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Liquid-Expanded to Liquid-Condensed Phase Transition in Polyelectrolyte Monolayers on the Aqueous KBr Solution. 1. Salt Concentration Dependence

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ABSTRACT: Fully quaternized poly(vinylpyridinium bromides) with three different *n*-alkyl chains were prepared by spontaneous polymerization. The surface pressure of the quaternized polymer monolayers spread at the air–water interface was measured as a function of KBr concentration. In the surface pressure (π)–surface area (A) (π–A) isotherm the absolutely flat portion corresponding to so-called liquid-expanded to liquid-condensed transition is simply a first-order transition for each polymer. At smaller A the π–A curves can be superimposed independent of the *n*-alkyl chain length and KBr concentration. The limiting area estimated from an extrapolation of the straight portion on the π–A isotherm to $\pi = 0$ shows that the pyridinium rings are attached flat on the water surface while hydrocarbon side chains are oriented vertically. Additional measurement of interfacial pressure of the quaternized polymer monolayer at the *n*-heptane–water interface demonstrates that the small negative cooperative cohesive energy (attractive force) mainly governs the existence of the flat portions in π–A isotherms. Qualitative comparison with some theoretical works can interpret the interfacial behavior of a polyion monolayer at the air–water interface.

Two-dimensional charged insoluble monolayers spread at the air–water interface are interesting from a fundamental and a practical point of view. Particularly, intensive attention has been paid to the two-dimensional phase transition. Two prominent phase transitions are well understood to occur in the surface pressure–surface area (π–A) isotherms under appropriate surrounding conditions, for example, temperature and salt concentration of water subphase. Most works on the phase transition have concentrated on fatty acid and phospholipid monolayers.[1,2] The so-called gas–liquid (G–L) transition at lower surface pressure is generally accepted to be a first-order transition. Another transition at higher surface pressure is usually denoted liquid-expanded to liquid-condensed (LE–LC) phase change. It was usually observed that the LE–LC transition occurs as a single slope change in the π–A isotherm. However, more recently Pethica and co-workers observed a completely horizontal portion in π–A isotherms of the LE–LC transition in fatty acids and phospholipid monolayers.[3,4]

Due to high solubillity in water and difficulty in forming films on the water surface, studies on polyelectrolyte monolayers have been lacking in comparison with nonionic polymer monolayers. To conquer this limitation several attempts have been performed by preparing (1) polymers with partially ionized chains such as random[5] and block[6,7] copolymers and (2) quaternized poly(vinylpyridine) with alkyl halides.[8]

Plaisance and Ter-Minassian-Saraga[8] systematically measured the surface pressure of poly(2-vinyl-5-methylpyridine) quaternized with hexyl or octyl bromide monolayers spread at the air–aqueous salt solution interfaces. Their π–A isotherms showed a dramatic change with variation of ionic strength or salt species, and the LE–LC transition was observed for the specific salts. However, they did not deeply study the LE–LC transition. Moreover, their samples were not fully quaternized.

In general, the 100% quaternization of poly(vinylpyridine) with *n*-alkyl halides was not attained if the *n*-alkyl chain length was long.[9] On the other hand, a mixture of 4-vinylpyridine and *n*-alkyl halide in a given solvent leads to the 100% quaternized poly(4-vinylpyridinium) salt by spontaneous polymerization[10] accompanied with the quaternization or protonation of the 4-vinylpyridine monomer.

In this paper we prepare fully quaternized poly(4-vinylpyridinium) salts from the spontaneous polymerization of 4-vinylpyridine and three different *n*-alkyl bromides. Surface pressure measurements of the resulting polyelectrolyte monolayers spread on aqueous KBr solutions are performed as a function of KBr concentration. The characteristics of their π–A isotherms will be discussed, focusing on the LE–LC transition as a function of *n*-alkyl chain length and KBr concentration.

