

# Unusual behavior of the specific heat of 2,6-lutidine in a porous medium: Orientational transition in a layer?

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Experiments reveal a dip on the temperature dependence of the specific heat in a mixture of 2,6-lutidine with water in a porous glass and also in pure 2,6-lutidine in a porous glass. This dip can be interpreted as a phase transition in a surface layer. © 1995 American Institute of Physics.

Experiments have shown that polar liquids which do not have mesogenic phases in their interior may form an orientationally ordered layer on a glass surface. The thickness of this layer can reach several hundred angstroms. Such layers have been observed in nitrobenzene, among several other substances.

Studying a mixture of 2,6-lutidine and water in porous glass, we observed an unusual behavior of the specific heat: a dip in a rather narrow temperature interval. We believe that this behavior can be explained in terms of a phase transition in a layer of lutidine which forms on the surface of the porous glass.

## 1. EXPERIMENTAL PROCEDURE AND RESULTS

For our study of the behavior of the specific heat near the critical mixing point of a binary mixture in a bounded volume, we selected a mixture of 2,6-lutidine and water with a lower critical mixing point in the interior at a critical temperature  $T_c = 33.644 \pm 0.001^\circ\text{C}$  and a critical concentration  $x_c = 0.29 \pm 0.01$  (this is the weight fraction of lutidine) in porous glass. The typical size of the pores of the glass matrix was  $d \approx 1000 \text{ \AA}$ ; the surface area of the matrix was  $\approx 5.2 \text{ m}^2$  (the specific surface area was  $s \approx 20 \text{ m}^2/\text{cm}^3$ ). The surface of the matrix was not subjected to any special treatment, aside from being held at  $T = 200^\circ\text{C}$  for about 2 h before the matrix was filled with the sample. The specific heat was measured in a scanning mode (the scanning rate was  $\approx 5 \text{ K/h}$ ) on a precision adiabatic calorimeter<sup>1</sup> with a cell volume of  $0.29 \text{ cm}^3$ . The apparatus was based on an Aksamit A data acquisition system.

In addition to the anomaly in the specific heat at  $T = 34.15^\circ\text{C}$ , associated with a separation transition, we observed a dip (Fig. 1), which can lie either above or below the separation temperature, depending on the lutidine concentration. The amplitude of the dip decreases with decreasing lutidine concentration, becoming comparable to the experimental error at  $x < 0.015$  wt. fraction of lutidine. It was found that this effect is not peculiar to the binary mixture: It also occurs in pure lutidine in porous glass (Fig. 2). This behavior of the specific heat is not observed in the interior anywhere in the range of measurement temperatures, from 0 to  $100^\circ\text{C}$ . The dip is therefore associated with two circumstances: the presence of the large glass surface and the presence of the lutidine.

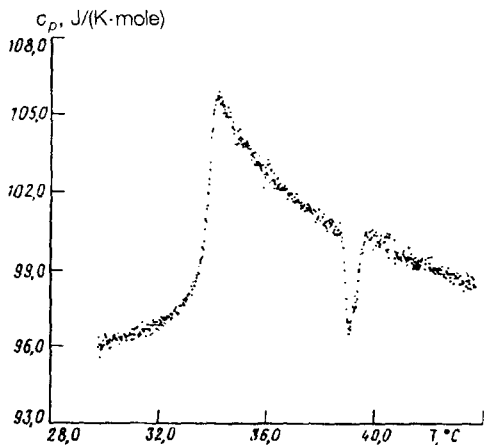


FIG. 1. Specific heat of a mixture of 2,6-lutidine and water in porous glass.  $d \approx 1000 \text{ \AA}$ ,  $s \approx 20 \text{ m}^2/\text{cm}^3$ ,  $x = 0.323$  mole fraction of lutidine.

To verify that the observed effect is exclusively a surface effect, we measured the specific heat of pure lutidine in porous glass with a matrix surface area  $\approx 26 \text{ m}^2$  (with a specific surface area  $s \approx 100 \text{ m}^2/\text{cm}^3$  and a typical pore size  $d \approx 100 \text{ \AA}$ ). The integrated heat of the dip increases in proportion to the surface area of the porous matrix (Fig. 3), although the amount of lutidine in the matrix is smaller by a factor of about 3. The specific heat of the effect in pure lutidine is  $(2.9 \pm 0.1) \times 10^{-3} \text{ J/m}^2$ . To study the equilibrium nature of this effect, we also carried out measurements at scanning rate of 0.3 and 20 K/h. The results were found to be reproducible within the experimental scatter of the points.

## 2. DISCUSSION OF RESULTS

What is the physical nature of this effect? The behavior of the specific heat near the dip is similar to a diffuse first-order phase transition with heat liberation. However, all known bulk phase transitions are accompanied by either an absorption of heat (a diffuse

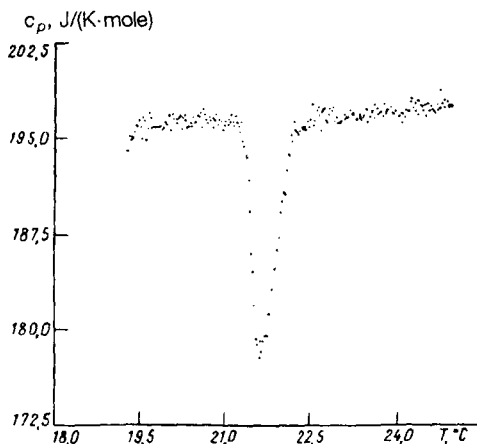


FIG. 2. Specific heat of 2,6-lutidine in porous glass.  $d \approx 1000 \text{ \AA}$ ,  $s \approx 20 \text{ m}^2/\text{cm}^3$ .

