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## TRANSITIONS IN CHEMICALLY BONDED ORGANIC PHASES ON SILICA SPECIFIC HEAT MEASUREMENTS BY ADIABATIC CALORIMETRY

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### SUMMARY

Heat capacity data of silicas chemically bonded to *n*-octyl, *n*-octadecyl, amino-butyl and 2,4-dinitroanilinobutyl groups, and of the bare silicas Merckosorb and Nucleosil, have been measured as a function of temperature by adiabatic calorimetry. By subtracting the heat capacity data of the corresponding bare silica, values for the bonded phases are obtained. The alkyl phases show second-order transitions within the examined temperature range, the enthalpy and entropy of which have been evaluated. The results are related to chromatographic solute retention behaviour on bonded silicas and compared with data for the corresponding organic compounds.

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### INTRODUCTION

Sufficiently dense layers of organic molecules, chemically anchored to a silica surface, show heat-induced structural alterations. These alterations are reflected in an anomalous solute retention-temperature behaviour in chromatographic columns.

Morel and Serpinet<sup>1</sup> examined the gas-liquid chromatographic (GLC) retention of hexane on octadecyl silica (4.4  $\mu\text{moles}$  of  $\text{C}_{18}$  per  $\text{m}^2$ ) and concluded that this layer "melts" within the range of 280–300°K. On a  $\text{C}_{22}$  alkyl silica (4.32  $\mu\text{moles}$  of  $\text{C}_{22}$  per  $\text{m}^2$ ), these authors found a melting transition at 313–321°K. A coating of 3% *n*-heneicosane caused a rise of this range by 20°, whereas a 6% coating of squalane (a branched  $\text{C}_{36}\text{H}_{74}$  alkane) virtually prevented solidification of the  $\text{C}_{22}$  layer<sup>2</sup>. Kessaissia *et al.*<sup>3</sup> examined the retention behaviour of permanent gases on  $\text{C}_3$ -,  $\text{C}_6$ -,  $\text{C}_{10}$ -,  $\text{C}_{16}$ - and  $\text{C}_{20}$ -alkyl silicas (3.3  $\mu\text{moles}/\text{m}^2$ ) which show two transitions at about 198 and 253°K, respectively, and a third one, at a temperature which is dependent on the length of the bound chain; the first two were related to glassy transitions occurring in polyethylene of 50% crystallinity.

Riedo *et al.*<sup>4</sup> have investigated transitions in *n*-alkyl silicas and in mixed

phases, consisting of anchored chains and various *n*-alkanes acting as wetting agents, by means of contact angle measurements.

Gilpin and Squires<sup>5</sup> concluded from the high-performance liquid chromatographic (HPLC) retention data of phenol and resorcinol on C<sub>8</sub>-, C<sub>9</sub>- and C<sub>10</sub>-alkyl silicas, using water as eluent, that on heating the alkyl phases expand to a bristle-like configuration. Recently, Hammers and Verschoor<sup>6</sup> discussed the transitions in LiChrosorb RP-18, surface concentration 4.4 μmoles of C<sub>18</sub> per m<sup>2</sup>, in water. It was shown that on heating up to 352°K an initially "rough" RP-18 surface layer of a rather high adsorptive strength steadily and irreversibly expands to a bristle-like phase. On subsequent cooling this phase reversibly collapses to a "smooth" layer of regularly associated alkyl chains with a relatively low adsorptive strength. The high transition end-point temperature of a dense C<sub>18</sub> bonded phase in water (compared to that in carrier gas) is due to the stabilization of the layer structure by hydrophobic association of the alkyl chain ends that are in contact with water.

Low temperature GC retention occurs as a result of solute adsorption to a "crystalline" alkyl layer<sup>1,2</sup>, whereas in HPLC columns<sup>6</sup> solute adsorption in the alkyl-water interfacial layer prevails at any temperature. As data obtained under both types of conditions can only lead to tentative conclusions about the structural alterations at the surface of the alkyl layer, we attempted to obtain further information by measuring the heat capacity of the alkyl bulk by adiabatic calorimetry. In order to examine the effects of chain length, measurements on a C<sub>8</sub> and a C<sub>18</sub> bonded phase were performed. Moreover, two polar phases have been investigated: silica chemically bonded to aminobutyl groups, which may form hydrogen bonds with residual silanol groups<sup>7</sup>; and silica chemically bonded to dinitroanilinobutyl groups, between which polar interactions can plausibly be assumed. [It has been shown that in apolar solvents this layer has a more or less tiled-roof structure of associated groups, which is (partly) perturbed on heating<sup>8</sup>.] The four selected adsorbents seem to cover the most important structural features of the bonded phases applied in GLC and HPLC.