Experimental Section

Materials. Poly(4-vinylpyridines) (PVP) quaternized with three different *n*-alkyl bromides such as *n*-hexyl bromide, *n*-octyl bromide, and *n*-dodecyl bromide were prepared by the spontaneous polymerization[10] of freshly distilled 4-vinylpyridine and *n*-alkyl bromide in distilled dimethyl cellosolve at around −15 °C. Three *n*-alkyl bromides were used without further purification. Reaction time was about $^1/_2$ year. With an increase in reaction time, quaternized polymers were precipitated. The product was washed several times by a large amount of dimethyl cellosolve. The polymers separated by filtration were dissolved in methanol and precipitated into excess distilled water. An additional dissolution (in methanol) and precipitation (in water) sequence was repeated to purify the polymers. They were dried under vacuum to remove water at room temperature.

The degree of the quaternization in the polymers was checked by elementary analysis.

Number-average molecular weights of the polymers were determined with a Knauer vapor pressure osmometer in methanol at 30 °C.

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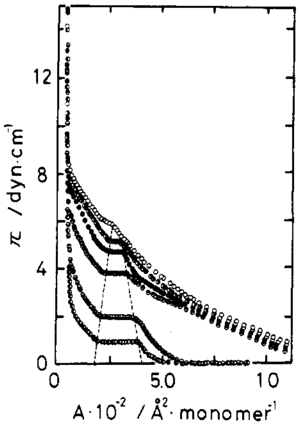

Figure 1. Surface pressure–surface area isotherms of the PVPC6 monolayer at the air–water interface as a function of KBr concentration at 25 °C: (○) KBr concentration C_s = 0.001 N; (◑) C_s = 0.003 N; (●) C_s = 0.01 N; (◓) C_s = 0.04 N; (◒) C_s = 0.1 N; (◐) C_s = 0.2 N.

4-ethyl-*N*-(*n*-hexyl)pyridinium bromide was used without further purification.

Deionized water was supplied from a Millipore Q-TM system. Spectral-grade methanol was used for a spreading solvent without further purification. Analytical grade KBr was used without further purification.

Method. The surface pressure of the quaternized PVP monolayer at the air–aqueous KBr solution interface was measured by the Wilhelmy plate method with a glass plate attached to a force transducer (Shinko Denki Co. Type 1301) fed into a home-built phase-sensitive amplifier. The surface pressure was determined with a precision of ±0.03 dyn/cm.

Monolayers were applied to the surface of the aqueous KBr solution in a Teflon trough (size 10 × 900 × 160 mm).[11] The methanol solution was delivered from a Terumo microsyringe and 30 min was allowed to evaporate methanol. Compression of monolayers was carried out successively with a Teflon barrier. The temperature of the aqueous subphase in the trough was controlled at 25 ± 0.1 °C by circulating thermostated water through a glass coil placed along the bottom of the trough.

The measuring technique of interfacial tension of the quaternized PVP monolayer spread at the *n*-heptane–water interface was the same as that for the air–water interface. The design of a trough was similar to that of Blight, Cumper, and Kyte.[12] The trough coated with Teflon has a dimension of 700 × 160 × 50 mm. The interfacial area was changed successively by using a Teflon ribbon attached to the movable barriers. We confirmed that methanol used as the spreading solvent has no effect on the interfacial pressure at the *n*-heptane–water interface. Temperature control of the oil and water phases in the trough was performed by adjusting room temperature to 25 ± 0.5 °C.

Results and Discussion

Poly(4-vinyl-*N*-(*n*-hexyl)pyridinium bromide) (PVPC6), poly(4-vinyl-*N*-(*n*-octyl)pyridinium bromide) (PVPC8), and poly(4-vinyl-*N*-(*n*-dodecyl)pyridinium bromide) (PVPC12) were prepared. The degree of quaternization of all three polymers was 100% and their molecular weights were determined to be 14 × 10³, 6.5 × 10³, and 20 × 10³ for PVPC6, PVPC8, and PVPC12, respectively. These polymers, attached with a relatively long *n*-alkyl chain, were found to be completely insoluble in water by examining their solubilities in water by UV spectroscopy. Therefore, they are expected to make a stable monolayer at the air–water interface.

