	sure, but no sample, at the mean temperature of the experiments, J/K
ϵ(as used)	energy equivalent of the standard calorimeter with additions for the heat capacity of the sample of ethylene carbonate and the heat capacity of the oxygen in excess of 30 atm abs at the referral temperature of the reaction (t_f), J/K
t_f	final temperature of the calorimeter for a given run, °C
ΔT	observed adiabatic temperature rise of the calorimeter system after ignition of the sample, K
Q(total)	total heat evolved to the calorimeter system (=ϵ(as used)ΔT), J
q(fuse)	correction for heat of combustion of fuse wire, J
$q(HNO_3)$	correction for heat released by forming nitric acid from nitrogen, oxygen, and liquid water, J
q(im)	correction for heats of combustion of impurities in sample, J
ΔE(cor to 28 °C)	correction to adjust observed heat of the bomb process from actual final temperature of each experiment (t_f) to common temperature of 28 °C, J
ΔE(cor, WC)	total "Washburn correction" (*4*) to reduce the observed heat of the bomb process to standard conditions having reactants and products in their thermodynamic standard states at 1-atm pressure and the common (isothermal) temperature selected, J
$\Delta E_c°$	change in energy due to idealized combustion reaction under standard-state conditions, J/g or kJ/mol as noted
ΔE_b	change in energy due to combustion of the sample itself under bomb conditions, i.e., after other thermal corrections to $-Q$(total), J/(gram formula weight)
Δn_g	change in number of moles of gas across the idealized combustion reaction
$\Delta H_c°$	isothermal enthalpy change for combustion of the compound with the reactants and products in standard states ("standard enthalpy of combustion") for a specified temperature, kJ/mol or kcal/mol as noted
n	number of moles of each product or reactant in the idealized combustion reaction used in correcting $\Delta H_c°$ from the selected final reaction temperature to 25 °C
$C_p°$	mean molar heat capacity at constant pressure, 25-28 °C, of a product or reactant in its thermodynamic standard state, kJ/(mol K)
$\Delta H_f°$(c)	standard enthalpy of formation of the crystalline compound for the reference temperature of 25 °C, kJ/mol or kcal/mol as noted

Registry No. Ethylene carbonate, 96-49-1.

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Solid-Liquid Phase Behavior of Nonadecylcyclohexane and Nonadecylbenzene

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The melting points of nonadecylcyclohexane (NDC) and nonadecylbenzene (NDB) have been determined to be 42.59 and 29.50 °C, and their freezing points, 29.97 and 24.94 °C, respectively. It is suggested that, analogous to the normal paraffins, these compounds form "rigid" (β) and "rotator" (α) phases in the solid state. In the present cases, however, the α phases are metastable and are formed directly from the melt as the result of kinetic factors. When the compounds stand for a sufficient length of time, the transitions to the more stable β phases are complete. The enthalpies of fusion of both phases for each substance have been estimated by using simple calorimetry and differential scanning calorimetry (DSC).

Introduction

Before initiating studies using NDC and NDB as liquid phases in gas-liquid chromatography, we decided to estimate their purities by using the cooling-curve method described by Rossini (*1*). It was soon discovered that each solid melts at a temperature considerably above that at which it freezes. Apparently there are (at least) two solid crystalline phases for these compounds, the less stable of which forms more readily from the melt. Upon standing, the crystal transforms into the more stable phase, which, when heated, melts at a higher temperature than that at which the liquid had solidified.

Because the enthalpy of fusion of the crystalline phase which is in equilibrium with the melt is required for purity estimation from the cooling curve, and because of the curious nature of these transitions, a study of the liquid-solid behavior of NDC and NDB was initiated.

Experimental Section

Cooling curves were obtained by using a MINCO platinum resistance thermometer (PRT), wrapped in copper screen, immersed in an insulated Pyrex tube containing the sample under study. A Rubicon potentiometer was used to oppose the emf drop across the PRT, and the imbalance was displayed on a

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Table I. Solid-Liquid Transition Temperatures and Purities Estimated from Cooling and Warming Curves

compd	t, °C	purity	t, °C	purity
NDC	29.97 ± 0.14	0.999	42.59 ± 0.05	0.945
NDB	24.94 ± 0.03	0.997	29.50 ± 0.04	0.982
C_{18}	28.12 ± 0.05	0.995		

1-mV chart recorder, as well as digitally by a Kiethley Model 177 microvoltmeter. The output from a stable power supply (2 mA) was measured by including a standard Leeds and Northrup 10.01 -Ω resistor in the PRT loop and measuring the emf drop across it before and after each cooling curve. The PRT was calibrated against a Leeds and Northrup certified PRT (Model 8163), and its resistance at the triple point of water was checked during the course of the measurements.

Enthalpies of transition were obtained in two ways: by using a simple, Dewar flask calorimeter, and by differential scanning calorimetry (DSC).