## EXPERIMENTAL

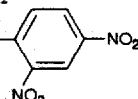
### *Adsorbent characterization*

The reference silicas were Merckosorb Si 100 (E. Merck, Darmstadt, F.R.G.) and Nucleosil 100-10 (Macherey, Nagel & Co., Düren, F.R.G.). The chemically bonded silicas LiChrosorb 10 RP-8 and RP-18 were supplied by Merck, whereas Nucleosil 10 NH<sub>2</sub> was obtained from Macherey, Nagel & Co. The latter was the starting material for 2,4-dinitroanilinobutyl silica (Nucleosil 10 DNAB), the preparation of which has been described previously<sup>8</sup>. The parent silicas have BET specific surface areas and mean pore diameters of 282 m<sup>2</sup>/g and 160 Å (LiChrosorb Si 100), and 388 m<sup>2</sup>/g and 180 Å (Nucleosil 100-10). The surface concentrations of the bound groups were determined by elemental analysis and are given in Table I. In view of the large RP-8 and RP-18 content, it cannot be ruled out that traces of water cause some polymerization of these alkyl layers during the silylation reaction.

### *Calorimetry*

The applied adiabatic calorimeter has been described in detail previously<sup>9</sup>. The

TABLE I  
CODE AND STRUCTURE OF THE EXAMINED BONDED PHASES

| Adsorbent                  | Bonded phase |   |   |
|----------------------------|--------------|---|---|
|                            | Code         | Structure   | Concentration<br>( $\mu\text{moles}/\text{m}^2$ ) |
| Merckosorb Si 100          |              |   |   |
| LiChrosorb 10 RP-8         | RP-8         | $-(\text{CH}_2)_7\text{CH}_3$   | 4.89  |
| LiChrosorb 10 RP-18        | RP-18        | $-(\text{CH}_2)_{17}\text{CH}_3$  | 4.39  |
| Nucleosil 100-10           |              |   |   |
| Nucleosil 10 $\text{NH}_2$ | AB           | $-(\text{CH}_2)_4\text{NH}_2$   | 2.13  |
| Nucleosil 10 DNAB          | DNAB         |  | 2.12  |

sample vessel was made of gold-plated silver (mass 28 g, internal volume 22  $\text{cm}^3$ ). For measurements below 90°K a new calorimeter was used. It was equipped with a gold plated copper vessel of mass 21 g and an internal volume 12  $\text{cm}^3$ . The heat capacities of the empty vessels were measured in separate runs and fitted with polynomial functions in overlapping temperature intervals of about 40°K. The standard errors of these fits did not exceed  $4 \cdot 10^{-3} \text{ J}/^\circ\text{K}$ . Small corrections for weight differences of the gold gaskets were applied.

The normal filling procedure includes sealing of the vessels in helium at 1000 Pa to enhance heat transfer. This procedure was not applicable to the present samples. No matter how careful the pressure was reduced, a sudden eruption in the finely divided powders (particle diameter 12  $\mu\text{m}$ ) almost emptied the vessels. Therefore, the vessels were closed after flushing the apparatus with helium at atmospheric pressure. The small correction for the heat capacity of the air-helium mixture in the vessels has been neglected. It will largely cancel when the data for the chemically bonded and the bare silicas are subtracted. Deterioration of the samples in air can be excluded; thermal stability of the phases in nitrogen and in air was established by thermal gravimetric analysis at 300–400°K.

The bare silicas were dried at 150°C for 3 days before use. The sample masses of the various materials ranged from about 2 to 4 g. An equilibration period of 2000 sec per measurement was maintained, which appeared to be sufficient in all cases. At a cooling rate of 75°K/h, consecutive experimental runs gave reproducible results. Hence, we conclude that the heat-induced structural changes discussed below are reversible under these conditions.