Figure 1 shows the π–A isotherms of PVPC6 spread on the aqueous solutions with six different KBr concentrations. We notice several features from these π-A isotherms. The π–A isotherms show an increase in surface pressure with decreasing KBr concentration at a constant area. This result is expected because the increase in the electrostatic repulsive force between charged segments should lead to an increase in π.

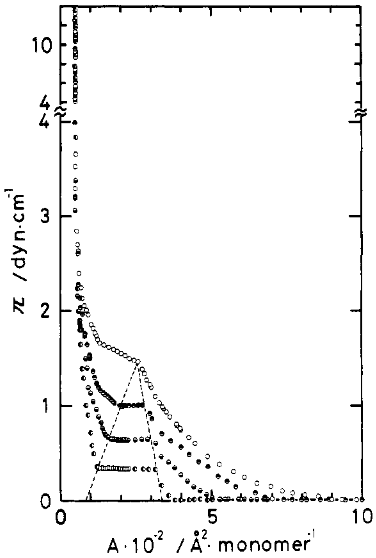

Figure 2. Surface pressure–surface area isotherms of the PVPC8 monolayer at the air–water interface as a function of KBr concentration at 25 °C: (○) C_s = 0.01 N; (◓) C_s = 0.04 N; (◒) C_s = 0.1 N; (◐) C_s = 0.2 N.

At large surface area [$A > 750$ Å²/(monomeric units)], corresponding to an expanded state of monolayer, the π–A isotherms of PVPC6 at concentrations of 0.1 and 0.2 N KBr are noticeably less expanded than those at the other concentrations of KBr. With decreasing A the salt concentration dependence of π is clearly observed, and finally the π–A isotherms are superimposed independent of KBr concentration. Below A = 50 Å²/(monomeric unit) the π–A plots show a nearly straight and very steep increase, indicating low compressibility in the monolayers.

Except for the concentration of 0.001 N KBr, all π–A isotherms have an absolutely flat portion. The flat portion starts at larger A and ends at smaller A as the KBr concentration increases. At the lowest KBr concentration (0.001 N) the π–A isotherm shows an apparently abrupt change of slope instead of the flat portion.

The flat portion of the π–A curves appears to correspond to the LE–LC transition. From the fact that π is constant even with changing A, the LE–LC transition is in fact first order. This finding is similar to the studies of Pallas and Pethica[4] for *n*-pentadecanoic acid and *n*-hexadecanoic acid monolayers at the air–aqueous HCl interface and for the dihexadecanoylphosphatidylcholine monolayer at the air–aqueous NaCl interface. The dashed line in the figure shows a coexistence curve connecting tie lines.

Changing the length of *n*-alkyl side chain varies the intermolecular, that is, chain–chain, interactions, such as the degree of hydrophobicity. Therefore, lengthening the chain enhances the cohesion in the monolayer film, i.e., leads to a more condensed π–A isotherm.[13]

In Figures 2 and 3 are shown π–A isotherms of PVPC8 and PVPC12 as a function of KBr concentration, respectively. Surface pressure is first detectable at a smaller A with increase in the *n*-alkyl chain length for the same concentration of KBr. The difference in π among the KBr concentrations at constant A becomes smaller with the length of the *n*-alkyl chain. The π–A isotherms of PVPC8 and PVPC12 also have absolutely flat portions. Thus even if the *n*-alkyl side chain is lengthened, the three quaternized PVP monolayers show flat portions in their π–A isotherms, indicating the first-order transition. The dashed lines in Figures 2 and 3 correspond to a coexistence curve

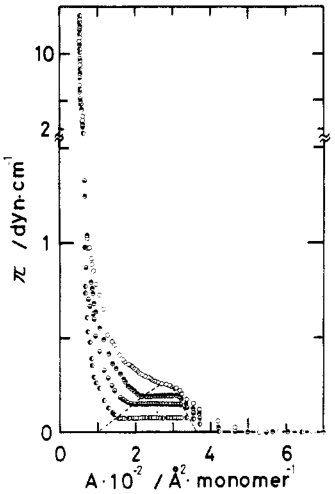

Figure 3. Surface pressure–surface area isotherms of the PVPC12 monolayer at the air–water interface as a function of KBr concentration at 25 °C. The symbols are the same as in Figure 2.

connecting ends of the flat parts for PVPC8 and PVPC12, respectively.

