

Monolayer Film Behavior of Polymers and Their Mixtures

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Synopsis

The monomolecular film behavior of polyvinyl acetate (PVAc), polyethyl acrylate (PEA) and mixtures of these ranging in concentration ratio of PEA to PVAc from 0.008 to 11.301 has been studied using a Langmuir-type film balance over an aqueous 0.01*N* HCl substrate. Hysteresis was observed in the compression-expansion cycle for PVAc. A discussion of polymer-polymer interaction in a mixed monomolecular film at an interface is presented. The extent of this interaction for films comprising PVAc and PEA has been determined in terms of deviations of the film area from the ideal behavior. The data are graphically presented over the given range of film composition. The data on the film areas of PVAc and PEA are discussed in terms of the molecular orientation of these polymers on the surface. A simple equilibrium thermodynamic treatment is applied to the data on mixed monolayer films. The implications resulting from this study are discussed.

INTRODUCTION

Monolayer studies have been used for a long time in investigations related to polymer interfacial behavior and the manner in which changes in polymer structure affect such behavior.¹⁻¹⁰ The poly(alkyl acrylate) and poly(alkyl methacrylate) series have been discussed in detail by Crisp.⁵ Cockbain and co-workers have reported the results of their studies on homologous polyethers.¹ Shereshefsky and co-workers have recently reported their work on monolayer surface pressure-area behavior of a series of succinate polyesters² and adipate polyesters.³ In all these studies the effect of polymer structure on polymer monolayer behavior has been discussed at length. The marked influence of polymer structure on polymer interfacial property is witnessed to a greater extent by the work of Ries and co-workers on poly(vinyl benzoate) and poly(vinyl acetate).^{7a} Here the replacement of the acetate group by the benzoate group results in a completely different orientation of the polymer on the surface. While poly(vinyl acetate) lies flat at the interface, poly(vinyl benzoate) assumes a vertical orientation. Blumstein and Ries recently reported their interesting work on linear, branched, and cross-linked insertion poly(methyl methacrylate).¹⁰

Monolayer film studies on polymer mixtures have not been conducted to any appreciable extent. In recent years attention has been directed to the study of such systems by Ries and Walker,⁸ by Beredjick and Ries,⁹ and by Ries and Beredjick.^{7a} Knowledge on the interfacial properties of copoly-

mers is presently equally lacking. Fowkes, Schick, and Bondi have reported their work on copoly(octadecene-vinyl acetate) and copoly(octadecene-vinyl alcohol).¹¹ Their results show that the copolymers possess better molecular packing ability than the corresponding physical mixtures. In the system poly(vinyl acetate)-poly(vinyl benzoate) referred to above evidence indicates that in the physical mixture of the two components the poly(vinyl acetate) molecule interferes with the poly(vinyl benzoate) molecule in so far as their interfacial behavior is concerned. In the equivalent copolymer system, however, there is apparently no such interference.

EQUIPMENT

Film Balance

This is a Central Scientific Company balance. It has been described in the literature in detail.^{7,8,12}

Improvements in the Original Equipment

The tray was coated (by fluidized-bed technique) with a thin layer of Teflon. This eliminated the need for the frequent waxing. The original mica float that had to be frequently waxed was replaced by a Teflon strip. The platinum ribbons attaching the float to the sides of the tray were also replaced by Teflon ribbons 25 μ thick. The Monel torsion wire was found to corrode under humid conditions and was thus replaced with a stainless steel wire (Malin's 0.010-in. diameter, hard temper).

Film compressions and expansions were conducted by means of a motor geared to a drive shaft carrying the barrier. The motor selected for this purpose has a braking device enabling instantaneous starting and stopping. In operation, the barrier traveled at a uniform speed of 12.5 mm./min. In an average run this corresponded to a compression rate of about 1.5 A.²/min. per polymer segment.

The film balance was placed in a dust-free housing constructed from a suitably modified dry box. A fan in conjunction with a high efficiency filter served to introduce dust-free air into the box prior to each run. The entire film balance assembly was mounted on a steel table designed to isolate structural vibrations. The steel table top, weighing 800 lb., was supported by four springs, one on each corner. A system of dashpots comprising four containers of grease as the viscous (damping) medium, one directly under each spring, served to dampen induced vibrations.

Differential Transformer for Torsion Measurement

Early work with the original equipment utilizing the pointer image alignment in a small mirror showed that this technique was not sufficiently sensitive to small changes in film pressure. A linear differential transformer (LVDT), used for monitoring small displacements, including those related to monolayer studies,¹³⁻¹⁵ seemed promising. This consists of a

