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Effects of Calcium Ions on Thermodynamic Properties of Mixed Bilirubin/Cholesterol Monolayers

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The mixed monolayer behavior of bilirubin/cholesterol was studied through surface pressure-area (π-A) isotherms on aqueous solutions containing various concentrations of calcium ions. Based on the data of π-A isotherms, the mean area per molecule, collapse pressure, surface compressibility modulus, excess molecular areas, free energy of mixing, and excess free energy of mixing of the monolayers on different subphases were calculated. The results show an expansion in the structure of the mixed monolayer with Ca^{2+} in subphase, and non-ideal mixing of the components at the air/water interface is observed with positive deviation from the additivity rule in the excess molecular areas. The miscibility between the components is weakened with the increase of concentration of Ca^{2+} in subphase. The facts indicate the presence of coordination between Ca^{2+} and the two components. The mixed monolayer, in which the molar ratio of bilirubin to cholesterol is 3:2, is more stable from a thermodynamic point of view on pure water. But the stable 3:2 stoichiometry complex is destroyed with the increase of the concentration of Ca^{2+} in subphase. Otherwise, the mixed monolayers have more thermodynamic stability at lower surface pressure on Ca^{2+} subphase.

Key words: Bilirubin/cholesterol, Mixed monolayer, Calcium ion, Thermodynamic property, Air/water interface

I. INTRODUCTION

Because of the existence of the membrane, the cell can assimilate nutrition from its environment, undertake metabolism, pass out messages, carry through energy transition, etc., so that the organism can carry out diversiform biologic function [1,2]. It is well known that the fundamental structure of biological membrane is a bilayer leaflet of lipids, stabilized by immersed proteins and carbohydrates [3]. Generally, lipids of animal cells contain three types: phosphatide, glycosphingolipid, and cholesterol [4]. Phosphatide is an important composition of biologic cell which can assemble ordered biologic membrane in an organism [5]. Cholesterol is the most abundant and widely distributed sterol in animal tissues, and it is also a major component of mammalian cell membranes. Since it is the precursor of bile salts and steroid hormones such as testosterone, it is functionally important in the human body [6]. The plaque formation on arterial walls can be induced by the high levels of blood cholesterol, which can lead to occlusion of arteries and death of heart muscle. Therefore, cholesterol also plays an important role in human pathology [7].

In the contemporary era, the diseases of various gallstones have attained more and more attention for their universalism and destruction in the human body. It is well known that gallstones are the products of pathologic biomineralization. The main components of mixed gallstones are cholesterol, bilirubin and its salts such as calcium bilirubinate [8,9]. The accumulation of bilirubin in blood and extravascular tissue usually acts as an available sign of a liver disease. Impaired secretion of bilirubin may indicate, a pathologic liver condition, e.g. a blockage of the common bile duct (as in gallstones) [10]. Bilirubin is involved in the formation of the black pigment gallstones, which is mostly made up of calcium bilirubinates in the human body. Copper bilirubinate acts as a free-radical scavenger in bile and protects phospholipids from peroxidation [11]. Moreover gallstones also contain organic substrates such as glycoprotein [12-14]. Fabricating gallstones *in vitro* is mostly important because it is very difficult to observe the nucleation and growth of gallstones in the human (animal), even simply *in vivo* bodies. So far, many investigations on the formation of gallstones have been limited to water and organic solvent systems [15], which differ from the human body environment.

Scientists have studied monolayers or Langmuir-Blodgett (LB) films consisting of these biological molecules in order to mimic the biological membrane [16-20]. Recent studies on bilirubin are reported due to its important role in biological systems [21-23]. Because the structure and biophysical properties of bilirubin molecules in ordered molecular assembles are different from that in bilirubin solution, the bilirubin monolayer can be applied in mimicking the mineralization process of gallstone formation. Ouyang *et al.* prepared

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and studied the characteristics of LB films of bilirubin and its derivatives [24-26], and investigated their orientation in the monolayers.