## RESULTS AND DISCUSSION

Randomly selected experimental results for Merckosorb (at 100–350°K) and for Nucleosil (at 10–350°K) are given in Table II. The heat capacities of the two silicas appear to be similar within error. Those for Nucleosil, from 30°K, and for Merckosorb, from 100°K, can be described by the polynomial:

$$C_p (\text{J}/^\circ\text{K} \cdot \text{g}) = -0.057 + 4.216 \cdot 10^{-3} T - 4.010 \cdot 10^{-6} T^2$$

TABLE II  
EXPERIMENTAL HEAT CAPACITIES OF THE BARE SILICAS

| <i>Merckosorb</i> |                                  |                 |                                  | <i>Nucleosil</i> |                                  |                 |                                  |
|-------------------|----------------------------------|-----------------|----------------------------------|------------------|----------------------------------|-----------------|----------------------------------|
| <i>T</i><br>(K)   | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K)  | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) |
| 100.43            | 0.31                             | 330.29          | 0.88                             | 8.90             | 0.003                            | 175.34          | 0.56                             |
| 113.65            | 0.36                             | 342.34          | 0.90                             | 12.35            | 0.007                            | 185.97          | 0.59                             |
| 121.88            | 0.39                             | 348.33          | 0.91                             | 15.01            | 0.010                            | 196.36          | 0.62                             |
| 133.60            | 0.43                             |                 |                                  | 21.21            | 0.051                            | 206.54          | 0.65                             |
| 141.09            | 0.46                             |                 |                                  | 24.26            | 0.068                            | 216.56          | 0.67                             |
| 155.53            | 0.50                             |                 |                                  | 31.58            | 0.089                            | 226.41          | 0.69                             |
| 165.98            | 0.53                             |                 |                                  | 40.35            | 0.11                             | 236.12          | 0.71                             |
| 176.16            | 0.56                             |                 |                                  | 51.62            | 0.15                             | 247.61          | 0.74                             |
| 199.11            | 0.62                             |                 |                                  | 60.27            | 0.18                             | 258.92          | 0.76                             |
| 211.82            | 0.65                             |                 |                                  | 70.02            | 0.21                             | 268.19          | 0.77                             |
| 230.47            | 0.69                             |                 |                                  | 77.02            | 0.24                             | 277.37          | 0.80                             |
| 248.71            | 0.73                             |                 |                                  | 86.81            | 0.27                             | 290.10          | 0.83                             |
| 257.72            | 0.75                             |                 |                                  | 99.55            | 0.32                             | 300.94          | 0.85                             |
| 269.56            | 0.77                             |                 |                                  | 111.05           | 0.36                             | 311.72          | 0.87                             |
| 278.36            | 0.79                             |                 |                                  | 121.74           | 0.40                             | 320.63          | 0.88                             |
| 295.75            | 0.83                             |                 |                                  | 131.86           | 0.43                             | 331.24          | 0.90                             |
| 305.81            | 0.84                             |                 |                                  | 141.56           | 0.46                             | 340.01          | 0.91                             |
| 311.18            | 0.87                             |                 |                                  | 153.21           | 0.50                             | 348.73          | 0.93                             |
| 321.18            | 0.87                             |                 |                                  | 164.44           | 0.53                             |                 |                                  |

