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CALORIMETRIC INVESTIGATION OF THE MONOLAYERS FORMED AT SOLID-LIQUID INTERFACE[*]

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Abstract

Heat capacity measurements have been made to investigate the formation of two solid monolayers each of *n*-pentane, *n*-heptane and *n*-dodecane adsorbed on graphite, one at submonolayer coverages and the other coexisting with the liquid. At submonolayer coverages the monolayers are found to melt respectively at 99.8, 151.6, and 217.3 K, well below the bulk melting points. The monolayers coexisting with the liquid melted at 205.6 for heptane and at 287.8 K for dodecane, whereas no evidence was obtained for pentane on the formation of such solid monolayer above the bulk melting point. The order persisting in the liquid near the interface depends upon the length of the molecules. The dodecane monolayers showed another transitions below the melting points both at submonolayer and multilayer coverages.

Keywords: adsorption, heat capacity, solid-liquid interface, solid monolayer

Introduction

The adsorption of molecules from the liquid onto solid surfaces is one of the most interesting interfacial phenomena to be studied. The behavior of adsorbed molecules is determined by the balance of adsorbate-adsorbate and adsorbate-substrate interactions. These interactions are often comparable so that there is competition between several possible phases with comparable Gibbs energy. The characterization of such phases, however, is not so easy because of the presence of the condensed phases surrounding the adsorbed layers. Applying ordinary scattering techniques, such as X-ray or electron diffraction, to the solid/liquid interfaces to obtain any structural information is problem partly of having adequate penetration to the buried interface and partly of having the sensitivity to distinguish the surface layer from the bulk phases. In this respect the solid/liquid interface is quite distinct from the solid/vapor and liquid/vapor interfaces.

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We have recently demonstrated that incoherent elastic neutron scattering is a powerful tool for identifying and characterizing monolayers adsorbed from pure materials and solutions [1–5]. This technique can provide unambiguous information on the presence of solid monolayers coexisting with liquid adsorbate. We have also demonstrated that coherent neutron diffraction is still applicable to such systems to determine the two-dimensional structure [1, 2, 5]. However, these neutron scattering techniques are time consuming and somewhat awkward measurements to perform. Therefore, it would be more convenient to be able to survey the thermal behavior of the adsorbed systems with calorimetry.

In this study, we apply an adiabatic calorimetry to such system not only to delineate the phase behavior but also to obtain the thermodynamic quantities in detail. Here, we deal with three linear alkanes, *n*-pentane (C_5), *n*-heptane (C_7) and *n*-dodecane (C_{12}), adsorbed on the surface of graphite. Specifically, we investigate the heat capacity of those adsorbed monolayers at submonolayer and multilayer coverages.

Experimental

The adsorbent used was recompressed exfoliated graphite, Papyex (Le Carbone Lorraine). The specific surface area of the two specimens used for the present study was determined to be 14.0 and 16.6 $m^2 g^{-1}$ by adsorption isotherm measurements using nitrogen. The graphite substrates were outgassed under vacuum in an oven at 400°C before packed into the calorimeter.

Alkanes were obtained from Wako Pure Chemical Industries, Ltd. The minimum assay claimed by the supplier was 98.0 for pentane and 99.0% for heptane and dodecane. Pentane was purified once by vacuum distillation, whereas the others were used without any purification. The purity of each material was checked by measuring the bulk melting point as described below. Known quantities of the adsorbates were added either directly from the vapor phase (for pentane) or under an inert atmosphere of helium using a microsyringe (for heptane and dodecane). After the introduction into the calorimeter vessel, the samples were annealed at a temperature just below the boiling point. When estimating the amount of adsorbate to add to the substrate we have used estimates of the surface area per molecule [6] and the specific surface area of the particular sample of graphite. In this manner we can prepare samples with coverages in terms of a number of equivalent monolayers. From now on we refer to equivalent monolayers as monolayers, but, in each case, the true quantities of adsorbates are given in Table 1. The accuracy of the measurements of the amount of adsorbates was better than ±1%.