From comparison with the π–A isotherms of three different quaternized PVP monolayers at the same KBr concentration, the flat region starts at smaller A with increasing the n-alkyl chain length. Of course, the absolute value of the surface pressure at the flat portion decreases with increasing length of the n-alkyl chain. At smaller A each π–A isotherm is superimposed and shows a very steep increase in π.

The steep increase in π where the molecules are closely packed gives the most quantitative information on molecular size and shape at the two-dimensional state. We can estimate the so-called limiting area by a method used to extrapolate the straight portion of the π–A isotherm back to $\pi = 0$ axis.[1] For a long alkyl chain compound monolayer such as a fatty acid, the limiting area is about 20 Å^2/(monomeric unit) and is almost the same as the cross sectional area in the bulk crystal determined by X-ray analysis.[14]

According to the traditional method the limiting area of the quaternized PVP monolayers was determined to be 48 ± 1 Å^2/(monomeric unit) independent of the length of n-alkyl chain and KBr concentration. This limiting area is fairly larger than that of the aliphatic chain monolayer and moreover is larger than the extrapolated limiting area of 34 Å^2/(monomeric unit) of the PVP monolayer at the air–water interface observed by Miller.[5] To interpret the observed limiting area, we should ask what the conformation of the quaternized PVP chains adsorbed at the air–aqueous KBr solution interface is. Since the strong KBr concentration dependence of the surface pressure for each quaternized PVP is due to a significant electrostatic repulsive force, a polar group such as the pyridinium ring is adsorbed lying flat on the surface of aqueous KBr solution while a n-alkyl chain protrudes out of the surface. The area of such a conformation is estimated by using a molecular model to be 48 Å^2/(monomeric unit). Agreement between the observed and calculated areas is fairly well.

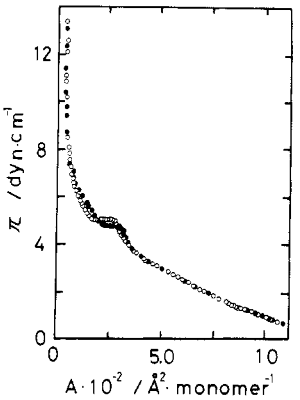

Figure 4. Surface pressure–surface area isotherms of the PVPC6 monolayer at the air–water interface for different salts: (○) 0.01 N KSCN; (●) 0.01 N KBr.

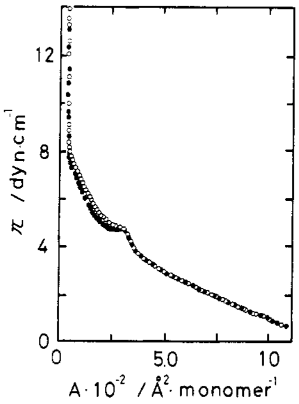

Figure 5. Comparison of interfacial pressure (○) and surface pressure (●) of the PVPC6 monolayer as a function of surface area for 0.01 N KBr at 25 °C.