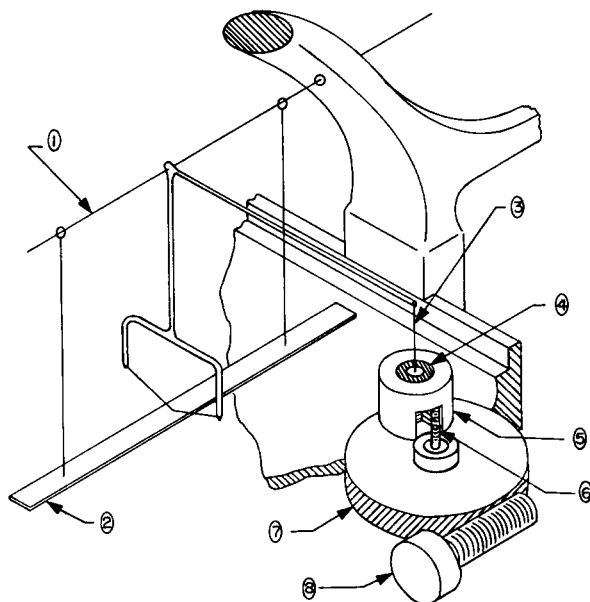


Fig. 1. View of vernier zeroing device (VZD) attached to the bridge part of the film balance, used for accurate determination of film pressure: (1) torsion wire; (2) Teflon float; (3) silk fiber suspension for transformer core; (4) linear variable differential transformer; (5) transformer housing; (6) #6-32 thd.; (7) worm gear; (8) adjustment screw.

core freely movable in an assembly of three equally spaced coils wound on a hollow drum. The relative displacement of the core inside the coil can be electrically measured with a high degree of exactness. Figure 1 represents a view of this equipment and its relation to the torsion wire of the film balance-bridge assembly.

The core of the LVDT was freely hung from the arm of the balance by a single silk fiber. The combined length of the core and the silk fiber was so adjusted that the lower end of the core extended roughly to the mid-point of the transformer coils. This represented an approximate zero setting. The transformer, with its extending leads, was mounted on a vernier zeroing device (VZD) designed and constructed for this purpose. The object of the zeroing device was to provide an accurate means for the zero setting of the LVDT and, hence, the balance. This was achieved through a vertical displacement of the transformer with respect to the suspended core by turning a manual adjustment screw. Each complete turn of this screw corresponds to 0.0032 in. of vertical displacement of the transformer. In use, linear displacement of the core, brought about as a result of torsion in the balance wire, gives rise to electrical output which, on balancing and conversion, will yield the film pressure. The balancing is achieved by a galvanometer through an Atcotran (Automatic Timing and Controls, Inc.) demodulator.

TECHNIQUE

The pressure π of a film on the surface of water is defined as the difference between the surface tension of the film-covered water and that of a clean water surface ($\pi = \gamma - \gamma_0$). The film was cast on water by spreading a measured volume of a solution of the desired material in a suitable solvent and allowing the solvent to evaporate. In the case of polymers the solvent was selected by keeping in mind both its solvent property as well as its vapor pressure. The concentration of the solutions was so adjusted as to provide a film well below a monolayer for approximately each 0.1 ml. dispensed. This was arrived at from a knowledge of the molecular weight of the material and an idea of its cross-sectional area. The solution was dispensed by a micrometer syringe capable of delivering 0.2 ml. and calibrated to measure 0.0002 ml.

Prior to casting the film the balance tray was each time wiped several times with a piece of damp untreated paper towel. The tray was then filled approximately up to the same mark with 0.01*N* aqueous HCl solution and the water swept several times with waxed aluminum strips in both directions on each side of the float. The water level was finally adjusted, and the balance set to a null position.

After the solution was spread, usually an interval of 15 min. was allowed for the solvent to evaporate. The temperature was then read and film compression initiated. At preselected intervals representing certain film areas, film compression (or expansion) was stopped, 2 min. allowed, the torsion wire readjusted to correspond to the null position, and the torsion read on the goniometer scale. This was then converted to dynes/cm. through calibration of the torsion wire.

Calibration

The calibration was conducted by measuring the torsion in the wire caused by hanging a series of known masses on the balance arm extending out in a perpendicular plane to the torsion wire. The calibration process was conducted both for loading and unloading successions, yielding 5.70 dyne/deg. and 5.68 dyne/deg., respectively. The mean of these two values was taken to represent the average. At the 95% confidence limit this has an uncertainty of no more than ± 0.05 dyne/deg. The conversion factors given here were obtained over a calibrating range of 300–1000 mg. (representing the range of mass hung from the balance arm and coinciding with the subsequent experimental conditions). In the lower calibrating range (0–300 mg.) the conversion factors were 5.65 dyne/deg. and 5.63 dyne/deg.

Reproducibility of the Data

The uncertainties in the reported film pressure π (dynes/centimeter), result from two sources: (1) the response of the microammeter to small torsions in the wire, and (2) the uncertainty in the effective length of

the float.¹⁶ The microammeter response limit was found to be within $\pm 0.2^\circ$ torsion. The uncertainty in the effective length of the float was calculated¹⁶ to be ± 0.5 cm. Employing the usual method for the propagation of errors,¹⁷ the uncertainty in the individual points representing the film pressure was calculated to be ± 0.05 dyne/cm. at low pressures (~ 1 dyne/cm.) and ± 0.8 dyne/cm. at higher film pressures. It was found however, that the reproducibility of the data from one experiment to another (Figs. 2–10) was actually better than this, i.e., ± 0.5 dyne/cm.

The uncertainty in the film areas A primarily resulted from the uncertainty (± 0.1 cm.) in the scale reading representing the length of the tray and its width (± 0.05 cm.). The calculated error in A is ± 0.0003 m.². This results in an uncertainty of ± 0.02 m.²/mg. in the individual values. The overall uncertainty from one experiment to another (Figs. 2–10) was found to be slightly higher. In a series of five experiments on the same system the standard deviation was calculated to be ± 0.016 m.²/mg. Twice this value is taken to represent the uncertainty in the reported values.

