The Effect of Monovalent Ions on a Langmuir Monolayer

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Introduction

It has long been understood that divalent ions in the aqueous subphase below a Langmuir monolayer aggregate toward the negatively charged surface of deprotonated headgroups, and alter the structure and properties of the organic monolayer. However, no effect of monovalent ions has ever been detected, and alkalis such as NaOH are routinely used to change the pH without concern about unintended effects [1].

Recently [2], a series of weak peaks has been observed in the diffraction pattern from fatty acid monolayers with divalent cadmium ions in the subphase, and assigned as a 2x3 supercell of the main monolayer. It is assumed that the cadmium ions form a superlattice underneath the organic monolayer. A later study, by our group, showed that there exists a small pH 'window' within which this superlattice is seen and in which the monolayer structure is chiral [3]. Since the interaction of the ions with the headgroup is very sensitive to the pH, it is instructive to study whether the monovalent ion introduced in raising the pH plays any role, and whether the ionic interactions can be affected or controlled by a proper choice of the alkali.

Methods and Materials

Heneicosanoic acid was spread on a series of basic dilute (10-4M) aqueous solutions of cadmium chloride. The pH was raised to 8.5 with the hydroxides of various group 1A elements: lithium, sodium, potassium and cesium. The temperature was held at 9°C and the film was compressed to a pressure slightly above zero. Because the organic monolayer is a powder, it was not possible to determine the in-plane components K_x and K_y individually, but only the combination K_{xy}.

Results

The K_{xy} positions remained constant for all the peaks in the diffraction pattern; however, quite unexpectedly, the intensity of each peak varied systematically as a function of different alkali species. Firstly, there was a remarkable enhance-ment in the intensity of the weak superlattice peak when cesium hydroxide was used. Different ions increased the intensity of the 'weak' peak from low to high in the order: Li^+, K^+, Na^+, Cs^+,. Secondly, the effect on the intensity of the main peaks varied from low to high in approximately the opposite order: Cs^+, Na^+, K^+, Li^+ The two extreme cases are shown in Fig. 1.

Discussion

These observations are more easily explained if the ‘superlattice’ peaks are not from a separate ionic lattice of Cd^{2+}, but are due to a variable modulation of the organic lattice. In that case, a gain in intensity of ‘superlattice’ peaks will be offset by a loss of intensity of the integer-order peaks.

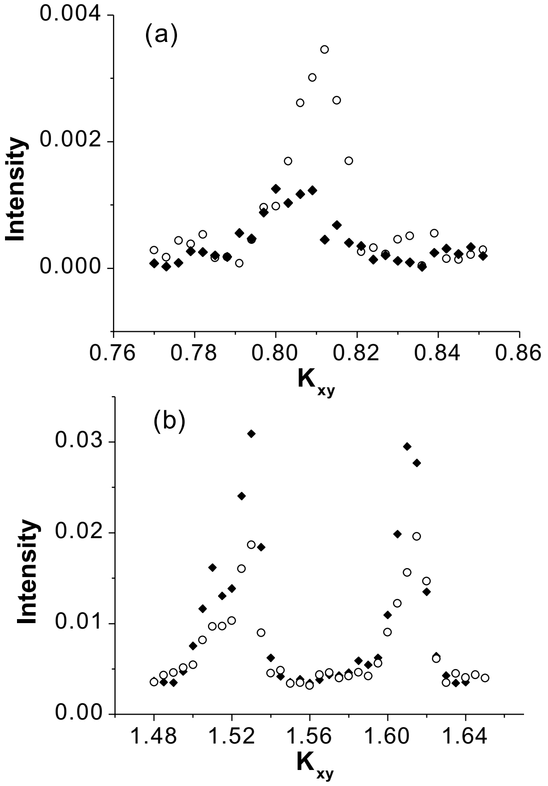

Fig. 1. Comparison of normalized diffraction intensities of (a) a superlattice’diffraction peak and (b) the main (integer order) peaks, with the monovalent ions cesium (o) and lithuim (♦).

Acknowledgments

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