Figure 4 shows the salt dependence of π–A isotherms of the PVPC6 monolayer at KSCN and KBr concentrations of 0.01 N. According to Plaisance and Ter-Minassian-Saraga[8] KSCN shows a selective binding to quaternized PVP monolayers. The π–A isotherm for KSCN also shows the flat portion, indicating a first-order transition. Both π–A isotherms are quite similar to each other except for the position of the phase transition region. The flat portion for KSCN starts at smaller A and the absolute value of the surface pressure at the flat part is relatively higher than for the value for KBr. Beyond the flat portion both π values cross at around 5 dyn/cm, corresponding to A = 250 Å^2/(monomeric unit). A further decrease of A increases π, π–A isotherms can be superimposed each other, and a solidlike monolayer is attained. Thus even for different salts we can confirm the LE–LC transition of the quaternized PVP monolayer as a first-order transition.

For the purpose of reducing the intermolecular interaction between long hydrocarbon chains of insoluble monolayers in two dimensions an oil–water interface is sometimes employed. The interfacial tension of PVPC6 spread at a n-heptane and aqueous 0.01 N KBr solution interface does not show the flat portion, but a kink is observed as shown in Figure 5. The π–A isotherm of PVPC6 at the air–water interface for the same KBr concentration is also displayed in the figure. The kink position of the interfacial area exactly corresponds to the starting point of the flat portion at the air–water interface. Below the kink point both π–A isotherms can be superimposed. Beyond the kink point the interfacial pressure shows an increase until two π–A isotherms are superimposed to make a solid type monolayer. This means that the difference in π–A isotherms between the air–water and oil–water interfaces is mainly contributed by the cohesive surface pressure π_s due to the van der Waals forces of attraction between hydrocarbon side chains.[1] Thus a small cooperative attractive force is sufficient to determine the flat portion in π–A isotherm at the air–water interface, i.e., a first-order transition. Some theoretical works also gave

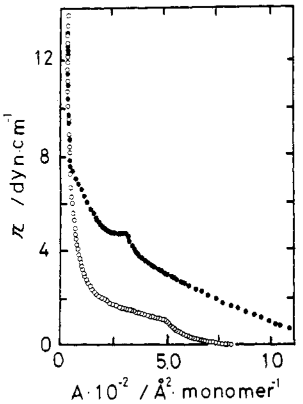

Figure 6. Surface pressure–surface area isotherms of 4-ethyl-*N*-(*n*-hexyl)pyridinium bromide (○) and PVPC6 (●) monolayers at the air–water interface for 0.01 N KBr at 25 °C.

the same conclusion for the interaction that leads to the LE–LC transition of lipid monolayers.[2]

To analyze further the nature of cooperativity of hydrocarbon side chains in polymers, we employ 4-ethyl-*N*-(*n*-hexyl)pyridinium bromide (EHPB) as an analogous monomeric compound of PVPC6. The surface pressure of an EHPB monolayer was measured at the air–aqueous 0.01 N KBr solution interface at 25 °C. Figure 6 displays the π–A isotherm of EHPB together with that of the PVPC6 monolayer at the same concentration of KBr. Around A = 750 Å^2/(monomeric unit) π of EHPB is first detectable and the π–A isotherm shows a kink, indicating the discontinuity in slope. The surface area at which the kink is observed is much larger than that for the starting point of the flat portion for PVPC6. The π value at the kink position is lower than that of the flat portion for PVPC6. It is clearly shown in Figure 6 that EHPB forms a less expanded monolayer than PVPC6, but the extrapolated limiting area of EHPB was determined to be the same value of 48 Å^2 as PVPC6. In the PVPC6 monolayer the comb-shaped arrangement of hydrocarbon side chains, which are ca. 3 Å apart, is expected to interact more cooperatively than the EHPB molecules at the air–water interface.

There have been a considerable number of theoretical works on the phase transition of monolayers at the air–water interface to explain whether the LE–LC transition is a first-order or second-order transition. Most theoretical treatments are concerned with the phase transition in lipid monolayers.[2] However, there is not a unique theoretical work to interpret the experimental data. Recently, Pethica and co-workers[3,4] have reported a first-order transition for the LE–LC change of some superpurified lipid monolayers by very careful measurements of their surface pressure. Thus our interesting findings also probably make a great contribution to the improvement of the theoretical treatment of the phase transition in monolayers.