POLY(VINYL ACETATE)–POLY(ETHYL ACRYLATE) MIXTURES

The poly(vinyl acetate) (PVAc) used was from an extremely narrow molecular weight sample with M.W. = 112,000.* The poly(ethyl acrylate) (PEA) was Thiokol's Thiacril-44, whose molecular weight was not available. Benzene solutions of the two polymers were first made (PVAc, 0.201 mg./ml.; PEA, 0.182 mg./ml.). Solutions containing various weight ratios of the two polymers were then appropriately prepared from these solutions.

Hysteresis Effects in the Poly(vinyl Acetate) System

Earlier experiments on other samples of PVAc had indicated the presence of hysteresis in its monolayer film compression–expansion cycle. In certain cases hysteresis has not generally been observed by some investigators^{5,8,18,19} and in others its presence or absence not mentioned at all.^{20,21} Hysteresis loops have, however, been obtained in the studies of adsorbed proteins.²² For this reason, as well as general interest in the monolayer behavior of polymers, this problem was investigated. The data covering this aspect of poly(vinyl acetate) are presented in graphical form in Figures 2–4. These determinations, as well as subsequent experiments, were made at temperatures that were subject to small increases at the time. During most of the experiments the temperature raised by about 1°C .; in some the change was smaller. The range of temperatures covering all the experiments reported was 22.5 – 27.5°C .

* This material was kindly provided by Professor John D. Ferry, University of Wisconsin. It has been analyzed by chromatographic separation in Japan with the apparent result that the number-average and weight-average molecular weights are identical within 1%.

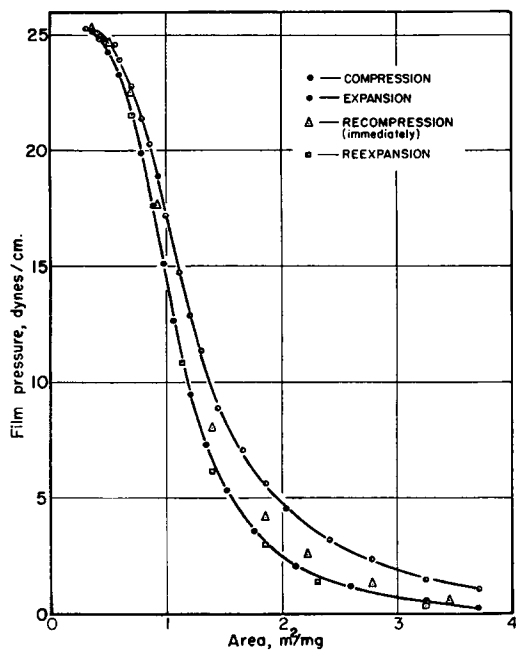


Fig. 2. Pressure-area isotherm of poly(vinyl acetate) (1-A-11).

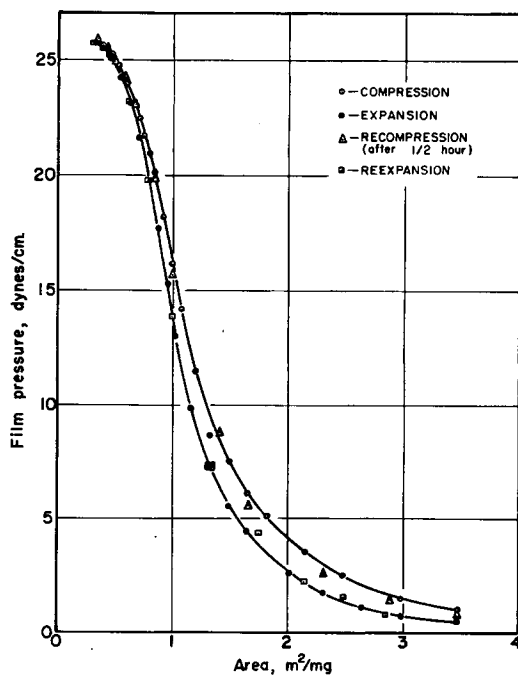


Fig. 3. Pressure-area isotherm of poly(vinyl acetate) (1-A-11).

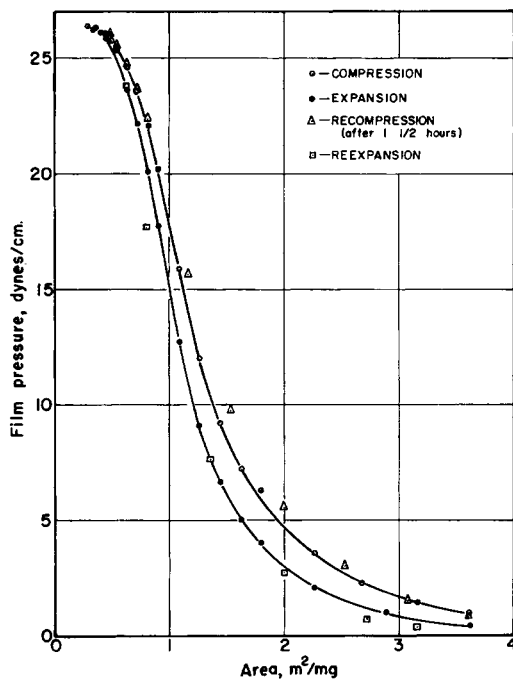


Fig. 4. Pressure-area isotherm of poly(vinyl acetate) (1-A-11).