Our group has investigated the monolayers of bilirubin, cholesterol, and their mixtures on pure water subphase and the glycoprotein adsorption into bilirubin/cholesterol mixed monolayers at the air/water interface [15,27,28]. In addition, Ca^{2+} exists in gall and coordinates with bilirubin in gallstone, so it is significant to study the effect of Ca^{2+} on cholesterol, bilirubin and their mixed monolayers for understanding the formation mechanism of gallstone and the interactions between Ca^{2+} and cell membrane. With this in mind, we studied the influence of Ca^{2+} on the thermodynamic properties of mixed bilirubin/cholesterol monolayers at the air/water interface and analyzed the mean area per molecule, collapse pressure, surface compressibility modulus, excess molecular areas, free energy of mixing and excess free energy of mixing by mathematical means using the data of surface pressure-area (π-A) isotherms. To our knowledge, investigations about the effect of Ca^{2+} on cholesterol, bilirubin and their mixed monolayers have not been reported up to the present.

II. EXPERIMENTS

Bilirubin (99%, Sigma), cholesterol (99%, Sigma), and $CaCl_2$ (A.R., Shanghai Chemical Reagents Co.) were purchased and used without further purification.

The water was obtained by reverse osmosis using a Milli RO-Milli Q system (Millipore), its pH and resistivity were 6.2 and 18 MΩ cm, respectively. Cholesterol and bilirubin were dissolved in chloroform with a concentration of 1.5 mmol/L. The mixed monolayers were prepared by spreading the mixed bilirubin/cholesterol solution onto the surfaces of various concentrations of $CaCl_2$ aqueous solution using a Microman-Gilson microsyringe which is precise to ±0.2 μL. The π-A isotherms were measured by WM-1 LB trough (South East University, China) with a continuous speed of 15 mm/min for two barriers. The accuracy of the surface pressure measurement is 0.1 mN/m. All work was carried out in a dust-free box at a temperature of 25 °C.

III. RESULTS AND DISCUSSION

A. π-A isotherms of mixed bilirubin/cholesterol monolayers on different subphases

The structures of cholesterol and bilirubin are shown in Fig.1. It is seen that the bilirubin molecule has more polar groups than the cholesterol molecule. The properties of a monolayer are related to the structure of the components. The π-A isotherms of the mixed bilirubin/cholesterol monolayers on pure water are shown in Fig.2(a). The curve of cholesterol monolayer (X_{BR}=0.0) indicates that cholesterol molecules form a condensed monolayer at the air/water interface. Its limited area per molecule is as about 40 Å^2 reported [29]. The bilirubin curve (X_{BR}=1.0) shows a transition form liquid-expanded phase to liquid-condensed phase at lower surface pressures. Its limited area per molecule is about 71 Å^2, which is consistent with reported data [30]. Bilirubin spread at the air/water interface as the folded ridge-title structure with intermolecular hydrogen bonds between the pyrrole and lactam functions of the dipyrrinone halves [30]. The isotherms of the mixed monolayers are located between the cholesterol curve and bilirubin curve. The π-A curves of mixed monolayers on Ca^{2+} subphase are shown in Fig.2 (b)-(d). It is seen that the shape of all the curves change *vs.* those on pure water. The bilirubin monolayer becomes condensed and collapse pressure ascends on Ca^{2+} subphase, but the collapse pressure of cholesterol monolayer and most mixed monolayers decrease conspicuously. With the increase of concentration of Ca^{2+}, the change of π-A curves is more notable. It is inferred that the properties of mixed bilirubin/cholesterol monolayers on Ca^{2+} subphase are apparently different from that on pure water, especially on 1.00 mmol/L Ca^{2+} subphase.

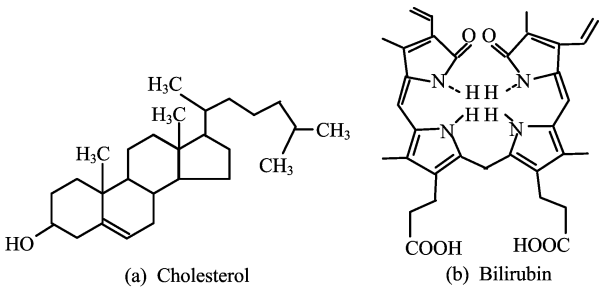

FIG. 1 Structures of cholesterol molecule and bilirubin molecule.

When the surface pressure is 20 mN/m, the mean area per molecule (A) on pure water and 1.00 mmol/L Ca^{2+} subphase is obtained and plotted with the mole fraction of bilirubin in Fig.3(a). The experimental data points show negative deviation from the ideal curve on pure water. This implies that an attractive interaction between bilirubin and cholesterol molecules exists in mixed monolayers. However, the deviation of A-X_{BR} curve is positive on 1.00 mmol/L Ca^{2+} subphase. The result is mainly attributable to the coordination between Ca^{2+} and the components of mixed monolayer.