Two different kinds of calorimeter vessels (designated as #9805 and #9806), both of which were constructed of copper, were used in this study: The one (#9805) contained 9.16 g of Papyex with a specific surface area of 16.6 $m^2 g^{-1}$ and the other (#9806) contained 9.21 g of Papyex with 14.0 $m^2 g^{-1}$. The former, which was used for pentane, equipped a small needle valve to permit evacuation of the inside and introduction of the sample vapor into it. The latter had no valve and was used for heptane and dodecane. In this case the liquid sample was put in under helium atmosphere.

Table 1 Summary of the coverages explored in this study for *n*-pentane, *n*-heptane and *n*-dodecane adsorbed on Papyex. The monolayer capacity (n_0) for each system is assumed based on the Groszek model [6]

Material (Vessel)	n/mmol	n/n_0
n-pentane	0.550	0.80
(#9805)	2.063	3.00
	4.821	7.01
n-heptane	0.363	0.80
(#9806)	3.178	7.00
n-dodecane	0.233	0.80
(#9806)	2.043	7.00

A platinum resistance thermometer (MINCO Products, Inc.) was attached to each calorimeter. They were calibrated by us at Osaka University on the basis of ITS-90 [7] by intercomparison with another standard platinum thermometer. The heat capacity of the adsorbed layers was determined from the difference between that of calorimeter, adsorbent, and adsorbate, and that of the calorimeter and adsorbent only. An a.c. bridge (H. Tinsley & Co., Type 5840D) was employed for the automatic temperature measurement.

Results and discussion

Purity of materials

Before presenting the results for the monolayers, it should be noted beforehand that the materials we used were pure enough at least for the present purpose. Figure 1 illustrates a plot of melting temperature *vs*. ($1/F$) for the samples, where F is the fraction melted. For these measurements, we used another calorimeter vessel (#9605) that we normally apply to bulk samples. It also equipped a platinum thermometer (MINCO Products, Inc.) calibrated based on ITS-90. The inner volume of the vessel was 15 mL and we used 0.1055 mol of pentane, 0.09193 mol of heptane and 0.05665 mol of dodecane for each measurement. The purity was determined to be 99.70, 99.85 and 99.57%, respectively. The values of the bulk melting temperature for 'pure' materials, which we obtain at $1/F=0$ by extrapolation (Fig. 1), are in excellent agreement with the selected values reported in reference [8].

Submonolayer coverages

According to our neutron diffraction study [5], the solid monolayers at submonolayer coverages form an island on the graphite surface. Moreover, the monolayer at 0.8 monolayers can safely be recognized as the one without any other monolayer or the bulk on top of it. In our calorimetry, the contribution of the monolayer to the total heat capacity was extremely small and depended upon the material, the coverage, the

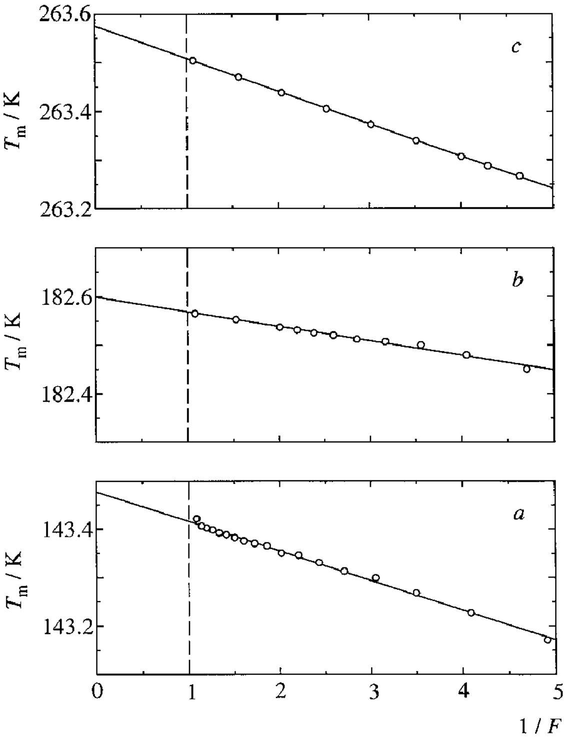

Fig. 1 A plot of melting temperature *vs.* (1/*F*) for the samples, where *F* is the fraction melted: a – *n*-pentane, b – *n*-heptane and c – *n*-dodecane