For charged monolayers Davies[15] pioneeringly proposed a surface equation of state at the air–water interface by modification of his treatment on charged films at the oil–water interface.[16] Derivation of the surface equation of state has been done by taking the electrical repulsion based on the Gouy–Chapman theory and the cohesive energy according to Guastalla[13] into account. From the theory of Davies the surface pressure for the charged monolayer is roughly proportional to the square root of salt concentration in the water subphase at larger surface area, where the contribution of the cohesive energy to the surface pressure is very small.

On the other hand, Gaines[17] showed a thermodynamic equation of state for an insoluble ionized monolayer on the aqueous salt solution using Gibbs dividing surface formalisms. Gaines' theory does not consider explicitly the origin of the forces (electrostatic or otherwise) that govern the behavior of charged monolayers.

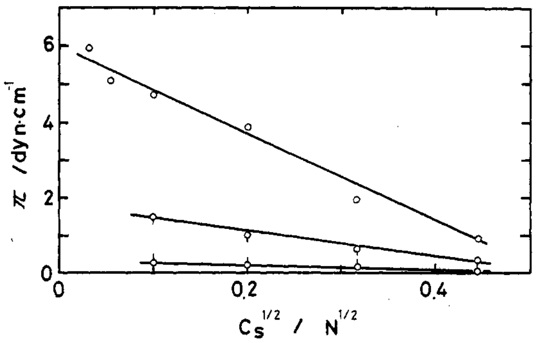

Figure 7. Plots of π at the flat portions in the π–A isotherm vs. the square root of KBr concentration: (○) PVPC6; (♀) PVPC8; (ȸ) PVPC12.

For the three quaternized PVP monolayers, up to the starting point of the flat portion, the surface pressure at the same KBr concentration is independent of salt species, oil–water and air–water interfaces, temperature.[18] This means that the surface pressure below the flat portion is mainly governed by the electrostatic repulsive force. Here, we can test the salt concentration dependence of π according to Davies' theory. For example, Figure 7 represents the surface pressure corresponding to the starting point of the flat portion plotted against the square root of KBr concentration. Within experimental error a straight line can be drawn for the respective quaternized PVP monolayers. Even for surface pressures in the same area below the flat portion, similar relations were obtained. However, Davies' surface equation of state for charged monolayers predicts no existence of the flat portion. On the other hand, in Gaines' theory a flat portion of the π–A isotherm can be realized by choosing adequate values of activity coefficients of the aqueous salt solution before and after the transition. Clearly, both theories cannot quantitatively interpret the measured data.

It was successful to describe the G–L transition in a simple fatty acid monolayer at the air–water interface in terms of the critical phenomena[19] and obtain the critical exponents.[20,21] Recently, some critical exponents have been shown to be reasonably consistent for the various paths of thermodynamic variables, such as pressure, salt concentration, and refractive index instead of temperature.[22] In our experiments the KBr concentration under isothermal conditions corresponds to a thermodynamic variable. However, there is no attempt to apply the idea of critical phenomena to the LE–LC transition. We will just try to analyze it according to the method for the fatty acid monolayer.[20,21]

In analysis we roughly regard the lowest KBr concentration as a critical point because the flat portion in the π–A isotherm of each quaternized PVP monolayer fully disappears. Such an estimation of the critical point leads to a lower value than a true value. Since the data points of PVPC8 and PVPC12 were less extensive than those of PVPC6, they were not used for comparison. The density gap between the ending and starting points of the flat portion is plotted double logarithmically against the difference in KBr concentration subtracted by the concentration of 0.001 N in Figure 8. The density corresponds to the reciprocal surface area. The exponent with the data was 0.31. This exponent is lower than 0.5 derived from the mean field theory[19] and larger than $^1/_8$ in the Ising model.[19] Estimation of the thermal compressibility defined