TABLE III  
EXPERIMENTAL HEAT CAPACITIES OF THE EXAMINED ALKYL SILICAS

| <i>LiChrosorb RP-8</i> |                                  |                 |                                  | <i>LiChrosorb RP-18</i> |                                  |                 |                                  |
|------------------------|----------------------------------|-----------------|----------------------------------|-------------------------|----------------------------------|-----------------|----------------------------------|
| <i>T</i><br>(K)        | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K)         | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) |
| 8.52                   | 0.010                            | 171.54          | 0.69                             | 84.72                   | 0.39                             | 265.66          | 1.27                             |
| 10.77                  | 0.020                            | 183.92          | 0.73                             | 95.85                   | 0.41                             | 269.92          | 1.28                             |
| 20.83                  | 0.062                            | 195.07          | 0.76                             | 111.20                  | 0.47                             | 275.46          | 1.27                             |
| 31.17                  | 0.10                             | 209.55          | 0.80                             | 120.82                  | 0.51                             | 282.25          | 1.23                             |
| 41.06                  | 0.14                             | 216.65          | 0.82                             | 130.08                  | 0.54                             | 289.67          | 1.20                             |
| 50.50                  | 0.19                             | 227.16          | 0.84                             | 143.44                  | 0.59                             | 294.62          | 1.18                             |
| 60.27                  | 0.23                             | 240.92          | 0.87                             | 156.08                  | 0.64                             | 302.09          | 1.18                             |
| 70.93                  | 0.27                             | 251.07          | 0.90                             | 165.04                  | 0.67                             | 310.89          | 1.17                             |
| 81.25                  | 0.31                             | 261.09          | 0.92                             | 174.86                  | 0.71                             | 315.27          | 1.18                             |
| 92.52                  | 0.36                             | 270.98          | 0.94                             | 180.62                  | 0.73                             | 325.17          | 1.20                             |
| 100.78                 | 0.40                             | 280.75          | 0.96                             | 200.34                  | 0.81                             | 331.37          | 1.21                             |
| 111.20                 | 0.44                             | 292.07          | 0.99                             | 210.43                  | 0.86                             | 335.09          | 1.22                             |
| 120.92                 | 0.48                             | 310.89          | 1.04                             | 220.79                  | 0.91                             | 345.02          | 1.25                             |
| 130.14                 | 0.52                             | 325.51          | 1.06                             | 226.59                  | 0.95                             | 352.66          | 1.26                             |
| 141.11                 | 0.57                             | 331.95          | 1.08                             | 245.67                  | 1.10                             |                 |                                  |
| 151.61                 | 0.61                             | 341.53          | 1.10                             | 252.02                  | 1.15                             |                 |                                  |
| 161.73                 | 0.65                             | 347.88          | 1.12                             | 260.02                  | 1.23                             |                 |                                  |

TABLE IV

## EXPERIMENTAL HEAT CAPACITIES OF NUCLEOSIL AB AND DNAB

| <i>Nucleosil AB</i> |                                  |                 |                                  | <i>Nucleosil DNAB</i> |                                  |                 |                                  |
|---------------------|----------------------------------|-----------------|----------------------------------|-----------------------|----------------------------------|-----------------|----------------------------------|
| <i>T</i><br>(K)     | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K)       | <i>C<sub>p</sub></i><br>(J/°K·g) | <i>T</i><br>(K) | <i>C<sub>p</sub></i><br>(J/°K·g) |
| 93.06               | 0.36                             | 209.66          | 0.72                             | 7.55                  | 0.004                            | 220.98          | 0.76                             |
| 98.41               | 0.39                             | 221.09          | 0.75                             | 9.68                  | 0.007                            | 241.27          | 0.82                             |
| 103.55              | 0.42                             | 232.37          | 0.78                             | 20.02                 | 0.052                            | 260.94          | 0.88                             |
| 108.55              | 0.45                             | 243.49          | 0.81                             | 33.71                 | 0.105                            | 280.97          | 0.94                             |
| 113.41              | 0.47                             | 254.49          | 0.83                             | 42.99                 | 0.14                             | 296.26          | 0.99                             |
| 122.81              | 0.51                             | 268.96          | 0.88                             | 53.02                 | 0.18                             | 309.63          | 1.03                             |
| 131.88              | 0.54                             | 282.05          | 0.90                             | 73.42                 | 0.25                             | 321.17          | 1.06                             |
| 140.69              | 0.56                             | 294.36          | 0.95                             | 93.10                 | 0.32                             | 340.76          | 1.12                             |
| 149.29              | 0.58                             | 308.07          | 0.99                             | 113.88                | 0.40                             | 348.53          | 1.15                             |
| 161.90              | 0.60                             | 318.41          | 1.03                             | 128.25                | 0.45                             |                 |                                  |
| 170.12              | 0.62                             | 328.68          | 1.07                             | 148.30                | 0.52                             |                 |                                  |
| 178.23              | 0.64                             | 338.84          | 1.12                             | 167.61                | 0.59                             |                 |                                  |
| 186.22              | 0.66                             | 345.56          | 1.15                             | 186.15                | 0.65                             |                 |                                  |
| 198.04              | 0.69                             | 352.25          | 1.18                             | 201.93                | 0.70                             |                 |                                  |

The standard error of this fit, based on 180 data, is equal to  $4 \cdot 10^{-3}$  J/°K·g. This equation was used to evaluate the heat capacity data for the various bonded phases. The experimental results for the chemically bonded silicas are given in the Tables III and IV, and represent random selections of roughly equally spaced data from the total experimental set.

