

The extent of molecular orientation at liquid/vapor interface of pyridine and its alkyl derivatives by molecular dynamics simulation

Mohammad Hadi Ghatee,^{a)} Amin Reza Zolghadr, Fatemeh Moosavi, and Leila Pakdel

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

(Received 7 May 2010; accepted 23 January 2011; published online 18 February 2011)

In this paper, molecular dynamics simulation was performed to investigate the liquid/vapor interfacial structure of neat polar liquids. Large-scale ensembles of liquid pyridine and its alkyl derivatives, 4-methylpyridine and 4-ethylpyridine, were simulated by classical molecular dynamics at 298 K. For the liquid system of low polarity, the surface density profile of the atoms meet exactly at the middle of interfacial region, and atoms of hydrophobic nature can be hardly discriminated from hydrophilic ones in either vapor or liquid sides. For a liquid system of high polarity, the density profile of atoms with different nature is highly discriminated all over the interfacial region, and as the polarity increases, a dense region of atomic density is clearly developed in the subsurface region. The recognized bivariate method was also used to study the molecular orientational distribution quantitatively. Orientational analysis of the three liquid systems indicates that the pyridine ring plane in the outmost surface tends to be vertical. Its tendency in the innermost interfacial region is parallel. The orientational states available to 4-ethylpyridine and pyridine are discriminated by predicting the possibility of a bisector-wise tumbling for the ring plane in pyridine and a side-wise tumbling in 4-ethylpyridine. The orientational distribution maps explain the trend of experimental surface tension and surface entropy. As the dipole moment of these liquids increases with the alkyl chain length, the surface structural profile changes from a regular definite one to a surface of complex atomic structure involving a dense phase near the interface. The development of dense region in alkyl derivatives is the result of segregation of molecules due to the alkyl group, which is captured and discriminated by molecular dynamics simulation even when the length of a short alkyl chain is increased by one carbon atom. © 2011 American Institute of Physics. [doi:10.1063/1.3554361]

I. INTRODUCTION

Knowledge of molecular surface structure of liquid state is one of the prime interests in surface science. It is required for understanding many phenomena including binary adsorption, spreading, and adhesion. Many important properties of liquids such as the solubility, the extent of liquid supercooling, the vapor pressure, etc., depend on the characteristics and structure of the liquid/vapor interface. Nature and structure of the liquid/vapor interface is also important for understanding the transport of chemical species across such interfaces. The molecular structure and geometry of the liquid system has the basic role in molecular orientation at the liquid surface, reminiscent state of minimum mechanical surface stress. Since the surface stress is subjected to the long-range interactions, surface properties are influenced by physical and thermodynamic properties of liquid bulk. Due to such long-range effects, surface layering may occur depending on the fluid molecular structure.

The composition of a liquid surface is different from the bulk due to unbalanced forces exerted on particles in this region, which requires the surface to contract to attain a state of minimum stress. Besides, the molecular polarity is responsible for specific molecular orientation at the interface

according to which the surface stress is optimized. Therefore, surface microscopic properties can be vastly related to surface thermodynamics, which may be viewed by surface entropy and surface energy. It turns out that the surface entropy, the negative of temperature dependence of surface tension, is an important tool for validating the surface composition and molecular orientation at the interface.

Vast varieties of experimental methods have been developed to study and investigate the surface structure. Techniques such as x-ray, ultraviolet photoelectron spectroscopy, and high-resolution electron energy loss are the usual methods used to study the near surface structure. Two other popular techniques are direct recoil spectroscopy and sum frequency generation with great insights.^{1,2} More recently, the technique of laser-induced fluorescence was used to detect gas-phase OH radicals formed at the gas-liquid interface and thus to determine the surface composition of some ionic liquids.³ Despite the current level of research activity, many of the properties of liquid surface remain to be elucidated.

Molecular dynamics (MD) simulation has been widely used to simulate the surface as well as bulk properties of liquids. MD provides useful information including time evolution of atomic coordinates of simple as well as complex liquids. The outcome accurately describes properties of the system of interest. Molecular dynamics has been used to simulate the interface of molecular systems, such as short-chain perfluoroalkanes and their alkane analogue. It has been tried

^{a)} Author to whom correspondence should be addressed. Electronic mail: ghatee@susc.ac.ir. Tel.: +98 711 613 7353, +98 711 228 4822. Fax: +98 711 228 6008.