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## Interaction between Insoluble Polymer Monolayers and Polyethylene Glycol in Aqueous Subphase at Air / Water Interface

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## Interaction between Insoluble Polymer Monolayers and Polyethylene Glycol in Aqueous Subphase at Air / Water Interface

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Blend polymer systems having miscibility in the bulk state, i.e. poly(methyl methacrylate)(PMMA)/poly(ethylene glycol)(PEG) and poly(vinyl acetate)(PVAc)/PEG systems were investigated at the air/water interface in terms of intermolecular and interfacial interactions. Both water and PEG aqueous solution were used as subphases.

**Keywords:** miscibility; air/water interface; deviation behavior

### INTRODUCTION

The miscibility in a binary polymer system at the air/water interface can be investigated by two approaches, either following change in the phase transition or plotting the mean area ( $A$ ) at a constant surface pressure( $\pi$ ) vs. the mole fraction of one component in the binary mixture[1,2]. If the plots have a linear relationship, the mixed films can be regarded as an ideal mixture or as a completely immiscible mixture with a phase separation. It has been established by Kawaguchi and Nishida that the deviation from the linear relation stems from the contribution of intermolecular interaction between both substances[2].

A negative deviation means that the mixtures are considered to be stable and miscible, whereas a positive deviation indicates that the mixtures are less stable than the components alone at the interface.

In this study, intermolecular and interfacial interaction in polymer blend systems poly(methyl methacrylate) (PMMA)/ poly(ethylene glycol) (PEG) and poly(vinyl acetate) (PVAc)/PEG were investigated at the air/water interface, in terms of the deviation from the additivity rule in the plot of mean surface area vs. the composition of the mixture. PEG aqueous solution was also used as a subphase instead of a pure water.

## EXPERIMENTAL

Monolayers were spread from the benzene solutions onto the distilled water or the aqueous PEG( $4.5 \times 10^{-5}$  mol/CH<sub>2</sub>CH<sub>2</sub>O) solution as a subphase. A LAUDA film balance was used for measuring  $\pi$  as a function of  $A$  at  $25 \pm 0.1$  °C through a compression rate of  $0.6 \text{ cm}^2/\text{sec}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the  $\pi$ - $A$  isotherms of the 50/50 mixtures of PMMA and PVAc as well as the homopolymers spread on the distilled water(A) and the aqueous PEG(B) and the mean surface areas are summarized in Table 1 as a function of PMMA mole fraction at 5 and 10 mN/m, in which different states of the monolayers with the molecular packing and the orientation are considered. PMMA was formed to be relatively condensed and compressible monolayers. In comparison to PMMA monolayers, PVAc showed relatively larger molecular area at the same surface pressure for both subphases, meaning that the PVAc was formed to be relatively expanded monolayers, being spread on both the distilled water and the aqueous PEG.

Table 1 exhibits that the surface area of the 50/50 PMMA/PVAc mixture shows slightly negative deviation from the additive values of the area for the homopolymer monolayers when they are spread on the aqueous PEG, whereas the areas show almost additivity values when they are spread on the distilled water, regardless of the surface

pressures. The negative deviation behavior stems from the interfacial and intermolecular interactions between either of or both the polymers, PMMA or PVAc, with PEG in the subphase. More condensed state behaviors in  $\pi$ -A isotherms were observed when the aqueous PEG was used for subphase rather than when the distilled water was applied for subphase.

**TABLE 1.** The mean surface area as a function of PMMA mole fraction for the mixtures of PMMA and PVAc. The data were taken from Figure 1.

Surface Pressure (mN/m)	Subphase	Surface area( Å <sup>2</sup> /repeating unit)		
		PMMA	Blend (50/50)	PVAc
5	aqueous PEG	15.2	19.0(19.3) <sup>a</sup>	23.4
	distilled water	16.3	22.7(22.65)	29.0
10	aqueous PEG	14.1	16.3(16.6)	19.1
	distilled water	14.9	18.2(18.3)	21.7

<sup>a</sup> Numbers in the parenthesis indicate calculated values from the additivity rule.

This fact may be ascribed to a more preferential intermolecular interaction between hydrophilic part of the polymer monolayer at the expanded state and PEG molecules in the subphase. It seems that PMMA or PVAc molecules can be closely packed each other at the air/aqueous PEG interface and form stable monolayers due to the molecular interaction between PEG and PMMA and/or between PEG and PVAc. The determination of miscibility for polymers in the monolayers at the condensed state is much more accurate than those at the expanded state.

Figure 2 schematically summarizes the condensed effect of  $\pi$ -A isotherms obtained on the aqueous PEG(B) as compared with those on the distilled water(A). In this figure, (a) shows simply the initial spreading state. In the expanded state (b), the polymer conformation on aqueous PEG is mainly affected by the interfacial and intermolecular interactions. Then, the monolayer is more packed than that on the distilled water and a shift to the lower pressures could be observed in the  $\pi$ -A isotherms obtained on the aqueous PEG. If a component in subphase has the interaction with each one in a mixture, it may be

expected that this acts as a compatibilizer in a blend. Then, in the condensed state (c), PEG in subphase can play as an interfacial agent for the mixed monolayer and a simple overlap of the  $\pi$ -A isotherms obtained on the aqueous PEG and on the distilled water can be observed. In this case, however, if there exists a chemical binding of

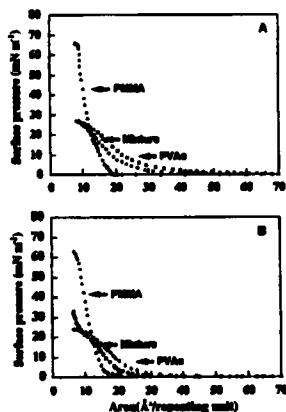


FIGURE 1.  $\pi$ -A isotherms for mixture of PMMA/PVAc(50/50 by mol) distilled water (A) and the aqueous PEG(B).

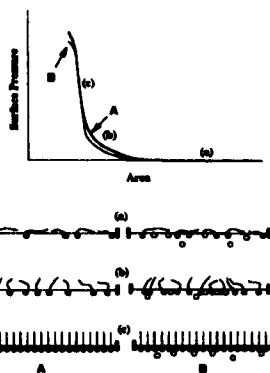


FIGURE 2. Schematic presentation of the polymer monolayer on the distilled water (A) and the aqueous PEG(B): (a) as-spread, (b) expanded, (c) condensed.

PEG with monolayer in the condensed state, a noticeable shift to lower pressures must be also observed in the  $\pi$ -A isotherm obtained on the aqueous PEG, as in the expanded state (b). Since the result in Figure 1 exhibits no shift in the condensed states for  $\pi$ -A isotherms of both PMMA and PVAc on the aqueous PEG as compared with the distilled water, the PEG binding does not exist in this work.

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