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# Energy and Entropy of Formation of Crystalline 1-Pentadecanoic Acid from the Ideal Gaseous Monolayer at the Air/Water Interface

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The Helmholtz free energies of compression of monolayers of 1-pentadecanoic acid at the air/aqueous HCl solution interface have been estimated from the two-dimensional gas region to the equilibrium spreading pressure at three temperatures. The free energies are used to obtain the energy and the entropy of formation of the crystalline fatty acid from an ideal two-dimensional gas at the aqueous interface. By comparison with published data on the sublimation of solid fatty acids, the energy and entropy of adsorption of the ideal three-dimensional fatty acid vapor to the ideal two-dimensional vapor at the air/aqueous HCl interface are estimated. The sum of the calculated changes of entropy for the loss of one degree of translational freedom and for the loss of the entire configurational entropy of the alkyl chain is close to the estimated standard entropy of adsorption.

## Introduction

The properties of monolayers of 1-pentadecanoic acid at the air/water interface have been studied in detail recently. The results have provided surface manometric standards for monolayer phase transitions, including the transition from solid crystal to monolayer at the equilibrium spreading pressure.[1,2] The so-called liquid-expanded to liquid-condensed phase transition was shown to be first order.[3] This transition is better described as a liquid to condensed transition. Thermodynamic functions for this transition and for the two-dimensional gas–liquid transition were also obtained.[4] The available data allow two further sets of estimates of interest, namely the second virial coefficients for the gaseous monolayers[5] and the thermodynamic functions for the formation of the three-dimensional crystalline 1-pentadecanoic acid from the ideal two-dimensional gaseous state in the monolayer. The thermodynamics of crystal formation is the subject of this paper.

## Experimental Section

The methods used to obtain isotherms for monolayers of 1-pentadecanoic acid on aqueous $10^{-2}$ mol dm$^{-3}$ HCl, for purifying the substances used and for controlling humidity and temperature have all been fully described.[1,2,6] The experimental precautions required to obtain accurate data include rigorous cleaning and purification, checking for spreading artifacts, and the use of monolayer expansion methods using sliding barriers. The results to be used in this paper we obtained in a series of experiments over a surface pressure range from 10 µN m$^{-1}$ to 20 mN m$^{-1}$ and a range of molecular areas from $3.5 \times 10^4$ to 20 Å$^2$ molecule$^{-1}$. The reproducibility of the pressures was ±1 µN m$^{-1}$

in the lowest pressures, ranging up to ±0.1 mN m$^{-1}$ at the highest pressures. The molecular areas were reproducible to ±2%.

## Results

The experimental results will not be recapitulated here. The largest components of the Helmholtz free energies of compression are from the isotherms in the gaseous region and from the two-phase transitions (gas to liquid and liquid to condensed).[3,4] Complete isotherms from $3.5 \times 10^4$ to 20 Å$^2$ per molecule reaching from the dilute (near-ideal) gas region to the equilibrium spreading pressure are available at 15, 25, and 30 °C. The dilute gas region is readily represented by a virial plot from which the second virial coefficient may be obtained.[5] At the dense end of the isotherms, at equilibrium with the crystal phase, the pressures are known accurately.[2]

The Helmholtz free energy of compression per molecule in the monolayer is given by

$$\Delta F = -\int_{A_1}^{A_2} \pi \, dA \tag{1}$$

where $\pi$ is the surface pressure and $A$ the area per molecule. We choose $A_1$ as $10^5$ Å$^2$ molecule$^{-1}$, at which area the monolayer is essentially ideal at all three temperatures. For purposes of integration, $A_1$ is readily accessible by a short extrapolation from the data at the highest experimental areas using a virial plot. We choose $A_2$ as 20 Å$^2$ molecule$^{-1}$ corresponding to the measured values on the films at the equilibrium spreading pressure. The imprecision in determining $A_2$ (~2%) introduces unimportant errors in the integral for the Helmholtz free energy. The integrations were performed graphically to give the results shown in Figure 1.

The variation of $\Delta F$ with temperature is linear. From the slope the energy and entropy for the compression are calculated. Since the chemical potentials of 1-pentadecanoic acid in the crystal and monolayer at the equilibrium spreading pressure are identical, the energy and entropy of compression calculated from the results of Figure 1 give the energy and entropy of formation of the crystal from an ideal monolayer at a standard state of $10^5$ Å$^2$ molecule$^{-1}$. The energy of crystal formation is calculated as −55 kJ mol$^{-1}$ and the corresponding entropy as −222 J mol$^{-1}$ K$^{-1}$. It is difficult to estimate the potential errors in these results. The plot in Figure 1 is quite linear and the integrations summarize numerous experimental results, tending to improve the statistical quality of the