The collapse pressure of the mixed monolayers with different compositions is a good indication of miscibility of their components [31,32]. The collapse pressures of bilirubin/cholesterol monolayers on pure water and 1.00 mmol/L Ca^{2+} subphase are plotted as functions of X_{BR} in Fig.3(b). The data on pure water shows a positive deviation from the ideal curve, which indicates that bilirubin and cholesterol are miscible in the condensed state of mixed monolayers. However, the miscibility

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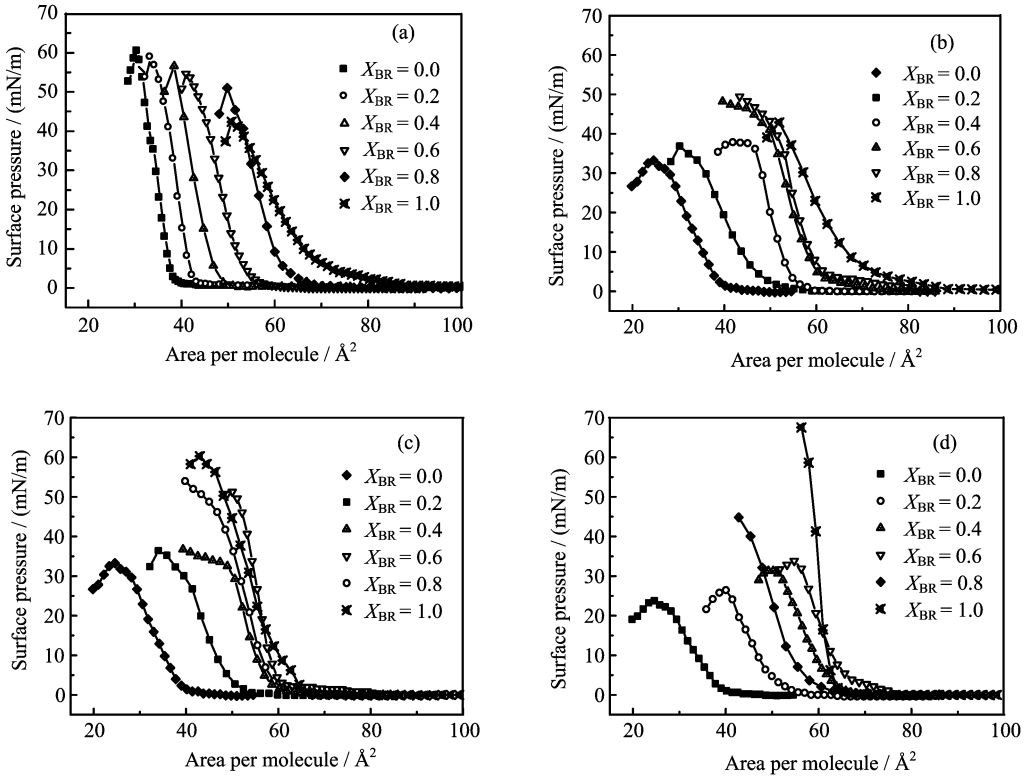

FIG. 2 Surface pressure-area per molecule isotherms of bilirubin/cholesterol monolayers on pure water (a), 0.01 mmol/L $CaCl_2$ solution (b), 0.10 mmol/L $CaCl_2$ solution (c), and 1.00 mmol/L $CaCl_2$ solution (d).

