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DYNAMIC PURITY DETERMINATIONS. II. SOME ADDITIONAL SYSTEMS

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Menadione and phenacetin systems were each prepared with a series of concentrations of materials of varying similarity to the host. The data indicate that the measured impurity is dependent upon not only the concentration but also the nature of the impurity. The determination of the actual beginning of melting by nuclear magnetic resonance results in more precise purity measurements.

In the previous paper [1], it was shown that one of the attributed causes of error in the determination of purity by differential scanning calorimetry or differential thermal analysis – lack of thermal equilibrium – is not a principal source of error. Further, the utility of determination of the solidus by nuclear magnetic resonance [2] was established. The latter arises from the need to distribute the energy represented by the temperature decrement at the completion of melting over the span of the melting process. If the very start of melting is not established clearly, there may be substantial error when that energy is distributed from the *inferred* starting temperature to the end of the process.

The difficulty of detection of the actual start of melting already exists in *ideal* systems at very low levels of impurity, because so small an amount of the eutectic composition needs be melted to dissolve the whole amount of impurity. As illustrated in Figure 1, the inability to detect the start of melting of relatively impure specimens may occur where solid solutions can form. As the temperature of a specimen of the indicated composition is heated through the solidus, it is only necessary to dissolve a *fraction* of the impurity because the major portion remains in solid solution.

Whereas in any system of practical concern, the impurities present are materials that were able to remain with the host material through any purification steps, isomers, degradation products, or reactants used in making the host material, the inevitable chemical similarity to the host renders solid solubility more probable than total (ideal system) insolubility. That is, ideal behavior is improbable when a manufactured chemical compound is tested for purity.

This investigation was undertaken to evaluate the errors from known components in systems of economic importance, namely menadione and phenyl salicylate.

* The data are taken from a dissertation presented in partial fulfillment of the requirements for the Doctor of Philosophy degree.

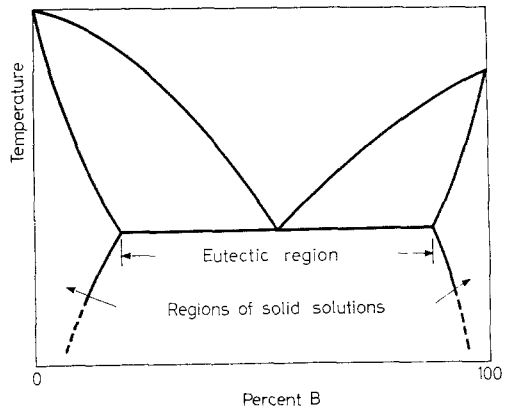

Fig. 1. Typical phase diagram for two components having some chemical similarity. The compositions with which purity measurements are concerned are in the solid-solution region

The systems were selected without concern for previous purity measurements to ascertain whether or not the procedures could be applied to any chosen system without substantial testing of that particular system. That is, systems that already had been shown to give good results were avoided. Some additional work on the phenacetin system was also done.

The materials chosen were menadione (1,4-naphthoquinone, 2,methyl-) and salol (phenylsalicylate or benzoic acid, 2-hydroxy, phenyl ester). In each case the starting materials and isomers were readily available. For menadione, the impurities introduced were naphthalene, 1-methyl-naphthalene, 2-methylnaphthalene, and *n*-tetracosane. For salol, the impurities added were phenol, salicylic acid and benzoic acid.

Because a product may have more than one impurity, combinations of the listed impurities were also tested. The potential problem is that the interaction of a second impurity may be with the first impurity as well as with the host material.

Experimental

Preparation

Commercial phenacetin was purified by zone refining until the best fractions chosen did not show detectable differences in their DSC curves or by liquid chromatography. Menadione was prepared by following Fieser's procedure [3], oxidation of 2-methylnaphthalene; it was purified by recrystallization (four times) from methanol. No impurities were detectable by DSC or reversed phase thin layer chromatography. Commercial phenyl salicylate was purified by zone refining then washing with water, methylene chloride and aqueous sodium carbonate.

Tests for reproducibility

The curves for the pure phenacetin or menadione could be overlaid and produced reproducible data. A specific test for reproducibility was made with phenacetin -0.50% acetanilide; the standard deviation in T_0 was 0.006°.

Successive curves for the pure salol could not be overlaid and an apparent decrease in purity was found. In fact, after the second freezing in place, a number of small peaks appeared superimposed upon the major peak. The material had crystallized in several places in the sample holder and the small peaks were the result of separate (in time) initiations of melting of the various bits of solid.

Preparation of mixtures

The major component was weighed on a semimicro analytical balance; the minor component was weighed on an electronic microbalance. The mixture was melted and stirred, then quenched by pouring it onto a slab of aluminum to preserve its homogeneity.