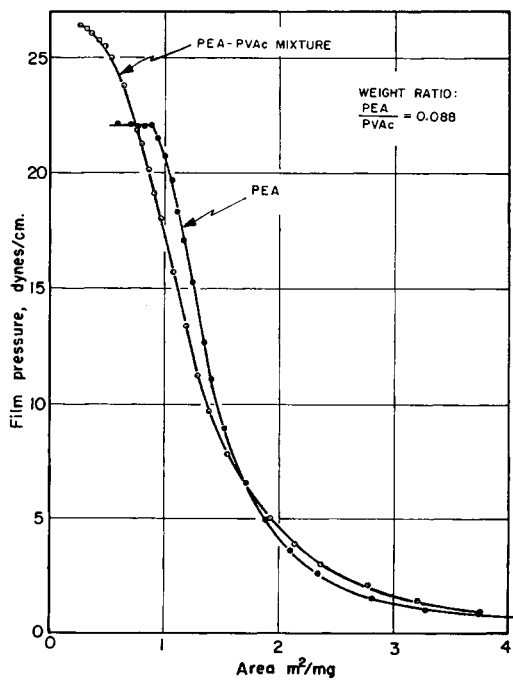


Fig. 5. Pressure-area isotherm of PEA-PVA mixture (weight ratio PEA/PVAc = 0.088).

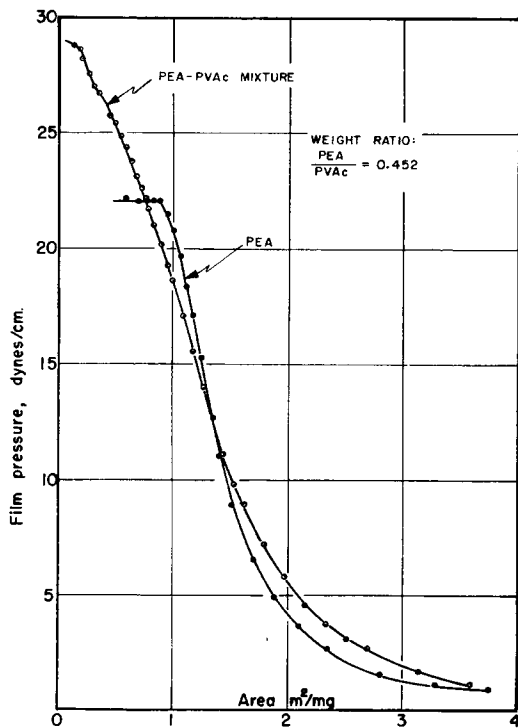


Fig. 6. Pressure-area isotherm of PEA-PVAc mixture (weight ratio PEA/PVAc = 0.452).

In the analysis that follows appropriate correction due to change in the temperature was made. All the analytically treated data were reduced to correspond to a temperature of 22°C. This was not done for the data presented graphically. In the treatment dealing with the poly(vinyl acetate)-poly(ethyl acrylate) mixtures the correction terms were derived from those of poly(vinyl acetate).

Data in Figure 2 represent the case where there was no time allowed to elapse between the half cycles, i.e., the film was expanded immediately upon compression and then immediately recompressed and reexpanded again. Hysteresis, as shown by the data on the film pressure-area determinations, definitely exists. It is noted that in the recompression half cycle the film pressure is lower. The reexpansion half cycle, on the other hand, follows that of the first expansion. The film collapse pressure is about 25.5 dyne/cm. at 22°C., in good agreement with reported values.^{5,8,18-20}

Figure 3 represents the data for the case where the recompression half cycle was conducted after allowing the film to remain in the expanded state following the first complete compression-expansion cycle. Here again hysteresis was observed. There was, however, a new trend developed in the recompression-reexpansion cycle which was attributed to polymer chain entanglement in two dimensions. Since such a process would be

time dependent, it was expected that by allowing the film to remain in the expanded state for some time the film pressure in the recompression half cycle should be higher compared to the case of immediate recompression (Fig. 2). As the data in Figure 3 indicate, this was observed to be the case. Film pressures were slightly higher in the recompression half cycle compared to the previous case. The data obviously do not throw any light on the mechanism of hysteresis. They indicate, however, that if the film expansion were to be conducted extremely slowly no hysteresis should be observed. It was noticed that the extent of hysteresis is smaller in the second

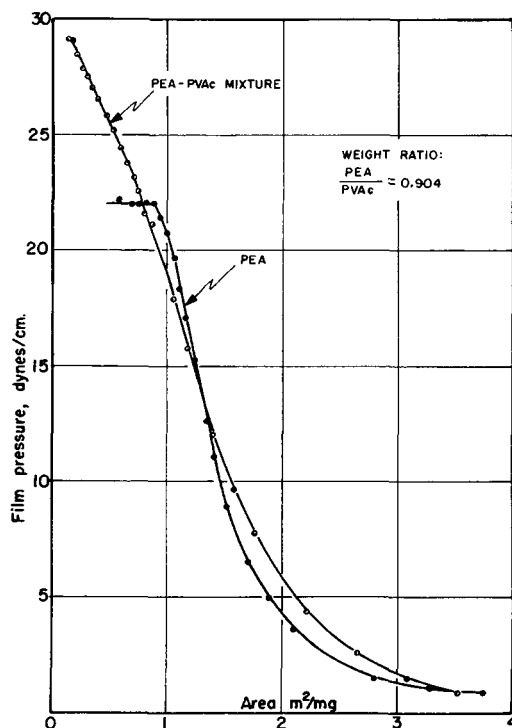


Fig. 7. Pressure-area isotherm of PEA-PVAc mixture (weight ratio PEA/PVAc = 0.904).

