The Liquid–Vapour Transition in Monolayers of n-Pentadecanoic Acid at the Air/Water Interface

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Using recently developed methods for surface manometry, the first-order two-dimensional phase transition from vapour to liquid in monolayers of ultra-pure n-pentadecanoic acid at the interface between air and aqueous 10^{-2} mol dm^{-3} HCl has been studied at temperatures from the triple point (17 °C) to 40 °C. Contrary to previous reports, the critical temperature is well above 40 °C. It was not possible with the apparatus and methods developed to date to determine the critical temperature, which is probably in the range of 50–60 °C. The latent heat of the phase transition was obtained as a function of temperature.

The phase transitions in monolayers of n-pentadecanoic acid have been studied in detail as part of a program to establish definitive criteria for surface manometry with insoluble monolayers at the air/water interface. Results published to date have established the equilibrium spreading pressures[1] and the characteristics of the liquid–solid (l/s) and liquid–vapour (l/v) transitions for n-pentadecanoic acid monolayers at 25 °C on aqueous 10^{-2} mol dm^{-3} HCl.[2,3] The spreading transitions for n-hexadecanoic and n-tetradecanoic acids on 10^{-2} mol dm^{-3} HCl have also been described,[1] and the thermodynamically predicted effects of electric fields applied normal to the interface in two-phase and single-phase regions of the isotherms for n-pentadecanoic and n-octadecanoic acids have been demonstrated.[4] These results have accounted for published variations in equilibrium spreading pressures and have demonstrated that the well known degenerate form of the so-called liquid-expanded to liquid-condensed transition is the result of a number of experimental artefacts.[3] This transition is, in fact, simply first-order in behaviour, and will usually correspond to a liquid–solid transition.

In this paper we examine the liquid–vapour transition in monolayers of n-penta-decanoic acid on 10^{-2} mol dm^{-3} HCl as a function of temperature. It will be shown that earlier estimates of the two-dimensional critical temperature[12,13] are too low owing to incorrect estimation of the densities of the coexisting phases as the result of incomplete experimental techniques. The new results are used to estimate the enthalpy of the transition.

Experimental

The techniques for surface manometry and for the purification of hexane, HCl, n-pentacanoic acid and water have been described in detail, as have the methods for controlling humidity and temperature.[2,5] These techniques have proved adequate for monolayer studies up to 40 °C. At higher temperatures we have not so far obtained reliable results because of problems in spreading and difficulties with the behaviour of photocells and related electrical circuitry at high water vapour pressures.

Salient features of the experiments presented here are the use of clear silica troughs

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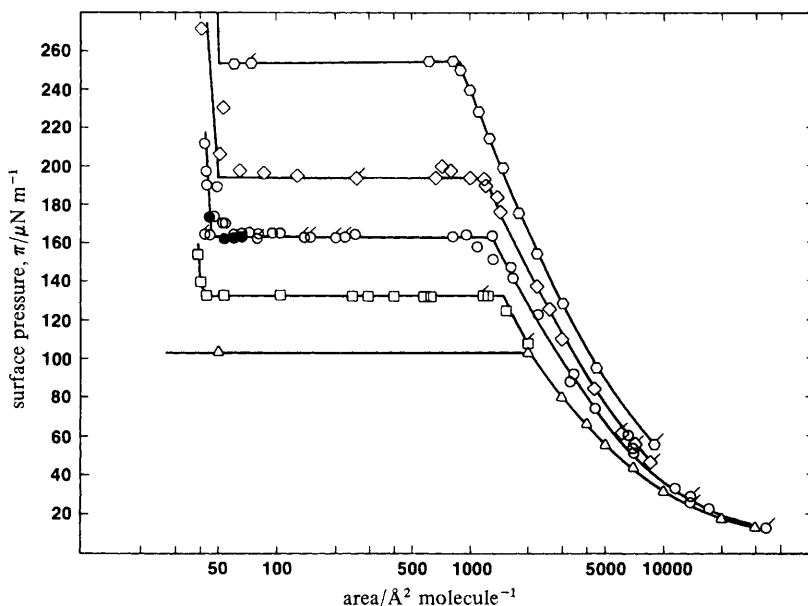‡ Present address: Electro-Biology, Inc., Fairfield, New Jersey 07006, U.S.A.