Preparation of specimens

The mixtures were pulverized. Weighed specimens were taken for the DSC work and sealed into sample holders. Unweighed specimens for NMR were prepared by pouring the powder into the sample tube to a depth of ca. 2.5 cm.

Acquisition of data

A DSC curve was obtained with both digital data acquisition (Perkin–Elmer Interface with Tektronix Programmable Calculator) and chart record. Values for T_0 and T_m were reported by the calculator and determined from the chart record by the procedure set forth in DSC-2 Manual [4].

Stepwise melting [5] was carried out on separate specimens.

The true solidus was obtained by first equilibrating the NMR tube at a temperature below the eutectic temperature, then advancing the voltage input to the heater in small increments, obtaining a plot over a principal peak of the major component after each equilibration. The area at several temperatures were determined and finally, from the intercept of the two segments [1], the solidus for that system was found.

Results and discussion

The detailed results may be found in the primary reference [6]. The essential information, $T_0 - T_m$, is tabulated for menadione in Table 1 and for phenacetin in Table 2. The data on salol require further study before publication.

The stepwise data are not included herein because they are not pertinent to the discussion of the effect of independent determination of the solidus. The stepwise purity data are in general agreement with the manually-calculated purities for the phenacetin systems but show some startling deviations for the menadione systems. The reason for the deviations is not clear.

Table 1

The quantity $T_0 - T_m$ for menadione with various levels of impurities naphthalene (N) 1-methylnaphthalene(α), 2-methylnaphthalene(β) and tetracosane(T) found by programmed calculation, by manual calculation from the chart record, and by correction of the starting point in the manual calculation from the solidus found by NMR

Substance	Calculator $T_0 - T_m$	Manual $T_0 - T_m$	NMR $T_0 - T_m$
Menadione +			
0.5 mole % N	0.20°	0.41°	0.29°
0.5 mole % α	0.21	0.51	0.38
0.5 mole % β	0.43	1.12	0.40
0.5 mole % T	0.43	0.26	0.27
0.5 mole % βN(0.25β+0.25N)	0.34	0.27	0.33
0.5 mole % $\beta\alpha$(0.25β+0.25α)	0.29	0.33	0.34
0.5 mole % βT(0.25β+0.25T)	0.56	0.07	0.32
Menadione +			
1.0 mole % N	0.37	0.80	0.52
1.0 mole % α	0.28	1.07	0.42
1.0 mole % β	0.32	1.18	0.48
1.0 mole % T	0.30	0.39	0.47
1.0 mole % βN(0.5β+0.5N)	0.46	0.72	0.49
1.0 mole % $\beta\alpha$(0.5β+0.5α)	0.51	0.52	0.48
1.0 mole % βT(0.5β+0.5T)	0.81	0.59	0.54
Menadione +			
5.0 mole % N	0.94	0.86	2.42
5.0 mole % α	0.80	2.59	2.41
5.0 mole % β	1.01	1.99	2.67
5.0 mole % T	0.46	1.90	2.65
5.0 mole % βN(0.5β+0.5N)	0.84	2.44	2.60
5.0 mole % $\beta\alpha$(0.5β+0.5α)	1.57	2.65	2.43
5.0 mole % βT(0.5β+0.5T)	1.15	2.72	2.40

Whereas the calculated purities are derived directly from the quantity $T_0 - T_m$, these values (nearer to the raw data) provide a valid and convenient set for comparison of methods. Further, some variations in programming or data reading could introduce minor differences in the values for a given curve but both values should be affected in the same direction. Variations in the quantity $T_0 - T_m$ are then close reflections of the real differences introduced by inhomogeneities in the sample or preparation of the specimen, by any transient deficiencies in programming or recording, or by any irreproducibility in the data collection and treatment. The data show general agreement, of course, but also are sufficiently diverse within a set that a pattern is difficult to perceive. Nonetheless, by ranking the results within each group, then summing the rankings, tetracosane is decidedly low in its $T_0 - T_m$ values for both menadione and phenacetin, both alone and with a second impurity. On the other hand, 2-methyl naphthalene is decidedly high in its $T_0 - T_m$ values.

Table 2

The quantity $T_0 - T_m$ for phenacetin with various levels of impurities acetanilide(A), benzamide (B), and tetracosane(T), found by programmed calculation, by manual calculation from the chart record, and by correction of the starting point in the manual calculation from the solidus found by NMR