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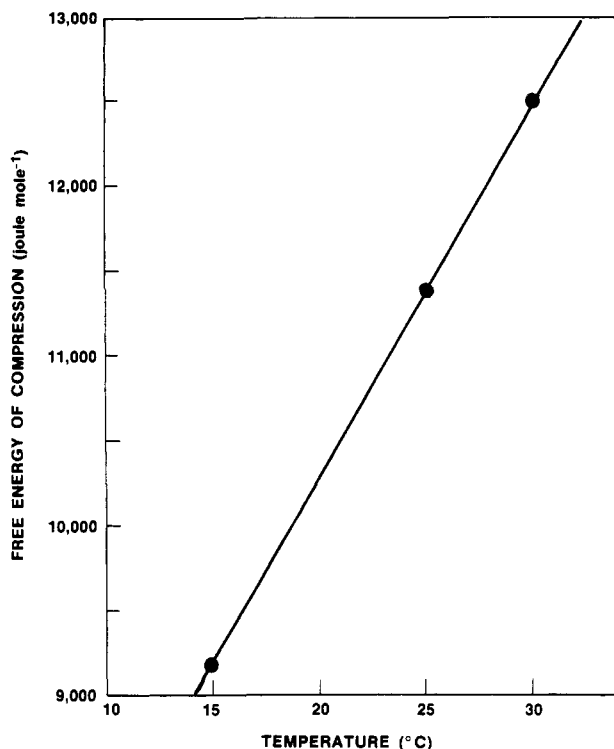(6) Pallas, N. R.; Pethica, B. A. *Colloids Surf.* **1983**, *6*, 221.

**Figure 1.** Helmholtz free energy of compression of a monolayer of 1-pentadecanoic acid from $10^5$ to 20 $Å^2$/molecule.

results. We accordingly estimate that the energy and entropy results are good to better than ±10%.

## Discussion

Davies and Malpas[7] report the sublimation vapor pressures and the derived enthalpies and entropies for a series of fatty acids with even number carbon atoms. Davies[8] also gives data on the sublimation of the odd-numbered fatty acids taken from an unpublished thesis by Thomas at the University of Wales in 1959. Plots of the heats and entropies of sublimation for the even-numbered acids show a reasonably linear trend with chain length, whereas the points are more scattered with the odd-numbered acids. Noting that the thermodynamic properties of paraffins and their derivatives form two series for odd and even numbers of carbon atoms,[9] we consider that the best estimates for the enthalpy and entropy of formation of crystalline 1-pentadecanoic acid from the ideal vapor will be given by averaging the values of the corresponding functions for the $C_{13}$, $C_{15}$, and $C_{17}$ acids given by Davies.[8] These enthalpies are close to the energies of sublimation, which are the same as the lattice energies but of opposite sign. We take 160 kJ mol$^{-1}$ for the energy of sublimation of 1-pentadecanoic acid, for comparison with 55 kJ mol$^{-1}$ for the energy of transfer from a crystal to an ideal two-dimensional vapor on the $10^{-2}$ mol dm$^{-3}$ HCl aqueous solution surface. Correspondingly we take 365 J mol$^{-1}$ K$^{-1}$ for the sublimation entropy of pentadecanoic acid to a standard state of 1 atm.

The experimental temperature range in the monolayer studies was from 15 to 30 °C, and in the sublimation studies from approximately 38 to 52 °C. Since the experimental results in either series show no variation of the energy and entropy with temperature, the comparison of the two sets

of results will be made on the basis of calculations at 25 °C. The crystals in contact with water will contain an unknown but very small amount of water, introducing minor corrections which will not be taken into account.

The energy of transfer from the crystal to the two-dimensional vapor (55 kJ mol$^{-1}$) is largely made up of the sum of the latent heats for the three-phase transitions corresponding to crystal to equilibrium monolayer at the spreading pressure[2] (17 kJ mol$^{-1}$), condensed to liquid monolayer[3] (18 kJ mol$^{-1}$), and liquid to vapor[4] (13 kJ mol$^{-1}$). The latent heats quoted are at 25 °C for the spreading and liquid–vapor transitions and at 27.5 °C for the condensed to liquid transition. Comparison with the energy of sublimation of the crystal to an ideal three-dimensional vapor from Davies[8] (160 kJ mol$^{-1}$) shows that the energy (or enthalpy) of adsorption of the three-dimensional vapor to form a two-dimensional vapor at the air/water interface is −105 kJ mol$^{-1}$. The entropies of formation of the crystal from three- and two-dimensional vapors in their standard states are −365 and −222 J mol$^{-1}$ K$^{-1}$, respectively. Hence the entropy of transfer from the ideal three-dimensional vapor at 1 atm to the ideal two-dimensional vapor at $10^5$ $Å^2$ molecule (corresponding to a surface pressure of 4.04 $\mu$N m$^{-1}$ at 25 °C) is −143 J mol$^{-1}$ K$^{-1}$.