Fig. 1. π *vs.* A isotherms for monolayers of n-pentadecanoic acid at the air/10^{-2} mol dm^{-3} HCl interface in the gaseous and liquid–vapour transition regions at several temperatures: □, 20; ○, 25; ◇, 30; ○, 40 °C. Single-shot spreadings indicated by ╱ as in ◔. Results by spreading from a crystal at 25 °C and subsequent expansion indicated by filled circles.[2] The isotherm at 15 °C (Δ) is for the solid–vapour transition below the triple point (data from Iwahashi, using the same experimental systems[15]).

which were roasted clean after each short series of experiments on a given day, the rigorous purification of water and monolayer substance (99.95% pure), spreading from n-hexane by single-shot or successive aliquots of fatty-acid solution, and the use of monolayer expansion methods using sliding barriers. The shapes of the isotherms were also confirmed by spreading monolayers from the solid in the absence of solvents followed by expansion using the barriers. Most of the results presented here were obtained by the Wilhelmy method, with glass plates in the absence of waxes or Vaseline. Some were measured with paper plates or by the use of a horizontal float and threads, with excellent agreement in surface pressures between the methods. None of the data were obtained by the commonly used monolayer compression method, which is a major source of large errors at low monolayer pressures. The reproducibility of the monolayer pressure is ± 1 μN m^{-1}, and the monolayer areas were reproducible to $\pm 2\%$, corresponding to the precision of the horizontal float method as described previously.[2]

Results and Discussion

The experimental results of the study of the l/v phase transition region for n-pentadecanoic acid monolayers on 10^{-2} mol dm^{-3} HCl at temperatures from 15 to 40 °C are collected in fig. 1. The experimental surface pressures (π) range is below 300 μN m^{-1}, and results were obtained out to 3.0×10^4 Å^2 molecule^{-1}. The triple point for n-pentadecanoic acid is close to 17 °C.[6-8] The isotherm at 15 °C thus represents a sublimation from the two-dimensional solid to vapour. In all cases the phase transitions are first-order, a conclusion confirmed by the large fluctuations in the surface potentials observed in the transition regions over the entire temperature range.[4, 8] The transition

Table 1. Experimental results for the liquid–vapour transition in n-pentadecanoic acid monolayers at the air/10^{-2} mol dm^{-3} HCl interface, and for the vapour–solid transition at 15 °C (molecular areas in the coexisting phases given in Å^2)

$T/$°C	π_{t}/μN m^{-1}	A(vapour)	A(liquid)
20	132	1500	41.5
25	162	1300	43.5
30	192	1200	47.2
40	252	850	51.0
15	102	2000	—

pressures and the molecular areas for the coexisting liquid and vapour monolayers are shown in table 1.