The Dewar flask was fitted with a cork stopper through which the sample could be inserted in such a way as to minimize any change in the heat leak during its introduction. The sample (20 g) was contained in a cylindrical metal can (originally containing 0.5 oz of Scotch Snuff, W. E. Garrett and Sons). The lid was soldered in place, and a length of $^1/_8$-in. copper tubing through which sample was introduced via syringe was soldered into its center. The tubing served as a support which held the can in the center of the Dewar flask when in place. Prior to insertion into the Dewar flask, the sample was maintained in a flowing helium bath inside a water thermostat, at a temperature above its melting point. The heat leak into the Dewar flask (containing 350 mL of magnetically stirred water at a temperature below ambient) was determined over 30 min and the sample was inserted.

The heat capacities of the Dewar calorimeter and of the metal can were obtained by measurng T_1, the initial temperature of the Dewar flask; T_2, the initial temperature of the can plus W g of water; and T_3, the final overall temperature, for several different values of W, via rigorous least-squares fitting of the data to the equation

$$(350 + C_{cal})(T_3 - T_1) = (W + C_{can})(T_2 - T_3) \qquad (1)$$

where C_{cal} and C_{can} are the heat capacities of interest.

Since the heat capacities of the liquid samples can be reliably estimated (*2*), but not those of the solid phases, it was decided to perform several runs with each hydrocarbon sample, keeping T_2 constant but varying the values of T_1. This allows estimation of the solid heat capacity as well as the enthalpy of crystallization via rigorous least-squares fitting of each set of temperatures to the equation

$$(350 + C_{cal})(T_3 - T_1) = \\ (C_{can} + C_s)(T_2 - T_{mp}) + \Delta H + (C_{can} + C_l)(T_{mp} - T_3) \qquad (2)$$

where everything is known but ΔH and C_s, the heat capacity of the solid phase in question.

The DSC used was a Perkin-Elmer DSC-2, in the Department of Materials Science and Engineering at Northwestern University.

The n-$C_{18}H_{38}$ (C_{18}) used as a reference herein was obtained from the Humphrey Chemical Co., the NDC from Chemical Samples Co., and the NDB from Wiley Chemical Co. (formerly Chemical Samples Co.). All samples were used as received.

Results

When either liquid was cooled, no solid phase was ever observed to form at the melting temperature. Instead, metastable solids were formed, and generally it was possible to observe the entire liquid–solid cooling curve before transition to the more stable crystal phase occurred. Table I presents temperatures of the four solid–liquid equilibria in question, as well as the melting point of C_{18}, included as a check on the apparatus and method. Since the more stable solid never formed directly from the liquid, the higher equilibrium temperature for each had to be determined from a warming curve by using samples that had stood long enough for the solid–solid transition to occur. The purities of NDC and NDB quoted in Table I were estimated from the cooling and warming curves by using the method of Rossini (*1*) and the appropriate enthalpies of fusion measured herein and given below.

Table II. Enthalpies of Fusion (cal g^{-1}) and Heat Capacities (cal g^{-1} K^{-1}) Used for Simple Calorimetry Results

compd	C_p^{l}	ΔH_f	C_p^{s}
NDC	0.522	47.7 ± 2.5	0.34 ± 0.14
NDB	0.506	25.6, 40.5[a]	
C_{18}	0.535	60.2 ± 2.2	0.35 ± 0.13

[a] See text.

Table III. Enthalpies of Fusion (cal g^{-1}) Estimated by DSC

compd	α→l	β→l	β→α
NDC	27.7 ± 0.4	48.5 ± 0.7	20.8 ± 0.8
NDB	25.7 ± 0.3	39.6 ± 0.6	13.9 ± 0.7

The results of the simple calorimetric determinations are presented in Table II, and those using DSC in Table III. Again C_{18} was included, in the simple calorimetry as a check of the apparatus and method, and in the DSC work as an internal standard to determine the "apparatus constant". The enthalpy of fusion of C_{18} was taken as 58.20 cal g^{-1} (*3*).

Discussion

There is good agreement between the melting point of C_{18} in Table I and the literature value of 301.3 K (3). Furthermore, there is no evidence of transitions below the melting point (from DSC scans) which come about as a consequence of the presence of C_{16} and/or C_{17} normal paraffin impurities in C_{18} (*4*). The melting range of NDC is given by Schlenk (*5*) as 41.9–42.4 °C, in good agreement with the value obtained from the warming curve in Table I. However, we were unable to reproduce the literature value for the melting point of NDB, 40 °C (*6*). A literature search leads us to believe that this value is not an experimental one but is probably based on a correlation of some kind.

It is worth noting that the estimates of purity based on the cooling curves are much more optimistic than those based on the warming curves. Gas-chromatographic analysis of the samples gives the following estimates of purity: C_{18}, 0.999; NDC, 0.947; NDB, 0.997. We can safely say that the estimate of purity for NDC based on the metastable solid–liquid equilibrium is seriously in error; it may be that the impurity is able to form a solid solution with the metastable phase, but not with the more stable (probably more tightly packed) phase. It follows that the equilibrium temperature may be somewhat higher than the 30.0 °C quoted in Table I.

