Preface

The thesis presents classical atomistic molecular dynamics (MD) simulation studies of the microscopic properties of surfactant aggregates at interfaces and the effects of ethanol on regular membrane properties. The thesis consists of two parts (Part A and Part B). In Part A, we have investigated the structural and dynamical properties of self-assembled monolayers of different types of surfactants adsorbed at air/water and oil/water interfaces. The distribution of ethanol in a model phospholipid membrane at different concentrations and its influence on the properties of the membrane have been studied in Part B.

Part A:

This part consists of six chapters. The primary focus of each of the chapters and the important findings obtained there from are highlighted below.

Chapter 1 presents a brief overview of the current status of knowledge on surfactant assemblies in solutions and at interfaces. Special emphasis has been given on highlighting the experimental, theoretical, and computer simulation studies on surfactant aggregates at vapor/liquid, liquid/liquid, and solid/liquid interfaces. Some important issues in this area and the scope of the present work are also discussed.

Chapter 2 discusses the microscopic structure and dynamics of monolayers of nonionic surfactant $C_{12}E_2$ (monododecyl diethylene glycol) adsorbed at the air/water interface using MD simulation methods. The simulation has been performed at a constant volume and at room temperature with a surface coverage corresponding to that at the critical micelle concentration or cmc. It is observed that there is a significant roughness developed at the interface, and the estimated average thickness of the adsorbed layer has been found to be in excellent agreement with experimental data. A strong tendency for the water molecules to form hydrogen-bonded bridged structures between the adjacent oxygen atoms of the oxyethylene headgroups has been noticed. This resulted in an exclusive preference for headgroup conformations with C–C bonds in gauche form. The translational and

dynamics in the hydration layer of a DMPC lipid bilayer have been explored. The calculations are carried out using the trajectory obtained from the DMPC bilayer simulation with a lipid/ethanol ratio of 1:1. It is noticed that in the presence of ethanol, the hydrogen bonds between the lipid phosphate groups and water molecules exhibit faster dynamics than that in the pure bilayer system. Both water and ethanol molecules have been found to form hydrogen bonds of equal strength with the lipid phosphate groups. Thus, the ethanol molecules can easily replace the water molecules bound to the phosphate groups, which results in shorter lifetimes and hence faster structural relaxation of phosphate–water (PW) hydrogen bonds in the presence of ethanol. It is further noticed that the reformation of broken PW hydrogen bonds is less significant in the presence of ethanol.