temperature and the calorimeter vessel used. For example, in the case of 0.8 monolayer samples, it was approximately 0.5% for any materials, irrespective of the vessel, over most of the temperature range except below 50 K and in the vicinity of the transitions where it became slightly larger. The resulting accuracy of the heat capacity measurement of such monolayers was estimated to be ±4% or better. The molar heat capacities determined for each material at 0.8 monolayers are illustrated in Fig. 2. The melting points of the solid monolayers were found to be 99.8 for pentane, 151.6 for heptane and 217.3 K for dodecane. They are substantially lower than those of the bulk solids (143.48 for pentane, 182.60 for heptane and 263.58 K for dodecane), which is normally observed in such two-dimensional system. For dodecane, an additional sharp anomaly due to a phase transition in the 2-D solid was found at 204.3 K, which is in contrast to the fact that the bulk solid exhibits no phase transition [8].

It should be pointed out that the molar heat capacities of all the monolayers at submonolayer coverages are substantially larger than that of the bulk solids [9]. For pentane, for example, the heat capacity of the solid monolayer at 50 K is 16% larger than that of the bulk solid [9] at the same temperature. One of the reasons for this is because of the softening of some of the intermolecular vibrations, which is evident

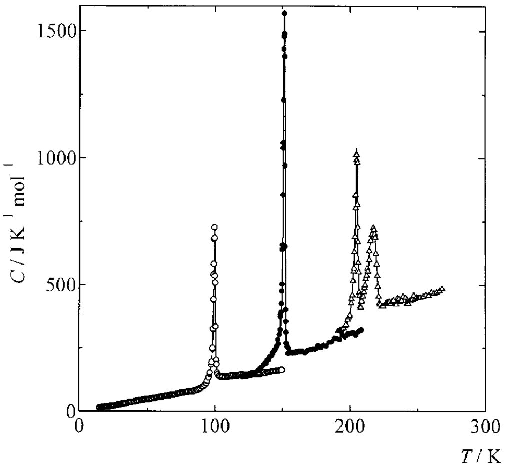

Fig. 2 Molar heat capacity as a function of temperature for 0.8 monolayers of *n*-pentane (o) , *n*-heptane (•) and *n*-dodecane (△) adsorbed on Papyex

when one considers the low-dimensionality. However, this could not explain the whole discrepancy successfully, particularly at higher temperatures. In fact, the difference becomes even larger. This could be ascribed to the floating of the monolayers away from the surface with increasing the temperature. One can describe this effect as a kind of desorption. However, so far we have no other experimental evidence on this.

Multilayer coverages

At higher coverages, the accuracy of the heat capacity measurement was much more improved. The molar heat capacity obtained for 7 monolayers of heptane is illustrated in Fig. 3. Also plotted in this figure is the intensity of incoherent elastic peak as a function of temperature for 10 monolayers of heptane [1]. At low temperatures, all the adsorbate is solid giving a strong elastic signal. As the bulk melting point is approached and crossed, the intensity falls significantly. Above the bulk melting point, there is still a significant residual intensity of the elastic peak. A simple calculation suggests that there is only a single layer adsorbed on the graphite [1] and that the molecules are predominantly lying their long axes parallel to the graphite surface, since Groszek's estimate of the area per molecule [6] was based on this molecular orientation. The residual intensity from the solid adsorbed layer is maintained to higher temperatures when the adsorbed layer melts and the elastic scattering falls to the level of the graphite background. This was clearly confirmed by the present heat capacity measurement: We observed a peak in heat capacity at 205.6 K. It should be noted here that the heat capacity results as well as the neutron scattering results clearly suggest premelting of the bulk solid. On the other hand, little can be said about the heat capacity anomaly at 150.3 K. It might be possible that some ma-