The heat capacity curve for the RP-8 phase in Fig. 1 shows a very broad

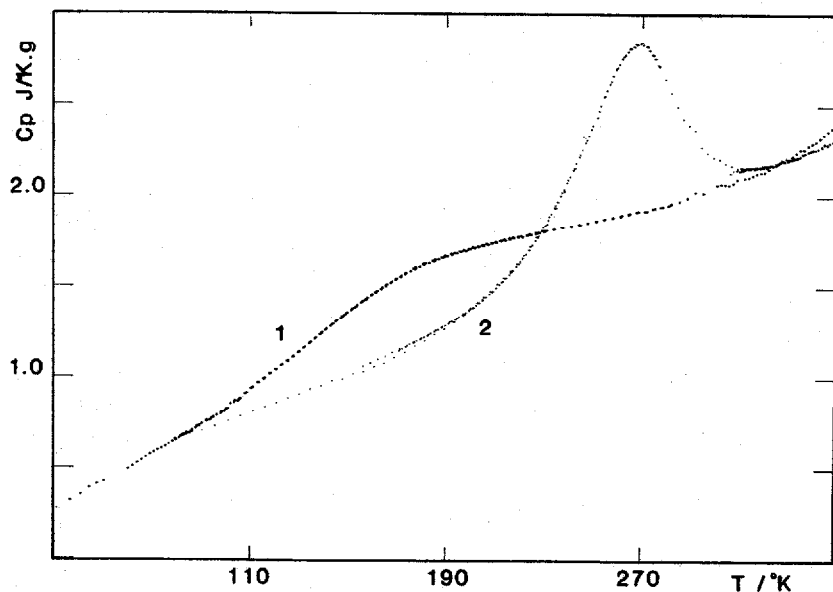


Fig. 1. Experimental heat capacity curves for the RP-8 (1) and the RP-18 phase (2) as a function of temperature.

transition ranging from 80 to 300°K, too large to construct an accurate baseline. By drawing a linear baseline between the data points at 70 and 310°K, rough estimates for the enthalpy and the entropy of the transition were obtained. Integration of the incremental  $\Delta C_p$  values yields  $\Delta H_{tr} \approx 41.8$  J/g, and of  $\Delta C_p/T$  values yields  $\Delta S_{tr} \approx 0.24$  J/°K · g.

The heat capacity curve for the RP-18 phase in Fig. 1 shows a pronounced second-order transition between 150 and 305°K with a maximum at 270°K. Its endpoint at 305°K is close to the melting point of *n*-octadecane (301.3°K). The baseline was computed using an iterative method. First, the data between 90 and 140°K and those between 310 and 350°K were fitted with linear regressions denoted by  $y_1$  and  $y_2$ , respectively. As a first approximation a linear baseline was used to estimate the transition enthalpy. An improved baseline was then computed at every experimental temperature,  $T$ , using the formula

$$\text{baseline value} = y_2 F + y_1 (1 - F)$$

wherein  $F$  is the fraction of the transition enthalpy at that temperature  $T$ . This procedure was repeated till no further change of the baseline occurred. The final result is presented in Fig. 2, together with the  $\Delta C_p$  curve. Integration yields  $\Delta H_{tr} = 57.3$  J/g and  $\Delta S_{tr} = 0.225$  J/°K · g.

Comparison of the calorimetric and the GC transition range of the RP-18 phase (150–305 and 280–300°K, respectively) shows that the RP-18 phase is only penetrable to solute molecules like hexane beyond a certain degree of thermal expansion. Distinct surface transitions in the solid state at 198 and 253°K, observed by