compression-expansion cycle. The effect should reduce even further if the film were allowed to remain in the expanded state for an extended time period. A third set of data representing the case where the film remained in the expanded state for 1½ hr. is graphically depicted in Figure 4. Here in the recompression and reexpansion half cycles the film pressures were slightly higher and slightly lower, respectively. These can only be explained by attributing them to "aging" of the film. The time taken for completing this experiment was about 6 hr., and it is highly possible that extraneous molecules originating from electrical cables in the box were adsorbed on the surface.

The pressure–area isotherm for poly(ethyl acrylate) is shown in each of the Figures 5–10. This is done in order not only to provide the data but also for comparison with those of its mixtures with poly(vinyl acetate) shown in the same figures. A few points regarding the monolayer behavior of this polymer in comparison with that of poly(vinyl acetate), having a similar but reversed ester group in its structure, may be useful. Poly(ethyl acrylate) film collapses at a pressure of about 22 dyne/cm., while poly(vinyl acetate) film collapses at about 26 dyne/cm. The areas at zero film pressure are 24 A.²/segment for PVAc and 30 A.²/segment for PEA. There is

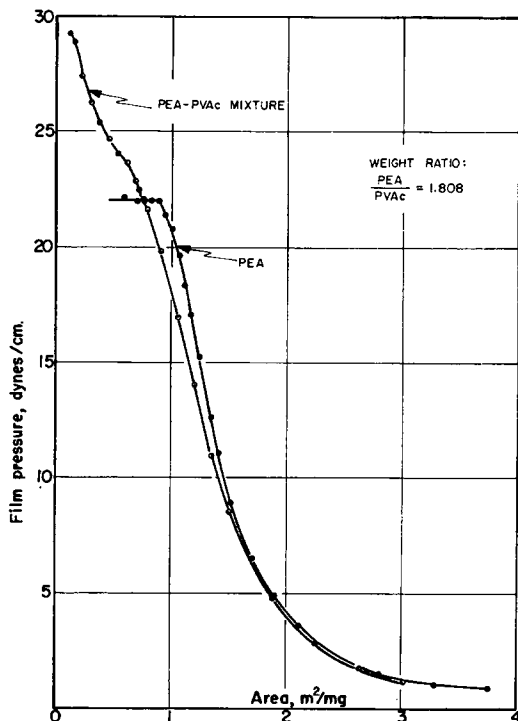


Fig. 8. Pressure–area isotherm of PEA–PVAc mixture (weight ratio PEA/PVAc = 1.808).

good agreement between the reported value⁵ for collapse pressure and the present determination. The area per polymer segment for PEA, however, is higher than that in the literature.⁵

The rates of change of film pressure on compression for poly(vinyl acetate) and poly(ethyl acrylate) in the linear region of their isotherms are, respectively, 17.01 and 19.86 dyne-cm.⁻¹ m.⁻² mg., the latter being nearly 17% higher than the former. Since chain rigidity in poly(ethyl acrylate) is not any greater than in poly(vinyl acetate), the difference is attributed to the greater interchain repulsive forces caused by the larger size of the ethyl compared to the methyl groups.

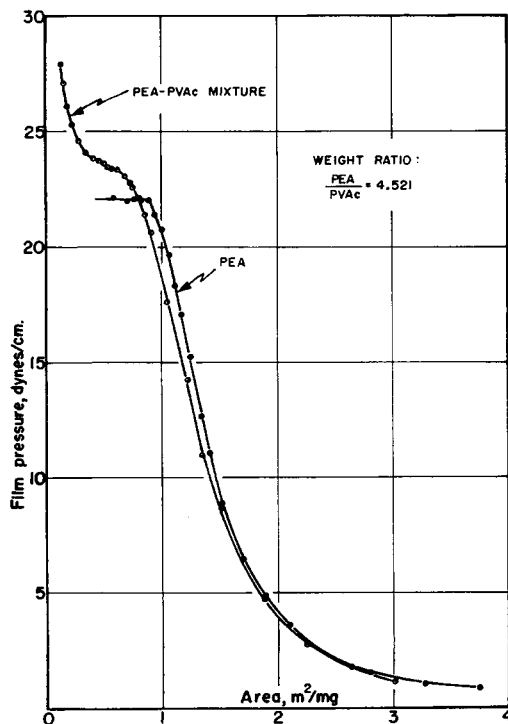


Fig. 9 Pressure-area isotherm of PEA-PVAc mixture (weight ratio PEA/PVAc = 4.521).

Because of similar structural features, e.g., the C=O and O—R groups in both polymers, the component of forces in the vertical plane to the surface should be the same in both molecules. The lower collapse pressure of the PEA is, therefore, attributed to the greater repulsion between the ethyl groups.