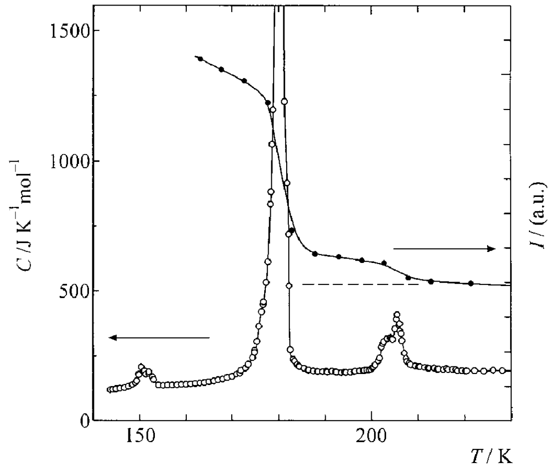

Fig. 3 Molar heat capacity as a function of temperature for 7 monolayers of *n*-heptane adsorbed on Papyex. The result of incoherent elastic neutron scattering [1] is also plotted, where the horizontal dashed line indicates the background level

terial stored in the pores or slits of the graphite substrate, if any, melts at such lower temperatures.

Figure 4 illustrates the molar heat capacity of 7 monolayers of dodecane as well as the incoherent elastic peak intensity for 5 monolayers. Both results showed premelting of the bulk solid. The heat capacity result clearly indicates that the solid monolayer existing with the liquid exhibits a phase transition at 283.2 K and melts at 287.8 K, whereas the neutron scattering result could not resolve those two anoma-

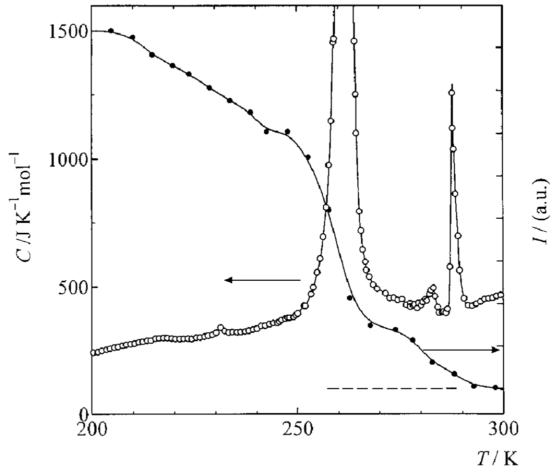

Fig. 4 Molar heat capacity as a function of temperature for 7 monolayers of *n*-dodecane adsorbed on Papyex. The result of incoherent elastic neutron scattering [1] is also plotted, where the horizontal dashed line indicates the background level

lies. Below the bulk melting point, one can notice a small peak and some bump in heat capacity, which is again possible effect of the material in the pores.

Unlike those two alkanes, pentane did not form any solid monolayer coexisting with the liquid: One can find some bump in heat capacity just below the bulk melting point both at 3 and 7 monolayer coverages (Fig. 5). This is presumably due to the monolayer melting: The solid monolayer of pentane already melts below the bulk melting point. A sharp anomaly at 127.9 K for 3 monolayers and at 129.0 K for 7 monolayers may be due to melting of the material in the pores.

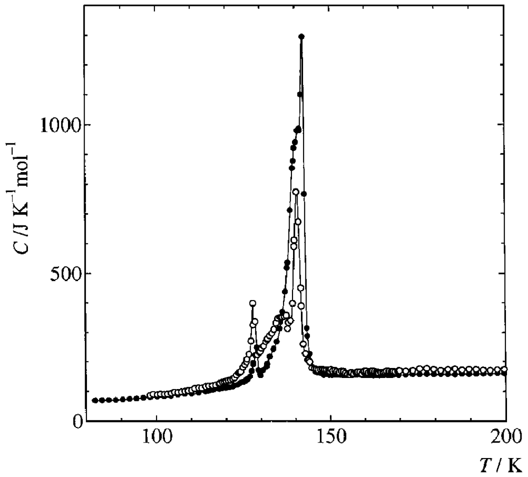

Fig. 5 Molar heat capacity as a function of temperature for 3 (○) and 7 (●) monolayers of *n*-pentane adsorbed on Papyex