Adam and Jessop[9] measured the l/v transition pressure at 20 °C, finding a value in fair agreement with the results given here. Their range of constant π was much narrower than shown in fig. 1, probably owing to impurities causing π to rise as the dense end of the transition is approached. Hawkins and Benedek[10] studied the transition for monolayers on water, which implies that the n-pentadecanoic acid in the monolayer was ionised to an extent depending on the surface density.[11] It seems probable that their measurements were also complicated by artefacts arising from impurities in their system. Kim and Cannell[12] examined the transition over a temperature range from 15 to 35 °C, and some features of their data agree well with the results presented here, particularly in the values of the transition pressure at lower temperatures. The densities of the coexisting phases given by Kim and Cannell are, however, different from those shown in fig. 1 and table 1. The range of the region of constant pressure they describe is much narrower than we find, giving high densities to the vapour and low densities to the liquid phases in coexistence. Kim and Cannell also give surface potentials for n-pentadecanoic acid, showing the range of fluctuations observed in the l/v transition region.[13] The upper and lower limits of these fluctuations can be used to estimate the highest density of the vapour phase and the lowest density of the liquid phase in coexistence at the one temperature at which surface potentials were measured (20.1 °C). We estimate these limiting densities as 10×10^{-4} and 150×10^{-4} molecule Å^{-2} as against 16.5×10^{-4} and 122×10^{-4} interpolated from their tabulated values obtained from surface pressure isotherms. Our results at 20 °C are 6.7×10^{-4} and 240×10^{-4} molecule Å^{-2} for the densities of the coexisting vapour and liquid phases, as indicated by our pressure isotherms and confirmed by surface potentials in our system.[8] We conclude that the results of Kim and Cannell are affected by residual impurities, particularly in their sample of n-pentadecanoic acid, for which no analysis was given. Their isotherms show a rise in surface pressure as the dense end of the phase transition is approached, much as we have observed for less pure samples than that studied in this paper.[2]

Because of their incorrect identification of the range of the l/v transition, Kim and Cannell concluded that the two-dimensional critical temperature (T_{c}) for n-pentadecanoic acid monolayers on 10^{-2} mol dm^{-3} HCl is 26.27 °C and went on to calculate several critical exponents from their data, concluding that mean field theory gives a good account of the coexistence envelope for the transition. As will be clear from fig. 1, the critical temperature is much higher than 40 °C, and we have not been able to reach the critical point with the apparatus used in this series of experiments. Attempts to work at 50 °C have given very unsatisfactory results. Another apparatus will be necessary either to protect the photocells and circuitry from the high water vapour pressures or to use
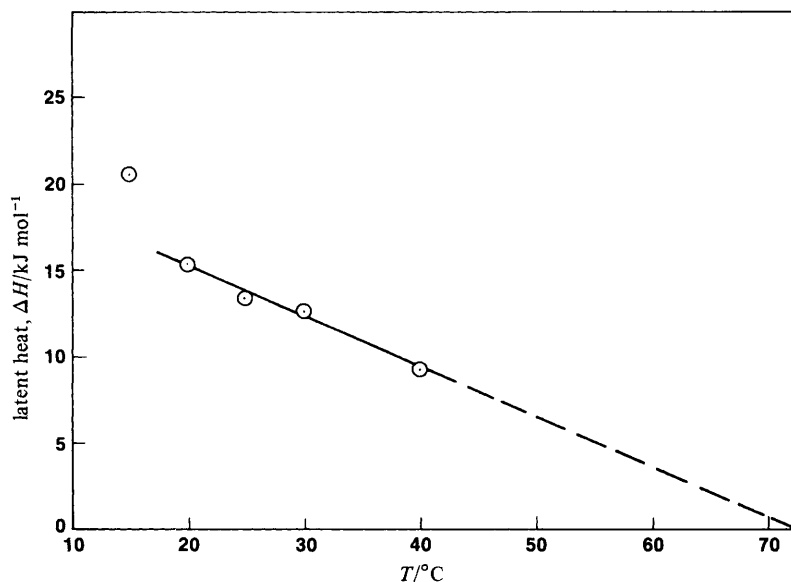
Fig. 2. The heat of vaporisation for the liquid–vapour transition in monolayers of n-pentadecanoic acid at the air/10^{-2} mol dm^{-3} HCl interface as a function of temperature. Note that at 15 °C the monolayer sublimates. The triple point is at *ca*. 17 °C.

alternative manometric methods. Spreading will also need further study at higher temperatures, and even if all these practical problems are solved the monolayer may prove either too soluble or too volatile to give useful results.