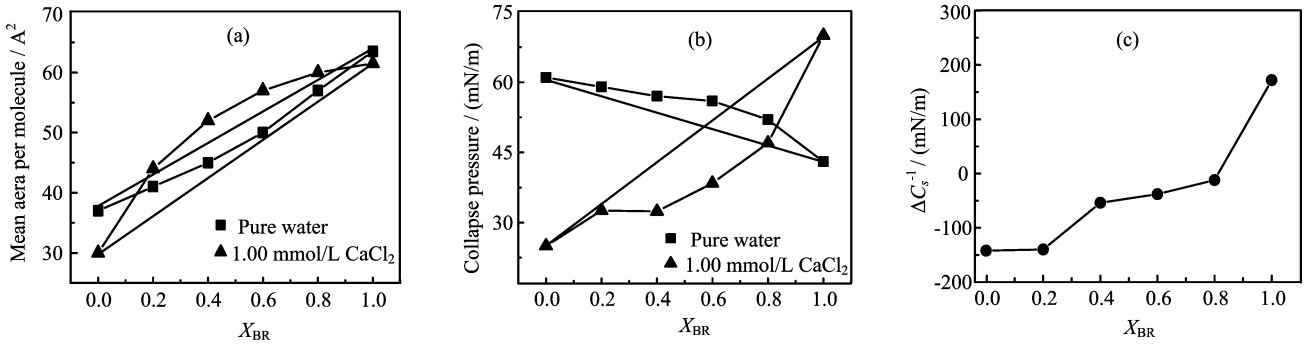

FIG. 3 Mean area per molecule (a), collapse pressure (b), and the change of the surface compressional modulies (c) as functions of composition for mixed monolayers on pure water and 1.00 mmol/L $CaCl_2$ subphase.

between bilirubin and cholesterol tails off, showing the negative deviation of collapse pressures from the ideal curve on Ca^{2+} subphase.

To make further study of the condensable behavior for mixed bilirubin/cholesterol monolayers on pure water and 1.00 mmol/L Ca^{2+} subphase, the surface compressional moduli (C_s) is analyzed. The C_s can be calculated as

$$C_s = -\frac{1}{A}\frac{dA}{d\pi} \quad (1)$$

where A is the area per molecule at indicated surface pressure, and π is the corresponding surface pressure. Data expressed as inverse function ${C_s}^{-1}$ are definite as the surface compressional modulies by David and Rideal [33]. The higher the ${C_s}^{-1}$ value is, the more condensed the monolayer is.

The ${C_s}^{-1}$ of cholesterol monolayer is 201.3 mN/m on pure water, and the ${C_s}^{-1}$ of mixed monolayers decreases as the X_{BR} increased. The ${C_s}^{-1}$ of bilirubin monolayer is only 42.9 mN/m. This suggests that the condensation of mixed monolayers should be prompted on pure water as cholesterol mole fraction increased. But the ${C_s}^{-1}$ values change on Ca^{2+} subphase. The deviation $\Delta{C_s}^{-1}$ of ${C_s}^{-1}$ on different subphases can be given as

$$\Delta {C_s}^{-1} = {C_{s1}}^{-1} - {C_{s2}}^{-1} \quad (2)$$

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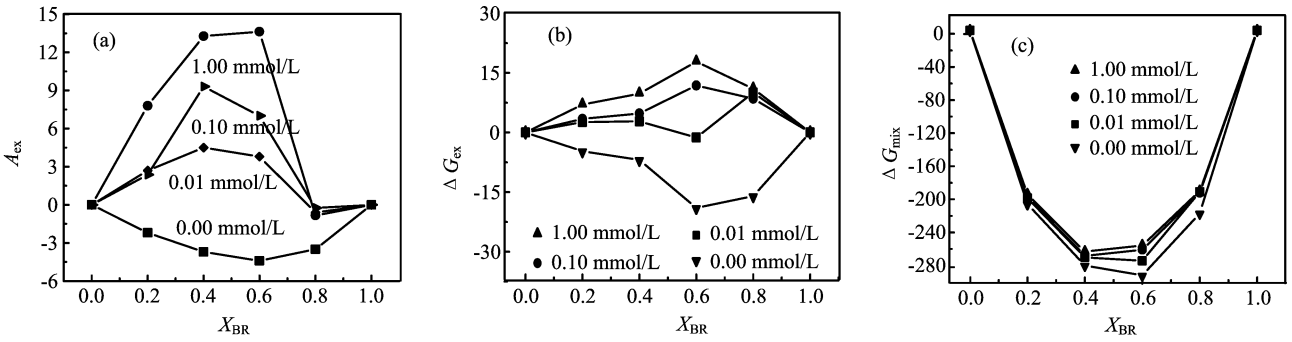

FIG. 4 Excess molecular areas (a), excess free energy (b), and free energy (c) as a function of composition of mixed monolayers on various concentration of $CaCl_2$ solution, when the surface pressure was 5 mN/m.

where C_{s1} and C_{s2} are the surface compressional moduli of monolayer on pure water and on 1.00 mmol/L Ca^{2+} subphase, respectively. The zero $\Delta {C_s}^{-1}$ means no effect of Ca^{2+} on the compression of monolayers. By means of Eq.(2), the $\Delta {C_s}^{-1}$ as a function of X_{BR} is shown in Fig.3(c). The $\Delta {C_s}^{-1}$ of cholesterol and bilirubin is -142 and 178 mN/m, respectively. In addition, the $\Delta {C_s}^{-1}$ value increases gradually from negative to positive with the increase of X_{BR}. This suggests that the effect of Ca^{2+} on mixed monolayers is weakened at low X_{BR} but enhanced at high X_{BR}.