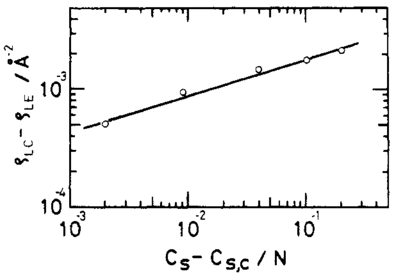

Figure 8. Double logarithmic plot of the density gap ($\rho_{LC} - \rho_{LE}$) between the liquid-condensed and liquid-expanded regions vs. the difference in KBr concentration ($C_s - C_{s,c}$) from 0.001 N.

as $\epsilon = -A(\partial\pi/\partial A)$ was performed by a polynomial fit, but there was considerable scatter in the calculated ϵ. Thus we could not determine the exponent by fitting the compressibility ϵ to power laws of the difference in KBr concentration from the critical concentration of KBr.

Conclusions

Poly(4-vinylpyridines) were fully quaternized with three n-alkyl bromides by the spontaneous polymerization of 4-vinylpyridine. At the air–water interface each poly(vinylpyridinium) salt attached with n-alkyl chain makes an insoluble and stable monolayer and shows a distinct flat portion, indicating a first-order transition for a liquid-expanded to liquid-condensed phase transition. The range of the flat portion in the π–A isotherms shifts with higher surface pressure and becomes narrower with decreasing KBr concentration. The origin of the force that governs a first-order transition is contributed by the small cooperative cohesive energy, i.e., cohesive surface pressure. This fact was confirmed by the measurement of the interfacial pressure of the polyelectrolyte monolayer at the oil–water interface.

Registry No. PVP·$H_3C(CH_2)_5Br$, 60595-47-3; PVP·$H_3C(CH_2)_7Br$, 76010-13-4; PVP·$H_3C(CH_2)_{11}Br$, 59950-03-7; KBr, 7758-02-3.

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Liquid-Expanded to Liquid-Condensed Phase Transition in Polyelectrolyte Monolayers on the Aqueous KBr Solution. 2. Temperature Dependence

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ABSTRACT: Surface pressure (π)–surface area (A) (π–A) isotherms have been obtained for a series of monolayers of poly(4-vinylpyridinium bromides) that were fully quaternized by three different n-alkyl chains (n = 6, 8, and 12) at the air–aqueous KBr solution interface as a function of temperature. In the π–A isotherm the flat portion corresponding to the so-called liquid-expanded to liquid-condensed transition, being simply a first-order transition, was observed even if the temperature changed. π–A isotherms condense with decreasing temperature. At higher KBr concentration a variation of the surface pressure with temperature was observed for the transition from liquid condensed to a solidlike film, whereas at lower KBr concentration a temperature dependence was also observed for the transitions from liquid expanded to liquid condensed as well as liquid condensed to solidlike film. The heats and entropies associated with the transition from liquid-condensed to liquid-expanded film were evaluated by applying the two-dimensional Clausius–Clapeyron equation. The values of these thermodynamic quantities were smaller than the previous data for lipid and polymer monolayers and decreased with decreasing temperature. The transition from liquid-expanded to liquid-condensed film was not easily interpreted in terms of the crystallization of the n-alkyl chain attached to poly(4-vinylpyridine) but was contributed by the freedom in the motion of the pyridinium ring adsorbed on the water surface.

A polyelectrolyte that gives an insoluble and stable polyelectrolyte monolayer spread at the air–water interface usually should contain two important characteristics: (1) a hydrophobic character, which is insoluble in the water subphase and makes a stable monolayer and (2) a hydrophilic character originating from charged group of the polyelectrolyte, which anchors the polyion to the water surface. Thus, an amphiphilic character will determine the surface pressure of polyelectrolyte monolayers.

Hydrophobicity related to cohesion due to the hydrocarbon components in the polyelectrolyte will be easily changed by varying thermodynamic parameters such as temperature, while electrical interaction such as an electrostatic force between charged groups strongly depends on salt concentration and the salt species in the water subphase.

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