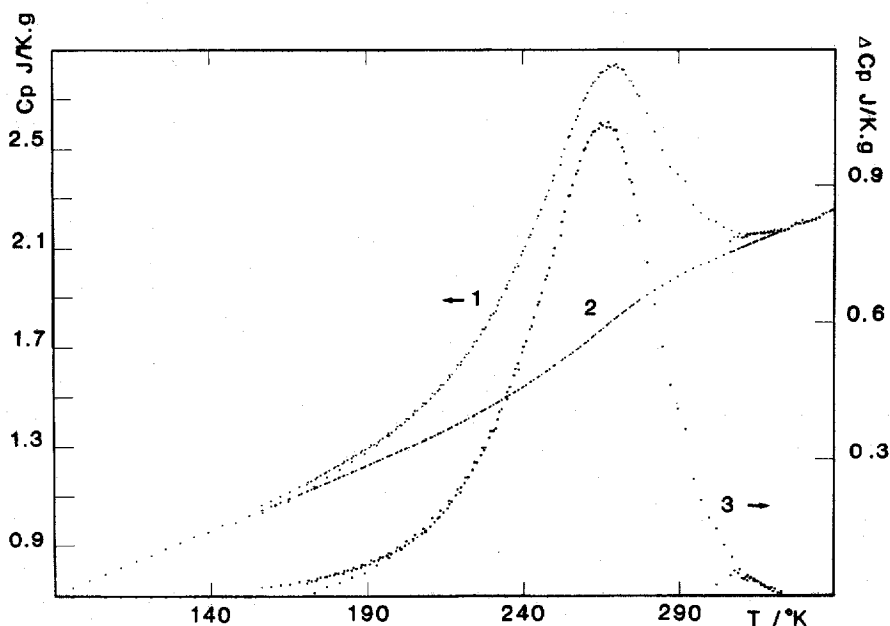


Fig. 2. Experimental heat capacity curves for the RP-18 phase (1) and for the computed baseline (2), and the resulting  $\Delta C_p$  curve (3) as a function of temperature.

Kessaissia *et al.*<sup>3</sup> on their home-made alkyl silicas, are not apparent from the heat capacity curves for our alkyl silicas. Obviously, the latter "crystallize" without a considerable amount of kink defects<sup>10</sup>. On the other hand, strictly regular crystalline phases of alkyl chains anchored to an irregular surface of a porous silica can hardly be expected. For that reason the transition range is broad, in particular for RP-8.

Comparison of the data for RP-18 and *n*-octadecane in Table V shows that the transition end-point of the former and the melting point of the latter are roughly similar. The same holds for the  $C_p$  values. In both respects, the RP-8 phase behaves differently in comparison with *n*-octane. This is expected because the bonding to silica will affect the thermal behaviour of a layer of short chains more strongly than that of a layer consisting of long chains. The bonding to silica significantly reduces the transition enthalpy and entropy, as is concluded from the ratios of the transition and melting data given in Table V.  $\Delta H_{tr.}/\Delta H_m$  is equal to 0.230 ( $C_8$ ) and 0.236 ( $C_{18}$ ), whereas the corresponding  $\Delta S_{tr.}/\Delta S_m$  ratios are 0.283 and 0.278, respectively. Note that these values are independent of the alkyl chain length.

TABLE V

THERMODYNAMIC DATA FOR THE BONDED PHASES AND THE CORRESPONDING ORGANIC COMPOUNDS

| Compound                           | Bonded phase |                  |                       |                         |            |                  |                           |                             |
|------------------------------------|--------------|------------------|-----------------------|-------------------------|------------|------------------|---------------------------|-----------------------------|
|                                    | $T$<br>(K)   | $C_p$<br>(J°K·g) | $\Delta H_m$<br>(J/g) | $\Delta S_m$<br>(J°K·g) | $T$<br>(K) | $C_p$<br>(J°K·g) | $\Delta H_{tr.}$<br>(J/g) | $\Delta S_{tr.}$<br>(J°K·g) |
| <i>n</i> -Octane <sup>13</sup>     | 90           | 0.82             |                       |                         | 90         | 0.74             |                           |                             |
|                                    | 300          | 2.23             |                       |                         | 300        | 2.05             |                           |                             |
|                                    | 216.36       |                  | 181.6                 | 0.84                    | 70-310     |                  | 41.8                      | 0.24                        |
| <i>n</i> -Octadecane <sup>14</sup> | 90           | 0.71             |                       |                         |            | 0.71             |                           |                             |
|                                    | 300          | 2.22             |                       |                         |            | 2.18             |                           |                             |
|                                    | 301.3        |                  | 243                   | 0.81                    | 150-305    |                  | 57.3                      | 0.225                       |
| <i>n</i> -Butylamine <sup>15</sup> | 300          | 2.65             |                       |                         | 300        | 2.95             |                           |                             |
| Dinitroaniline                     |              |                  |                       |                         | 90         | 0.42             |                           |                             |
|                                    |              |                  |                       |                         | 300        | 1.76             |                           |                             |

The heat capacity curves for the aminobutyl (AB) and 2,4-dinitroanilinobutyl (DNAB) phases are given in Fig. 3. Owing to the relatively small weight fraction of AB groups on Nucleosil, the estimated error of the  $C_p$  data is rather large: about 10% at 90°K and 5% at 300°K. As a result there is no conclusive evidence for a transition around 130°K, but the onset of a transition at 250°K is significant; it may be connected with the desorption of amino groups from the silica surface. It is estimated that about 4  $\mu\text{moles}/\text{m}^2$  of residual silanol groups are present on AB silica, which will have a strong affinity to the amino groups. Recently, Grime and Sexton<sup>11</sup> have suggested this type of interaction on the basis of enthalpimetric titration curves for aminopropyl silica. X-ray photoelectron spectra obtained by Carley *et al.*<sup>12</sup> seem to point to adsorbed aminopropyl groups as well.