B. Effects of the concentration of Ca^{2+} on thermodynamic properties of mixed monolayers

The interactions between the components of the mixed monolayers can be examined by plotting the excess molecular areas of the mixture, A_{ex}, as a function of X_{BR} under isobaric conditions. A_{ex}, which is also a measure of nonideality [34,35], is given by

$$A_{ex} = A_{1,2} - X_1 A_1 - X_2 A_2 \tag{3}$$

where $A_{1,2}$ is the mean area per molecule of mixed monolayers, A_1 and A_2 are the area per molecule of pure monolayer of components 1 and 2, respectively, and X_1 and X_2 are their corresponding molar fractions in the mixed monolayers. Thus, a linear correlation between the molecular area and the molar fraction of one component means either immiscibility or miscibility with nearly ideal behavior, A_{exc}=0. Deviation from the additivity rule, whether negative or positive, indicates miscibility and nonideality [36]. In Fig.4(a), the A_{ex} as a function of X_{BR} shows negative deviation on pure water. For a mixed monolayer, it always results in a negative A_{ex} if attractive intermolecular force or geometric accommodation (efficient packing) occurs [37]. This demonstrates mutual compatibility between bilirubin and cholesterol formed in their mixed monolayers. The formation of stable bilirubin/cholesterol mixed monolayers on pure water subphase is attributed to the multi-interactions, such as the hydrogen bond between the polar groups of bilirubin and cholesterol, van der Waals forces of hydrophobic chains between bilirubin and cholesterol molecules, etc. But on Ca^{2+} subphase, the coordination interaction of Ca^{2+} with double carboxyl groups of bilirubin is stronger than that with the hydroxyl group of cholesterol, and is also stronger than the hydrogen bond between bilirubin and cholesterol. Therefore, the combination of bilirubin with cholesterol molecules is abated. The positive A_{ex} on Ca^{2+} subphase confirms that the mutual compatibility between bilirubin and cholesterol is weakened.

The interactions between the components and the thermodynamic stability of mixed monolayers can be investigated from the calculation of excess free energy of mixing, ΔG_{ex}, or free energy of mixing, ΔG_{mix} [38-40]. For a process of two single-component monolayers to form a mixed monolayers at a constant surface pressure and temperature, the expression for ΔG_{ex} is given as

$$\Delta G_{ex} = \int_0^{\pi} (A_{1,2} - X_1 A_1 - X_2 A_2) \mathrm{d}\pi \tag{4}$$

Thus, the ΔG_{ex} can be calculated from the π-A isotherm. The relation gives the ΔG_{mix}:

$$\Delta G_{mix} = \Delta G_{id} + \Delta G_{ex} \tag{5}$$

where the ideal free energy of mixing, ΔG_{id}, can be calculated from the equation:

$$\Delta G_{id} = kT(X_1 \ln X_1 + X_2 \ln X_2) \tag{6}$$

where k is the Boltzmann's constant and T is the temperature. From Eq.(4), we deduced that if the two components were immiscible (phase separated) and followed the additivity rule, the integrand $(A_{1,2} - X_1 A_1 - X_2 A_2)$ and ΔG_{exc} should be equal to zero at any pressure and molar fraction. The nonzero ΔG_{exc} indicates that mixing is taking place. As can be seen from Fig.4(b), the negative ΔG_{ex} for all bilirubin/cholesterol monolayers on pure water became positive as the concentration of Ca^{2+} increased in suphase, which is consistent with the thermodynamic conditions for miscibility and strong interactions in the mixed monolayers. Apparently, the

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changes of ΔG_{ex} resulting from the coordination between Ca^{2+} and the components of monolayers are more evident with the increase of the concentration of Ca^{2+} from 0.01 mmol/L to 1.00 mmol/L.