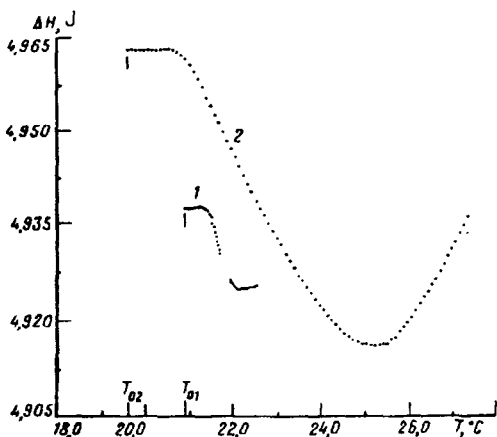


FIG. 3. Behavior of the enthalpy of 2,6-lutidine in different porous glasses near the dip on the curve of the specific heat:  $\Delta H = H(T) - (\partial H / \partial T)_{T=T_{0i}}(T - T_{0i})$ . 1— $d \approx 1000 \text{ \AA}$ ,  $s \approx 20 \text{ m}^2/\text{cm}^3$ ; 2— $d \approx 100 \text{ \AA}$ ,  $s \approx 100 \text{ m}^2/\text{cm}^3$ .

$\delta$ -function in the specific heat), if this is a first-order transition, or an anomalous increase in the specific heat or an abrupt jump in the case of second-order phase transitions. In other words, the behavior of the specific heat near bulk phase transitions is the opposite of that which we have observed here. This behavior of the specific heat cannot be explained by Landau's phenomenological theory. We therefore suggest that the dip in the specific heat of lutidine is due to a distinctive feature of a transition in a surface layer.

A layer of lutidine adsorbs on the surface of the glass matrix. This conclusion follows from the shift of the separation curve for the mixture of 2,6-lutidine and water in porous glass, toward higher concentrations, in comparison with the separation curve in the interior. It was established in Refs. 2 and 3 that polar benzene-monomonsubstituted liquids (nitrobenzene, aniline, and acetophenone) form homeotropically oriented layers on a lyophilic glass surface. Lutidine belongs to this class of liquids. We therefore suggest that a layer of lutidine which forms on the surface of porous glass is also orientationally ordered. Possible phase transitions involving an interaction of the liquid with the surface, of a wetting type (a transition from a macroscopically oriented layer on the surface to a microscopic layer) or involving a change in orientation (from homeotropic to inclined) of the lutidine dipoles with respect to the glass surface, do not lead to a dip in the specific heat. The reason for the singularity-like decrease in the specific heat may be an abrupt change in the surface energy or a deformation of the oriented layer (in this case the thermal effect should depend on the size of the pores, but no such dependence is observed experimentally). At the very least, the specific heat of the dip is on the same order of magnitude as the surface energy.

Formally, the total (measurable) specific heat  $C$  can be written as the sum of a bulk part  $C_b$  and a surface part  $C_s$ :  $C = C_b + C_s$ . In a sense, it is the surface component of the specific heat which exhibits the unusual behavior. This assertion is demonstrated by Fig. 3, which shows the enthalpy of lutidine versus the temperature near the dip; the regular part, associated with the bulk specific heat, has been subtracted here. The decrease in enthalpy is evidence of heat evolution, which leads to the dip in the measured specific

heat. The temperature interval of the dip is apparently governed by the inhomogeneity of the surface, which is equivalent to an impurity in the case of a bulk phase transition.

We also measured the specific heat of nitrobenzene in porous glass with a typical pore size  $d \approx 100 \text{ \AA}$ . At  $T \approx 145^\circ\text{C}$ , we observed a dip on the plot of the specific heat versus the temperature, as in lutidine. In this case, however, the dip spanned a broader temperature interval, and the specific heat was larger ( $\approx 10^{-2} \text{ J/m}^2$ ). These differences may be due to the sizes of the dipole moments of the lutidine and nitrobenzene molecules. We cannot say just which specific mechanism could lead to such an unusual behavior of the specific heat. There are no theoretical hints here. However, the observation of a dip in the specific heat of lutidine and nitrobenzene, which are polar liquids, is evidence that this observed effect is somewhat general.

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<sup>1</sup>L. V. Entov *et al.*, *Int. J. Thermophysics* **14**, 221 (1993).

<sup>2</sup>B. V. Deryagin *et al.*, *Dokl. Akad. Nauk SSSR* **262**, 853 (1982) [*Sov. Phys. Dokl.* **27**, 121 (1982)].

<sup>3</sup>B. V. Deryagin and Yu. M. Popovskiĭ, *Kolloidn. Zh.* **44**, 863 (1982).

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