The heat capacity curve for DNAB is very smooth. From 100 to 350°K the data can be described with the polynomial:

$$C_p \text{ (J/°K·g)} = -0.33 + 1.017 \cdot 10^{-2} T - 2.842 \cdot 10^{-5} T^2 + 5.915 \cdot 10^{-8} T^3$$

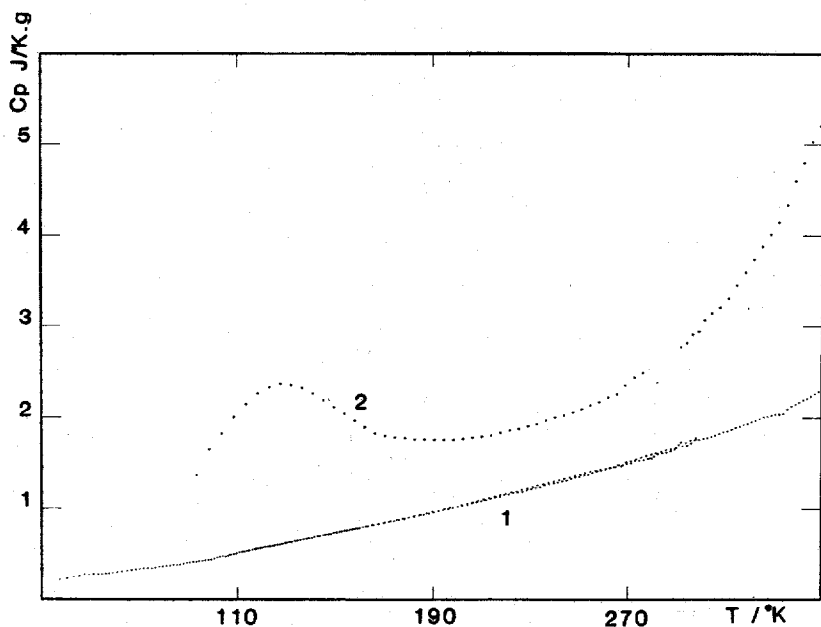


Fig. 3. Experimental heat capacity curves for the 2,4-dinitroanilinobutyl phase (1) and the aminobutyl phase (2) as a function of temperature.

The standard error of this fit is equal to  $0.01 \text{ J}/^\circ\text{K} \cdot \text{g}$ . The increase of the  $C_p$  data with increasing temperature will be largely due to a steady decrease of the polar interactions in the associated layer of dinitroanilino groups and the resulting enhanced freedom of motion of the DNAB groups. This explanation is compatible with the slow relaxation of the layer structure after abrupt temperature jumps, reflected in solute adsorption data on DNAB silica in apolar eluents, at 283, 298 and 313°K (ref. 8).

## CONCLUSIONS

Adiabatic calorimetry has proved to be an excellent method to examine the thermodynamic bulk properties of bonded phases, provided the mass of organic material in the sample is larger than 100 mg.

Dense layers of *n*-octyl and of *n*-octadecyl groups bound to porous silica show second-order transitions between 70 and 310°K and 150 and 305°K. These transitions show some similarity with a melting process, in particular for the octadecyl phase. On the other hand, the transition enthalpy and entropy values of both alkyl phases are only one fourth of the melting enthalpies and entropies of the corresponding *n*-alkanes. Transitions due to "kink defects" are not apparent in dense octyl and octadecyl phases. The transition end-point of RP-18 is very similar to that of RP-8 and close to that observed from GC retention data on a  $C_{18}$  phase of comparable density.

The aminobutyl and the dinitroanilinobutyl phases do not show second-order transitions at temperatures up to 350°K. The increase of the heat capacities with



increasing temperature on these phases is largely attributed to a decrease of hydrogen bonding on the former, and of polar interactions between the DNAB groups on the latter, accompanied by an increase in motional freedom of the bound ligands.

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