In Fig.4, the greatest negative deviations of A_{ex}, ΔG_{ex}, and ΔG_{mix} from ideality are observed for the system containing 60% bilirubin. Therefore, the highest thermodynamic stability corresponds to the formation of 3:2 stoichiometry complexes ($M_{bilirubin-cholesterol}$, like a molecule) in the mixed monolayer. According to Ref.[27], bilirubin molecules within monolayer on pure water subphase should have a closed packed structure with vertical position after being compressed. Moreover, cholesterol molecules can self-assemble a stable monolayer not by compression, and these molecules should arrange in vertical position at air/water interface. Owing to the interactions between cholesterol and bilirubin, the complex between vertically oriented cholesterol molecule and vertically oriented bilirubin molecule can be an organized self-assembly at the air/water interface. Due to the stronger hydrogen bond between polar groups of bilirubin molecules and the steric effect, a stable complex with 3:2 stoichiometry between bilirubin and cholesterol formed. So the orientation freedom in bilirubin was hindered and the ordering degree of bilirubin molecules arranged at the air/water interface increased.

However, the multi-interaction among Ca^{2+}, bilirubin and cholesterol makes the calcium ions attached or inserted into the bilirubin/cholesterol monolayer as shown in Fig.5(b). As a result, the hydrogen bonds between bilirubin and cholesterol molecules are weakened, and the 3:2 stoichiometry complexes are also destroyed in mixed monolayers.

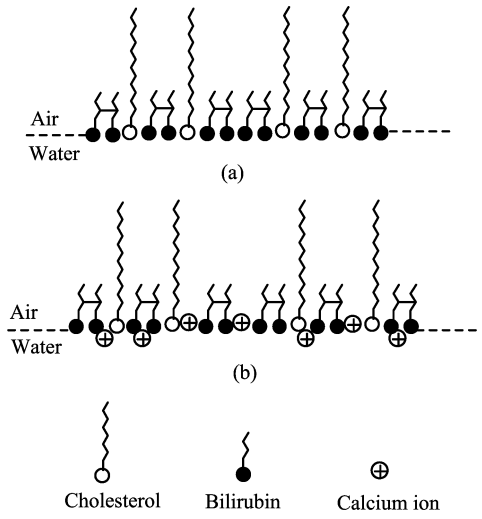

FIG. 5 The array of bilirubin and cholesterol molecules in mixed monolayer on pure water (a) and on Ca^{2+} subphase (b).

C. The properties of mixed monolayers at different surface pressures

The mean area per molecule and the thermodynamic properties of mixed monolayers were investigated at various surface pressures (2, 5, 10, and 20 mN/m). The deviations from additivity of mixed monolayers on pure water are shown in Fig.6(a), in which large negative deviations from additivity are observed at 2 and 5 mN/m. The deviation becomes smaller at 10 mN/m and is close to zero or becomes positive at 20 mN/m. The negative A_{ex} signifies good miscibility as well as favorable intermolecular interactions between cholesterol and bilirubin at low surface pressure (2 and 5 mN/m), but the miscibility becomes poor at 10 and 20 mN/m. Interestingly, all the A_{ex}-X_{BR} curves are similar in Fig.7(a), which indicates that the coordination between Ca^{2+} and the components of mixed monolayers is not influenced apparently by the surface pressure.

The values of ΔG_{ex} and ΔG_{mix} as a function of X_{BR} at various surface pressures (2, 5, 10, 20 mN/m) on pure water are shown in Fig.6 (b) and (c). The greatest deviations of all ΔG_{ex}-X_{BR} and ΔG_{mix}-X_{BR} curves from ideality are observed for the system containing 60% bilirubin. It shows that the 3:2 stoichiometry complexes are organized self-assemblies by interaction between molecules, which is not induced by the surface pressure. In Fig.7(b), when the surface pressure increases, the positive ΔG_{ex} of the mixed monolayers also increases on 1.00 mmol/L Ca^{2+} subphase. Apparently, the inner-tension of the coordination between Ca^{2+} and components is enhanced because of the close distance between molecules when the mixed monolayers are compressed. The negative deviations of ΔG_{mix} become less with surface pressure increasing in Fig.7(c), which suggests that the mixed monolayers are more stable at lower surface pressure on Ca^{2+} subphase.

