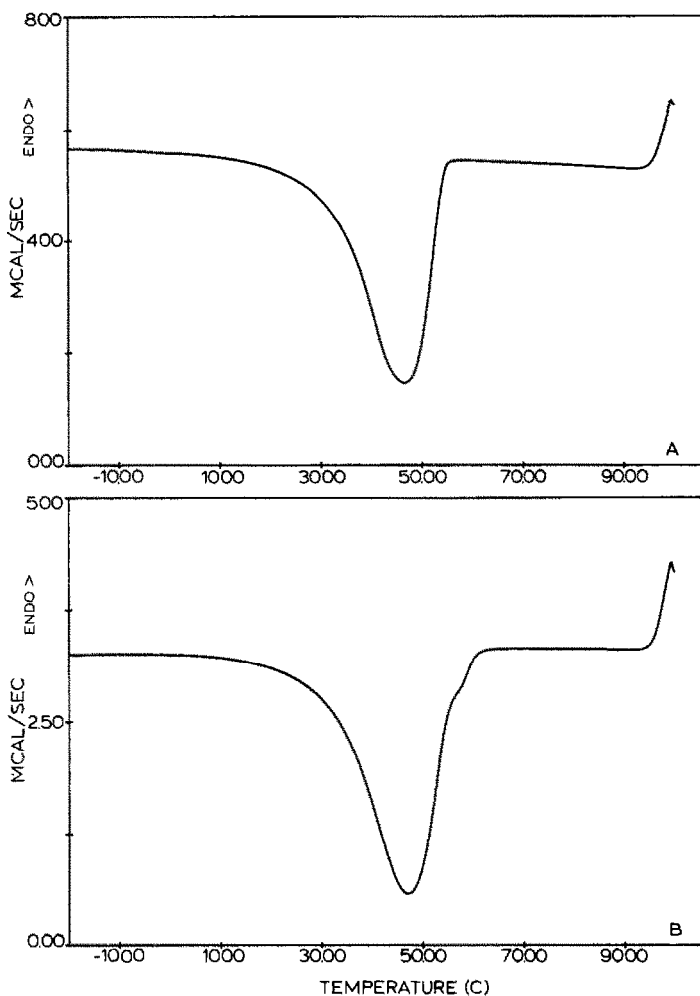


Fig. 4. DSC scans of two different mixtures of microcrystalline/paraffin/mineral oil. (A) 21/49/30 ratio, (B) 35/35/30 ratio.

not needed to add precision to this value, since it already lies within the precision of the method. However, in this case the wax/wax ratio is unknown. To resolve this issue consider Fig. 5. It can be seen that there is a qualitative difference between these scans even though the percentage of oil in each mixture is high. Thus, it is possible to identify the wax ratio contained in the sample even at high oil contents.

These two examples cover the two extreme cases which would be encountered in practice. It can be seen that the weight fraction of each of the ingredients is obtainable in both situations. Thus, all intermediate mixtures will also be characterizable using the method described. This has been found to be true in practice.

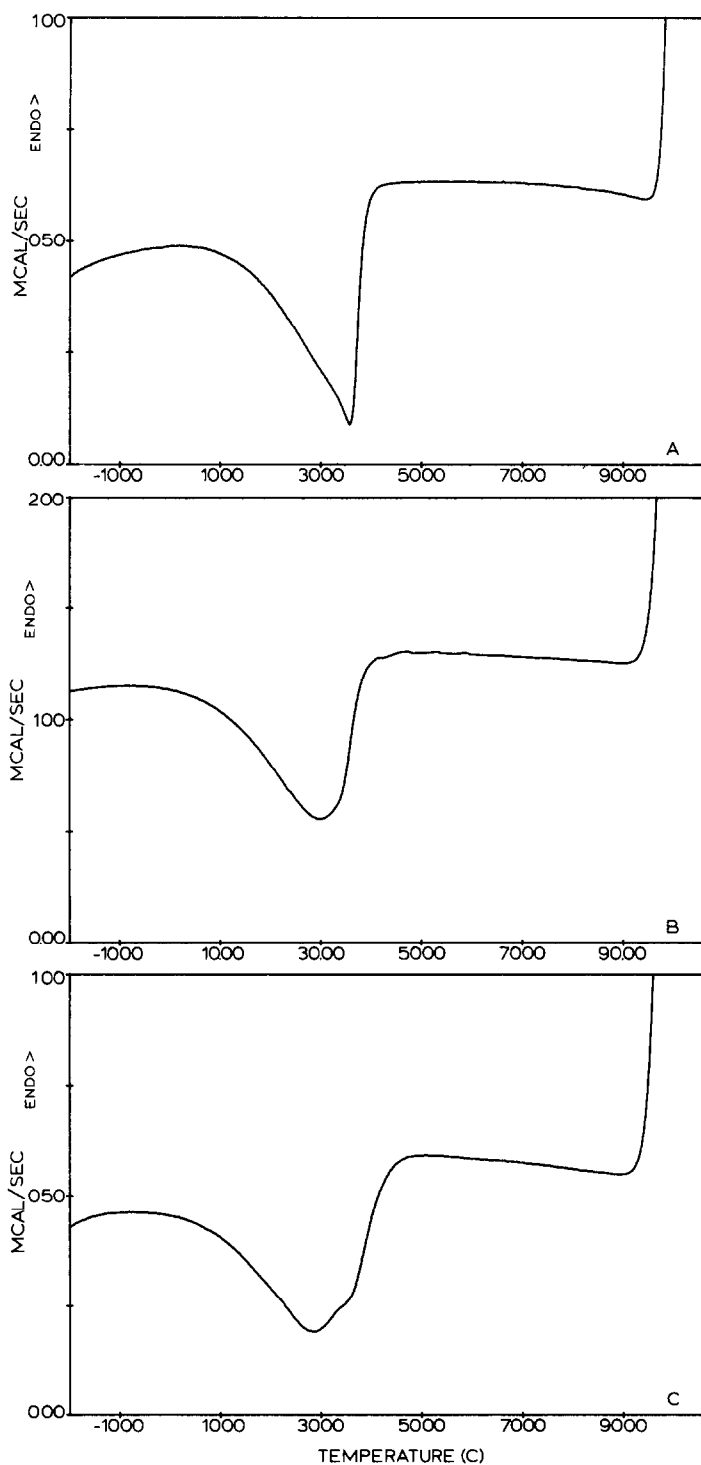


Fig. 5. DSC scans of three different mixtures of microcrystalline/paraffin/mineral oil. (A) 3/7/90 ratio, (B) 5/5/90 ratio, (C) 7/3/90 ratio.

SUMMARY

It is shown that quantitative estimates of ingredient levels can be obtained for microcrystalline/paraffin blends using only heat of crystallization data.

A method is also described which will allow the estimation of all three ingredient levels in a microcrystalline/paraffin/mineral oil mixture using a simple DSC scan of the sample. The method involves two steps:

(1) a comparison of peak shape to standard scans. Different wax/wax ratios yield characteristic shapes from which the ratio of the sample under study can be identified.

(2) A calculation of percentage oil from the measured heat of crystallization. This information along with the data from step (1) yields all three ingredient levels.

It is shown, by example, that this method can be used for the entire range of ingredient levels.

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