Over the range 20–40 °C the l/v transition pressure varies very linearly with temperature by 6.0 μN m^{-1} K^{-1}. Kim and Cannel give 6.7 μN m^{-1} K^{-1} over a smaller range of temperatures up to 26 °C. From the two-dimensional form of the Clausius equation for the transition pressure (π_t)

$$\frac{\mathrm{d}\pi_t}{\mathrm{d}T} = \frac{\Delta H}{T\Delta A}$$

where ΔA is the difference in molecular area across the transition, the enthalpy of evaporation (ΔH) for the transition may be calculated, as shown in fig. 2. ΔH varies linearly with temperature, corresponding to a difference in the constant-pressure heat capacity between the vapour and liquid states of 300 J mol^{-1} K^{-1}. The linear variation of the transition pressure continues to 15 °C, where the transition is a sublimation. The estimated sublimation heat is shown on the figure. It lies off the line for the heats of the l/v transition, allowing a rough estimate of the heat of the solid–liquid transition at 3.5 kJ mol^{-1}.

From the results shown in fig. 2, an extrapolation may be made to zero ΔH, as would apply at the critical temperature. The temperature so obtained is 71 °C. If the usual pattern of ΔH variation with temperature near T_c applies, then T_c will be well below 71 °C. Another estimate of T_c can be made by assuming that the critical exponent β for the dependence of the density difference across the transition ($\Delta\Gamma$) on the temperature near the critical point is 0.5, as required by mean-field theory,[14] and using the data from table 1 to extrapolate to zero $\Delta\Gamma$. From the densities at 30 and 40 °C the value of T_c so obtained is 51 °C. A value 10 °C or more above the highest temperature for which a reliable experimental isotherm has been measured seems acceptable from a consideration of the isothermal compressibilities (K) of the two-dimensional vapour at the
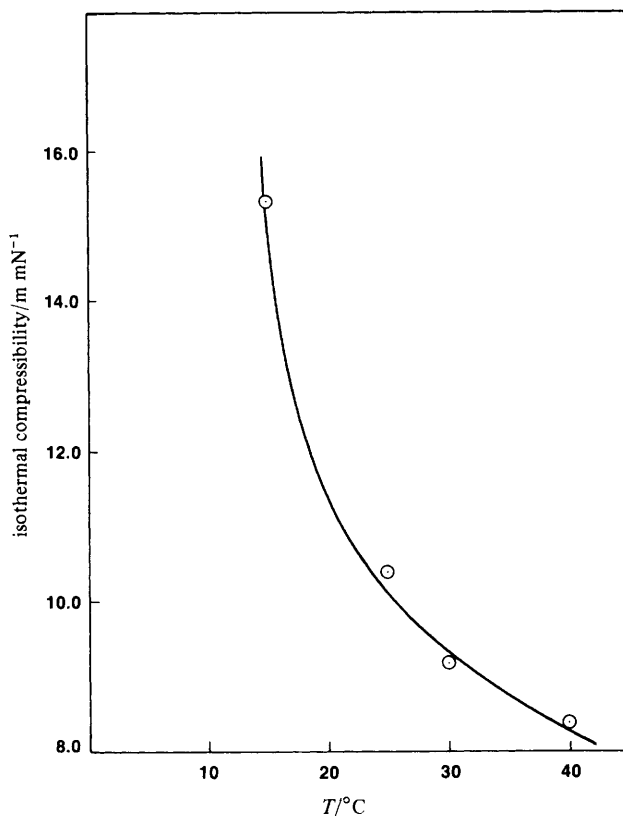
Fig. 3. Isothermal compressibilities for n-pentadecanoic acid vapour at the transition pressure at several temperatures. Compressibilities estimated graphically as the limiting slope at the transition from the isotherms of fig. 1. The data are insufficient for an estimate at 20 °C.

transition pressures, as estimated graphically and shown in fig. 3. Near the critical point K will rise rapidly to infinity. At the experimental temperatures K falls with increasing temperature, with some indication of reaching a minimum. Taking all these leads, T_c is probably in the region 50–60 °C, near the melting point (54 °C) for the solid fatty acid and in a difficult range for future experiment. There is little guidance in the data on the applicability of mean field or Ising theory to the transition.

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