IV. CONCLUSION

From a detailed analysis of surface pressure-area isotherms of mixed bilirubin/cholesterol monolayers, it is concluded that the miscibility of bilirubin and cholesterol decreased with the increase of the concentration of Ca^{2+} in subphase. The non-ideality of mixed monolayers is evident in the mean area-composition and the collapse pressure-composition figures. The mixed monolayers exhibited noticeable negative deviation on pure water and positive deviation on Ca^{2+} subphase. This data suggests that the attractive interactions between bilirubin and cholesterol should be displaced by the multi-interaction among Ca^{2+}, bilirubin, and cholesterol, so the molecular packing of bilirubin/cholesterol monolayers that exist on pure water is hindered on Ca^{2+} subphase because of the coordination between Ca^{2+} and the components. Furthermore, the free energy and the excess free energy of mixing-composition curves indi-

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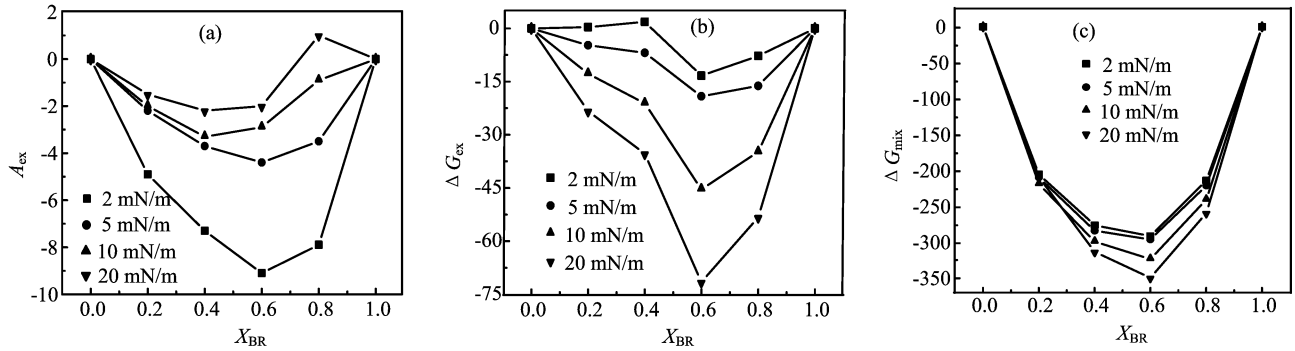

FIG. 6 Excess molecular areas (a), excess free energy (b), and free energy (c) as a function of composition of mixed monolayers at various surface pressures on pure water.

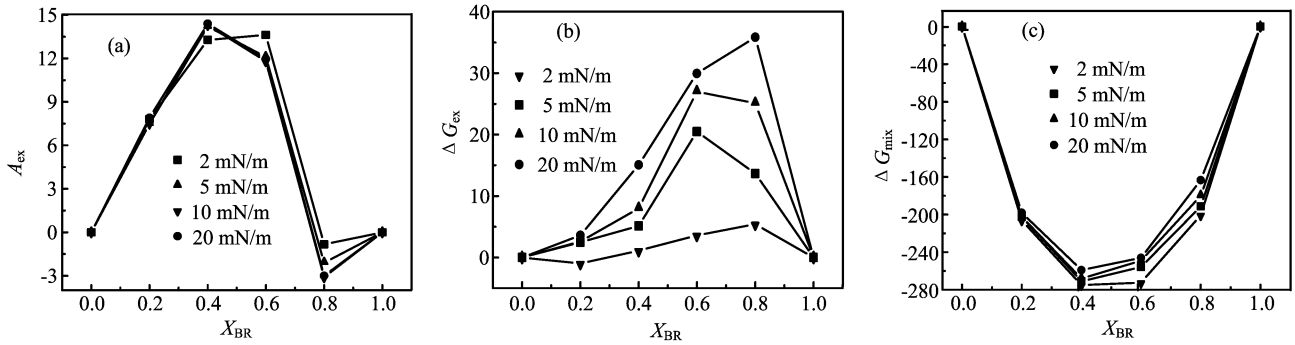

FIG. 7 Excess molecular areas (a), excess free energy (b), and free energy (c) as a function of composition of mixed monolayers at various surface pressures on 1.00 mmol/L Ca^{2+} subphase.

cate that the mixed monolayers become less stable as the concentration of Ca^{2+} increases in subphase.

V. ACKNOWLEDGMENTS

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