Film Pressure of Polymers and Their Mixtures

Figures 5–10 depict the pressure-area isotherms for poly(vinyl acetate)–poly(ethyl acrylate) mixtures, the weight ratio of the latter polymer to the former ranging from 0.088 to 11.301. In the discussion and deductions that follow a correction was applied and all data were reduced to correspond to 22°C. In the pressure range 2.5–12.5 dyne/cm. the correction term for the PVAc film area is 0.03 m²/mg.-°C.; in the range of 12.5–22.5 dyne it is 0.02 m²/mg.-°C. For poly(ethyl acrylate) no appreciable correction was needed. These correction terms were applied to the case of the mixtures. Since the values employed in the calculations were those read from the graphs either directly or by extrapolation, the uncertainties resulting from such a correction were not regarded as serious.

Polymer-Polymer Interaction at the Interface. In Table I are recorded the monolayer film areas at zero film pressure for various mixtures of these

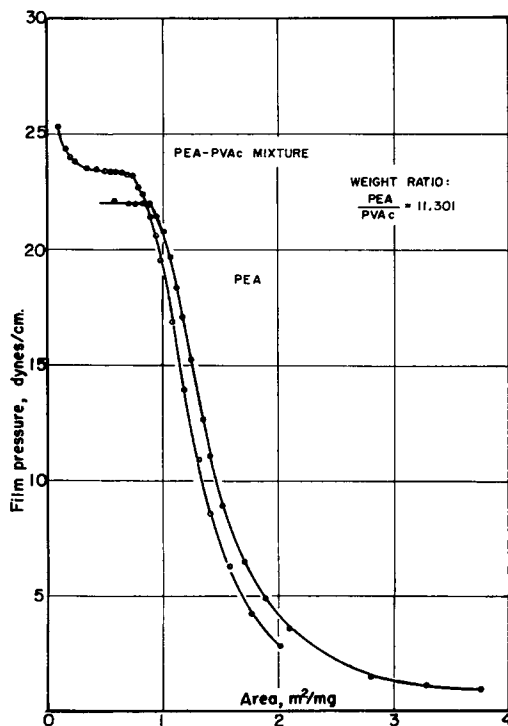


Fig. 10. Pressure-area isotherm of PEA-PVAc mixture (weight ratio PEA/PVAc = 11.301).

polymers. One interesting fact emerges from these data: The film area of the polymer mixture under zero pressure goes through a maximum as composition changes. Before pursuing this point further, it would be appropriate to briefly discuss the general trend that might be expected in the behavior of mixed films. In a multicomponent, physically mixed

TABLE I
Film Areas Under Zero Pressure for PEA-PVAc Mixtures at 22°C.

Film composition		
Wt. ratio PEA/PVAc	Ratio of the number of PEA/PVAc repeating units	Film area A_0 , m. ² /mg.
0 (PVAc)	0	1.64
0.088	0.08	1.81
0.452	0.39	1.98
0.904	0.78	2.06
1.808	1.56	1.85
4.521	3.89	1.77
11.301	9.72	1.65
∞ (PEA)	∞	1.83

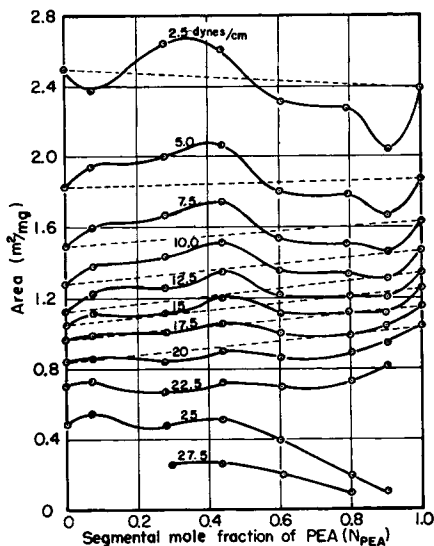


Fig. 11. Monolayer film areas of PEA-PVAc mixtures at various film pressures; temperature 22°C.

polymer film where the components are molecularly dispersed, it is probable that the behavior of the mixed film is proportional to the composition but, due to the changes in molecular environment, there will be differences in the orientation and packing of each component. In cases where strong interactions exist, this difference is quite manifest.²³ This seems to be somewhat expected also in situations where the interaction between the components is weaker.²⁴ Where the components are immiscible, giving rise to micelles or islands, it is expected that the molecular environment of each molecule will not be substantially altered by the presence of the other. In such a situation it is expected that the ideal mixture rule $P = \sum_i p_i N_i$, where P is the total property, p_i the property, and N_i the mole fraction, respectively, of the i th component, will apply. Applying this rule to the film surface area, A_m ,

$$A_m = A_1 N_1 + A_2 N_2 \quad (1)$$

of the mixture one would generally be able to predict the extent of departure from ideality and hence the interactions. It should be noted, however, that while such departures are a strong indication of the presence of interaction and hence miscibility between the two components, agreement with an equation such as eq. (1), for a two-component system, does not necessarily imply lack of mixing. While mixing may occur, it is not always true that it should result from or be accompanied by interaction between molecules. Cases of strong interaction and miscibility between alcohols or acids with amines have been observed^{24,25} In utilizing eq. (1) one needs to know the molecular weight of each species in the mixture and thus the mole fractions.

TABLE II
Monolayer Film Areas of PEA-PVAc Mixtures
at Various Film Pressures at 22°C.