Ordering near the interface

The temperatures, enthalpies and entropies of the monolayer transitions obtained in this study are summarized in Tables 2, 3 and 4 for pentane, heptane and dodecane, respectively. To determine the enthalpies and entropies, we assumed a base line in the heat capacity. The uncertainty does not exceed 5% of the absolute values. The values reported for bulk solids [8] are also listed in the Tables. One can find that the total entropies of the monolayer transitions are much smaller than the bulk melting entropy for all the alkanes investigated here, particularly at submonolayer coverages, indicating that the significant amount of order exists at the interface. It is interesting to know how far such surface effect reaches. When we compare the values obtained for pentane between 3 and 7 monolayer coverages (29.4 and 42.3 J K^{-1} mol^{-1}, respectively), a simple calculation gives us the mean melting entropy for the uppermost 4 layers as (42.3×7–29.4×3)/4=52.0 J K^{-1} mol^{-1}), which is still 11% smaller than the bulk value (58.55 J K^{-1} mol^{-1}). This means that the effect reaches beyond the 3 layers away in such linear molecules. It is also interesting to know how much effect is left in the adsorbate near the interface. When we take the difference in the transition entropies between 7 monolayers and the bulk (16.3, 27.8 and 40.2 J K^{-1} mol^{-1} for pen-

Table 2 Summary of the transition temperatures, enthalpies and entropies obtained for *n*-pentane adsorbed on Papyex

Coverage	*T*/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
0.8 monolayers	99.8	1.36	13.8
3 monolayers	127.9		
	140.5	3.90	29.4
7 monolayers	129.0		
	142.3	6.06	42.3
Bulk [8]	143.48	8.401	58.55

Table 3 Summary of the transition temperatures, enthalpies and entropies obtained for *n*-heptane adsorbed on Papyex

Coverage	*T*/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
0.8 monolayers	151.6	3.52	23.4
7 monolayers	150.3	0.24	1.6
	180.3	7.67	42.7
	205.6	0.96	4.7
		8.87	49.0
Bulk [8]	182.60	14.030	76.83

Table 4 Summary of the transition temperatures, enthalpies and entropies obtained for *n*-dodecane adsorbed on Papyex

Coverage	*T*/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
0.8 monolayers	204.3	2.00	9.8
	217.3	2.52	11.7
		4.52	21.5
7 monolayers	262.5	24.75	94.5
	283.2	0.22	0.8
	287.8	1.24	4.3
		26.21	99.6
Bulk [8]	263.58	36.84	139.77

tane, heptane and dodecane, respectively) which we can regard as a measure of the order left over the 7 layers, we notice that the order amounts to approximately 3.5 J K^{-1} mol^{-1} for each carbon atom. This is fairly large, corresponding to 30% of the bulk melting entropy for each carbon atom (approximately 11.5 J K^{-1} mol^{-1}). Such order exists in the liquid within the 7 layers near the interface.

Conclusions

The heat capacity measurements on heptane and dodecane at the interface of the liquid and a graphite substrate confirm the formation of solid monolayers above the bulk melting point. This parallels the behavior previously observed [1] by incoherent elastic neutron scattering as well as coherent neutron diffraction. Pentane, on the other hand, does not form the solid monolayer coexisting with the liquid. At submonolayer coverages, the monolayer melts well below the bulk melting point for all the alkanes. The transition entropy as well as the transition enthalpy is much suppressed in the monolayers and the effect reaches far and away from the interface. The amount of order persisting in the liquid near the interface depends upon the length of the molecules. For dodecane, the calorimetry indicates a new transition just below the monolayer melting both at submonolayer and multilayer coverages.

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