Using the relevant forms of the Sackur–Tetrode equation for the translational entropies in three- and two-dimensions at the chosen standard states gives a difference of only −19 J mol$^{-1}$ K$^{-1}$. The decrease in entropy on transfer from the three-dimensional to the two-dimensional vapor is therefore 124 J mol$^{-1}$ K$^{-1}$ more than expected from the translational restriction. This excess loss of entropy is almost exactly 14 $R$ ln 3, equivalent to the loss of the configurational entropy of the chain. Whether this implies that the chains are extended on the surface at low density with substantial potential barriers to conformation changes due to van der Waals interaction with the water is uncertain since the contributions from the head group and vicinal water are unknown.

Clint et al.[10] have estimated the standard enthalpies and entropies of adsorption of short-chain 1-alkanols from the vapor to the surface of unacidified water, using experimental data on the solubilities of the alkanols in water, the surface tensions of dilute alkanol solutions, and the vapor pressures of the pure alkanols. The dependence of the estimated enthalpies and entropies on chain length up to $C_5$ is quite linear. Making the large extrapolation to $C_{15}$ gives the enthalpy of adsorption of 1-pentadecanol vapor to water as −120 kJ mol$^{-1}$, similar to the corresponding enthalpy for 1-pentadecanoic acid (−105 kJ mol$^{-1}$).

For the entropies of adsorption, the large extrapolation to $C_{15}$ gives approximately −200 J mol$^{-1}$ K$^{-1}$ for 1-pentadecanol for the standard states used in this paper, as compared to the value of −143 J mol$^{-1}$ K$^{-1}$ given above for 1-pentadecanoic acid. The thermodynamic calculations for the alkanols involve several assumptions. The saturated solutions of each immiscible alcohol in water are assumed ideal and the corresponding heats of dilution are taken as zero. Close examination of the surface tension–concentration data for the alcohol solutions suggests that the initial slopes are underestimated at lower temperatures and longer chain lengths. The best that may be concluded from these comparisons is that the estimated thermodynamic changes on adsorption of pentadecanol are similar to those for the fatty acid.

Further insight into the interpretation of the contribution of the alkyl chain to the adsorption of 1-penta-

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decanoic acid vapor to the two-dimensional state would be provided by thermodynamic data on the adsorption of the vapors of *n*-alkanes to the liquid water interface. The data available, however, are conflicting. Jones and Ottewill[11] give standard heats and entropies of adsorption for four *n*-alkanes ($C_5$ to $C_8$) derived from measurements over a range of temperatures of the lowering of the surface tension of water as a function of alkane vapor pressure. Extrapolating their standard enthalpies of adsorption to a $C_{14}$ chain length gives approximately $-58$ kJ mol$^{-1}$, much smaller than the estimate for 1-pentadecanoic acid given above.

The standard entropies of adsorption of the alkanes given by these authors vary little with chain length and are said to correspond closely with the loss of one degree of translational freedom only. These negative entropies of alkane adsorption, for the standard states used here, are about one-eighth of the corresponding entropy of adsorption for 1-pentadecanoic acid vapor. This strongly suggests that their results are unreliable, not least because configurational terms would be expected to give a chain-length dependence for the entropy of adsorption.

Later data for adsorption of alkane vapors to liquid water at lower surface and vapor pressures than those given by Jones and Ottewill were reported by Hauxwell.[12] These data are also for the four *n*-alkanes from $C_5$ to $C_8$ and have been analyzed to give a consistent set of standard

thermodynamic functions for adsorption.[12,13] Extrapolating the standard enthalpies to a $C_{14}$ alkane chain length gives about $-80$ kJ mol$^{-1}$, below the value obtained above for 1-pentadecanoic acid ($-105$ kJ mol$^{-1}$), suggesting a contribution to the enthalpy of adsorption from the carboxyl group. The extrapolation to $C_{14}$ chain length is reasonably acceptable since these *n*-alkane adsorption enthalpies extrapolate to near zero at zero chain length. Extrapolation of the standard entropies of alkane adsorption obtained from Hauxwell's results (adjusted to the standard states used here) to longer chain lengths gives an estimate of $-130$ J mol$^{-1}$ K$^{-1}$ for a $C_{14}$ alkane vapor. This value may be compared to $-143$ J mol$^{-1}$ K$^{-1}$ for the adsorption of 1-pentadecanoic acid. The difference between these two values, if significant, may indicate that the carboxyl group contributes to the loss of entropy on adsorption of the vapor.

**Registry No.** HCl, 7647-01-0; 1-pentadecanoic acid, 1002-84-2.

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