π , dyne/cm.	Segmental mole fraction of PEA in PVAc N_{PEA}							
	0	0.0747	0.2800	0.4376	0.6086	0.7954	0.9037	1.000
2.5	2.49	2.36	2.63	2.59	2.30	2.27	2.02	2.38
5.0	1.82	1.93	1.99	2.05	1.79	1.77	1.66	1.88
7.5	1.48	1.59	1.66	1.73	1.53	1.50	1.45	1.62
10.0	1.28	1.37	1.43	1.50	1.35	1.33	1.31	1.46
12.5	1.12	1.22	1.25	1.32	1.21	1.20	1.20	1.34
15.0	1.04	1.10	1.11	1.19	1.11	1.12	1.12	1.25
17.5	0.96	0.98	1.00	1.04	0.99	0.98	1.04	1.15
20.0	0.84	0.86	0.84	0.89	0.85	0.88	0.94	1.04
22.5	0.70	0.72	0.66	0.71	0.69	0.72	0.79	—
25.0	0.48	0.53	0.46	0.50	0.39	0.19	0.10	—
27.5	—	—	0.24	0.26	0.19	0.08	—	—

In the case of PEA the molecular weight was not known. In the calculations the polymer segmental mole fraction was, therefore, used. This represents the fraction of the repeating units for each component over the total. In Figure 11 polymer mixture areas are plotted at several film pressures. The extent of the deviation from linearity is a measure of interaction and thus miscibility of the polymers (Table II). The values representing the ordinate were directly read from Figures 2 and 5–10. Several important points are revealed from these plots: (a) there is interaction existing between poly(vinyl acetate) and poly(ethyl acrylate) molecules at the interface; (b) contribution to the film area due to interaction is both positive and negative and follows more or less the same trend irrespective of the film pressure; (c) deviation from eq. (1) is smaller in the film pressure range 12–22 dyne/cm. and increases in the lower film pressure region. This range corresponds approximately to the linear region of the pressure–area isotherms of the mixtures.

Interpreted in terms of molecular orientation and interaction, these would mean that at the interface the two polymers form a more homogeneous and molecularly dispersed phase at low film pressures than at the higher values. As the pressure is increased, each polymer chain will undergo reorientation compatible with the new conformational environment of the components of the mixture. The data represented in Figures 2–10 show that close packing of the polymer chains is generally attained at about 10 dyne/cm. This is approximately the pressure where the linear portion of the pressure–area isotherm begins. It is associated with the close packing and, hence the coming into effect, of inter- and intramolecular interactions. Data plotted in Figure 11 show that in the range where these forces become operative, molecular orientation of a type equivalent to a decrease in the degree of mixing of the polymer components begins to occur. Such reorientations need not necessarily result in actual separation of the com-

ponents. The implication would be the existence of a two-dimensional phase structure where polymer interactions are minimized. Electron diffraction studies of such films should reveal more direct information on their structure.

The discussion of mixed-polymer monolayers at an interface and their interaction and stability may be further pursued from the equilibrium thermodynamic point of view. If the systems comprising the polymer mixtures in the film form represent true equilibria, and not rate-dependent processes, one may compare the monolayer area, A_0 (obtained by extrapolation of the linear region of the isotherm to zero pressure) with the calculated partial mole area, \bar{A} , for each component. If the chemical potential of one of the components, say, PEA, is μ_2 , this being defined as $\mu_i = (\partial F / \partial n_i)_{P, T, n_j}$, and its chemical potential in the thermodynamic standard state is μ° , then

$$\mu_2^s = \mu_2^\circ + RT \ln a_2^s \quad (2)$$

where a_2^s is the activity of component 2 on the surface. If the chemical potential of this component in its excess phase is μ_2^* and π represents the surface or film pressure at which this component separates out of the film, at equilibrium $\mu_2^s = \mu_2^*$. Therefore, one may write

$$\mu_2^* - \mu_2^\circ = RT \ln a_2'^s + \pi \bar{A}_2 \quad (3)$$

Here the a' term refers to the activity at which component 2 separates out of the film. The term $\pi \bar{A}_2$ is the surface energy of component 2 per mole. Replacing the activity term by the product of the mole fraction and the activity coefficient terms, rearranging and differentiating, one obtains

$$\bar{A}_2 = -RT [(\partial \ln N_2'^s / \partial \pi) - (\partial \ln f_2 / \partial \pi)] \quad (4)$$

If we assume that the activity coefficient remains independent of film pressure π , eq. (4) becomes:

$$\partial \ln N_2' / \partial \pi = -\bar{A}_2 / RT \quad (5)$$

Thus if $\ln N_2'$ is plotted versus π , the pressure at which excess component 2 is squeezed out of the film, a straight line should result. This plot is represented in Figure 12. Because of difficulties involved in estimating π from the graphs, the data in Figure 12 are approximate. The segmental area, \bar{A}_2 , of PEA was calculated from the slope of the line [eq. (5)] to be 35 A.²/repeating unit. This is in good agreement with the directly measured value of 30 A.².