The enthalpy of fusion of C_{18} measured by simple calorimetry (Table II) is within experimental error of the accepted value (58.2 cal g^{-1} (*3*)).

The method (described in the Experimental Section) used successfully for C_{18} and NDC gave very poor results for NDB. The explanation came to light after completion of the DSC experiments: its solid–solid transition is slow, and the time required for its completion increases as temperature increases. For the NDB runs, the initial Dewar flask temperature varied from 2.83 to 15.58 °C, and the solid material in the can at the end of the intermediate runs apparently consisted of varying amounts of the two solid phases in question. If we use the simple approximation that the solid heat capacity for NDB is the same as that of the liquid, and calculate a value for the enthalpy of fusion (from eq 2) for each of the seven runs for this compound, the results vary from 40.5 cal g^{-1} for the lowest temperature run to 25.6 cal g^{-1} for the highest. Comparison of these values with the DSC results in Table III indicates that the solid–solid transition was essentially complete at the end of the former and had not yet begun in the latter, a fortunate coincidence.

The DSC results in Table III stand in reasonable agreement with those in Table II. The NDC apparently goes through both transitions during the course of the simple calorimeter experiment.

It is well-known that normal paraffins containing from 19 to 36 carbon atoms undergo solid–solid phase transitions at temperatures not too far below their normal melting points (*3*, *7*, *8*). A general classification refers to the higher temperature solid phase as a "rotator" phase, denoted α, in which the molecules rotate about their long axes; and the lower temperature phase (actually comprising different crystal types for different chain lengths), in which that rotation is severely restricted, is denoted β. It seems likely that the two solid phases observed in the present study are manifestations of the same phenomenon, with the exception that the presence of the six-membered ring at the end of each chain appears to have interfered with the stability of the α phase to the extent that the β phase, when heated, goes directly to the liquid phase. That is, if the chains are loose enough to rotate, they are loose enough to come apart from one another. The α phase has been relegated to a metastable existence and appears only ephemerally when the liquid is cooled, the solidification process being kinetically controlled.

By coincidence, the C_{18} chosen as an internal reference in this study displays the same behavior on cooling, except that its metastable phase is much less stable than that of either NDC or NDB relative to its more stable phase. About half of the runs using DSC in which C_{18} liquid was cooled displayed supercooling, the onset of a relatively slow exotherm, and a sudden burst of heat. Mazee (*4*) refers to a metastable melting point for C_{18} at 300.7 K, 0.7 K below its normal melting point. Apparently in the case of C_{18} also, the rotator phase is, under conditions which are not well-defined, more readily formed from the melt than the more rigid β phase. It was impossible, however, to observe complete crystallization of the C_{18} α phase before spontaneous transformation to the β phase.

In the case of NDC, the DSC trace for cooling the liquid showed two completely isolated exotherms, the first being the liquid to α phase transition, and the second, the α to β transition. The latter is not an equilibrium transformation, and its peak could be observed even after cooling was stopped after the first transition. When an attempt was made to remelt the α phase of NDC immediately after its crystallization, the spontaneous α to β exotherm superimposed itself on the emerging endotherm. Thus in NDC, the α phase enjoys a greater stability relative to its phase than in C_{18}, and it may be ascribed to a greater difficulty associated with the cyclohexyl group's finding its niche in the β phase relative to a methyl group's ability to do so in the more nearly symmetric normal paraffins.

In the case of NDB, the DSC cooling trace showed only the liquid to metastable solid transition, unless the sample was cooled to temperatures near 0 °C. Only then was a second exotherm, analogous to the one in NDC, observed. Furthermore, it was a simple matter to reheat the α phase back through its transition to liquid without interference from the α to β transition. Apparently the β phase of NDB is the most difficult of the three substances studied to reestablish once it has been thermally disrupted.

This observation may be related to the fact that the literature melting pont for NDB was never observed in the present study. Our contention is that no one has actually observed it, though it may well have a "thermodynamic" existence. That is, if the 40 °C value is based on the melting points of the homologues of NDB, then, *if NDB exhibited the same crystal structure as those homologues*, its melting point would be 40 °C. We have not succeeded in observing that particular crystal phase.

Finally, it should be mentioned that a third crystal phase of NDB was occasionally observed in the DSC traces, but only on a freshly prepared sample. It never reappeared once the sample had been melted and recooled, even after standing for 2 weeks. When observed, its endotherm was always accompanied by a "shoulder" due to the β to liquid transition, so that reliable values for its melting point and enthalpy of fusion could not be obtained, but they are approximately 32–33 °C and 47 cal g^{-1}, respectively. Comparison of this enthalpy of fusion with those in Table III makes it tempting to call this "new" phase the β phase. Clearly X-ray work on these solids is called for in order to unravel their structures.

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Registry No. NDC, 22349-03-7; NDB, 29136-19-4.

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