Substance	Calculator $T_0 - T_m$	Manual $T_0 - T_m$	NMR $T_0 - T_m$
Phenacetin +			
0.5 mole % A	0.01°	0.05°	0.32°
0.5 mole % B	0.01	0.42	0.28
0.5 mole % T	0.01	0.05	0.22
0.5 mole % (0.25B+0.25A)	0.05	0.11	0.31
0.5 mole % (0.25B+0.25T)	0.02	0.14	0.31
Phenacetin +			
1.0 mole % A	0.01	0.19	0.56
1.0 mole % B	0.03	0.56	0.61
1.0 mole % T	0.04	0.13	0.47
1.0 mole % (0.5B+0.5A)	0.12	0.25	0.52
1.0 mole % (0.5B+0.5T)	0.17	0.44	0.45
Phenacetin +			
5.0 mole % A	0.75	1.48	2.15
5.0 mole % B	1.03	1.98	2.34
5.0 mole % T	0.01	1.57	1.42
5.0 mole % (2.5B+2.5A)	0.90	1.35	2.02
5.0 mole % (2.5B+2.5T)	0.61	1.41	2.07

It is worth noting that 2-methyl naphthalene is the starting material for menadione whereas *n*-tetracosane, a straight-chain hydrocarbon, is quite dissimilar. For phenacetin, benzamide shows typically high $T_0 - T_m$ values. Again, its structure is quite similar to that of phenacetin. The means and the ranges for the several data sets are shown in Table 3 for menadione and Table 4 for phenacetin.

Table 3

Mean values and ranges of $T_0 - T_m$ (from Table 1) from menadione for each level of impurity added. Three data points have been discarded via the Q-test

Concentration		Calculator	Manual	NMR
0.50%	Mean	0.35°	0.31°	0.33°
	Range	0.36	0.44	0.13
1.00%	Mean	0.37	0.75	0.49
	Range	0.22	0.71	0.14
5.00%	Mean	0.97	2.38	2.51
	Range	1.11	0.82	0.22

Table 4

Mean values and ranges of $T_0 - T_m$ (from Table 2) from phenacetin for each level of impurity added. Three data points have been discarded via the Q-test

Concentration		Calculator	Manual	NMR
0.50%	Mean	0.02	0.09	0.29
	Range	0.04	0.09	0.10
1.00%	Mean	0.07	0.31	0.52
	Range	0.16	0.43	0.16
5.00%	Mean	0.84	1.56	2.15
	Range	0.42	0.63	0.32

The mean values – even with the variation within the sets – should show a progression in values proportional to the increasing concentration. For neither menadione nor phenacetin do the automatically acquired and treated data show a reasonable agreement. The manual calculations from the chart record shows substantially better agreement and the NMR-corrected manual data show the best agreement. In nearly all cases, the range for the NMR-corrected data is smaller than for either of the other sets; it is very probable that the uncertainty in the starting point for integration engenders some variation in $T_0 - T_m$ and that a definitive value from the NMR determination of the liquidus vitiates the uncertainty and thereby diminishes the range of calculated values.

Conclusions

For the systems tested, there is evidence that the measured impurity content is in some cases dependent upon the nature of the impurity as well as its concentration. The implication for practical measurements is that ideality cannot be assumed. Even so, the fact that there is variation in response does not imply that dynamic thermal methods are inappropriate; it does imply, however, that the effects of the probable impurities should be verified.

The use of nuclear magnetic resonance to ascertain the true solidus results in data that reflect the purity more precisely. This does not imply that NMR should be used as a part of every purity determination but it does make available a means of testing the applicability of the ideal-system treatment. A systematic study of a system of commercial importance may enable applications of suitable corrections to routine DSC measurements for that system.

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References

1. B. KAWALEC, J. J. HOUSER and P. D. GARN, J. Thermal Anal., 25 (1982) 259.
2. E. F. G. HERINGTON and I. J. LAWRENSON, J. Appl. Chem., 19 (1969) 337.
3. L. F. FIESER, J. Am. Chem. Soc., 61 (1961) 2559.
4. Model DSC-2 Differential Calorimeter Manual, Perkin—Elmer Corporation, Norwalk, Connecticut, USA.
5. H. STAUB, W. PERRON, Applications of a New Quantitative DTA System to Purity Analysis, Mettler Instrumente AG, Greifensee, Switzerland (1972).
6. T. F. HABASH, Dissertation, The University of Akron, Akron, Ohio, USA, 1981.

ZUSAMMENFASSUNG — Es wurden Menadion- und Phenacetinsysteme mit je einer Konzentrationsreihe von Zusatzstoffen, der Matrix in verschiedentlichem Ausmaß ähnlich, hergestellt. Die Ergebnisse zeigen an, daß die gemessene Verunreinigung nicht allein von ihrer Konzentration, sondern auch von ihrer Natur abhängig ist. Genauere Reinheitsmessungen erfolgen aus der Bestimmung des wahren Schmelzanfangs mittels kernmagnetischen Resonanzmessungen.

Резюме — Менадион и фенацетин были получены с различной концентрацией примесей, изменяющих их свойства. Данные показали, что измеренная чистота зависит как от концентрации, так и от характера примеси. Определение с помощью ЯМР истинного начала плавления дает более точные измерения чистоты.