By using the segmental mole fraction, N_i (seg), instead of the usually defined term N_i (where the number of molecules rather than the number of repeating units is used) one would note that there is some error introduced into the equation and hence the plot (Fig. 12). By defining the mole fraction of the PEA as $N_2 = n_2 / (n_1 + n_2)$ and its segmental mole fraction as N_2 (seg) = $n_2' / (n_1' + n_2')$, where n refers to the actual number of

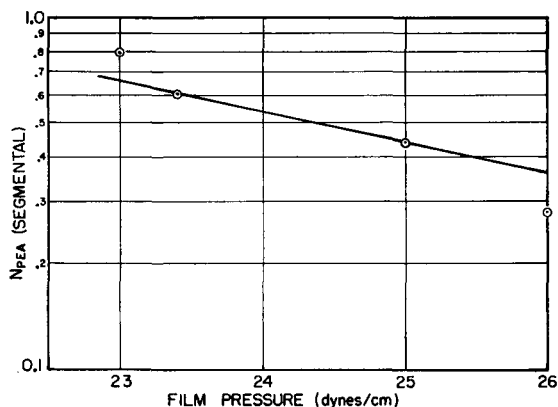


Fig. 12. Variation of the film pressure at which one component (PEA) of the mixture separates with film composition.

molecules of the polymer and n' to the number of repeating monomer units in the polymer, one may derive the relation:

$$\ln N_2(\text{seg}) = \ln N_2 + \ln \left(\frac{1}{z_1} \right) \left[\frac{z_1 m_1 M_1 + z_2 m_1 M_2}{m_1 M_2 + m_2 M_1} \right]. \quad (6)$$

Here M and z refer to the molecular weight of the repeating unit and the number of these per polymer chain (subscript 1 referring to PVAc and 2 to PEA); m represents the mass of the polymer per unit mass of the mixture. Equation (6) may be transformed to

$$\ln N_2(\text{seg}) = \ln N_2 + \ln \left(\frac{1}{z_1} \right) \left[\frac{z_1 M_1 (m_2/m_1) + z_2 M_2}{M_1 (m_2/m_1) + M_2} \right]. \quad (7)$$

If the two polymers have the same number of segmental units per polymer chain, i.e., if $z_1 = z_2$, then obviously $\ln N_2(\text{seg}) = \ln N_2$. Since the molecular weight, M , of any polymer, is equal to $M = zM$, eq. (7) may be rewritten as

$$\ln N_2(\text{seg}) = \ln N_2 + \ln \left(\frac{1}{z_1} \right) \left[\frac{M_1 (m_2/m_1) + M_2}{M_1 (m_2/m_1) + M_2} \right] \quad (8)$$

Replacing m_2/m_1 by x , this becomes

$$\ln N_2(\text{seg}) = \ln N_2 + \ln \left(\frac{1}{z_1} \right) \left[\frac{M_1 x + M_2}{M_1 x + M_2} \right] \quad (9)$$

For dilute solutions of one polymer in the other, i.e., for small values of x ,

$$N_2(\text{seg}) = N_2(z_2/z_1) \quad (10)$$

and the points in Figure 12 should be displaced by a constant amount. At higher concentrations, however, since M_1 for the present sample of PVAc

is about 1,400 times as large as M_1 , the second term on the right-hand side the equation becomes a governing part, and the straight line will be curved gradually and displaced in the positive direction of the ordinate.

It will be of interest to note that in eq. (4) at the collapse pressure π_0 of the pure component, N_2' would represent the solubility of that component in a two-dimensional phase. The point of intersection of the straight line, in Figure 12, with the ordinate at this pressure will thus represent the solubility of this polymer component in the film. It is also of interest to note that in the range of composition ratio of 0.45–0.90 the isotherm for the mixed film is represented by a straight line, indicative of a new phase structure. The collapse pressure of this film is higher than that of either component (Figs. 6 and 7). The implications resulting from this concept are as follows.

(a) Polymer–polymer interaction and hence compatibility at the interface can be studied. For the system PVAc–PEA compatibility was observed through a wide range of concentration and at various film pressures up to the point of collapse.

(b) Similar studies of polymers in the presence of plasticizers can be undertaken to learn about the behavior of extended or plasticized systems when these are present at an interface. Furthermore, the study with plasticized systems will throw light on the behavior of plasticizers in general.

(c) If a system comprising a polymer mixture is present at an interface, it is important to know both how and to what degree the interfacial behavior is governed by the polymer–polymer interaction and by the composition.

(d) Incorporation of film studies of the type presently being discussed with information derived from surface potential studies on metallic or aqueous substrates will lead to an understanding of the role of polymer orientation and interaction on the surface.

(e) Film balance studies have shown²⁶ that good film-forming properties and high collapse pressures are characteristic of many corrosion-preventative compounds. This is obviously related to the fact that the first adsorbed molecular layer of a corrosion-preventing agent is the only one that can react chemically with a metal surface. The function of anti-rust additives has been the subject of many investigations,²⁷ but details of formation, structure, and behavior of protective films are still obscure.

(f) It is possible, as reported by Ries and co-workers, to use such techniques to differentiate between stereochemical configurations in polymers^{6,9} and to study the interfacial behavior of their mixtures.⁹ It is also possible to differentiate in an analogous manner between graft and block copolymers.⁹ Furthermore, surface pressure–area measurements can suitably be extended to the comparative study of copolymers and homopolymer physical mixtures of equivalent composition.¹¹

Polymer Orientation and Adhesion at the Interface. By assuming a certain polymer conformation at the interface and by taking into account the possible interactions that exist between a polymer and a surface, it is

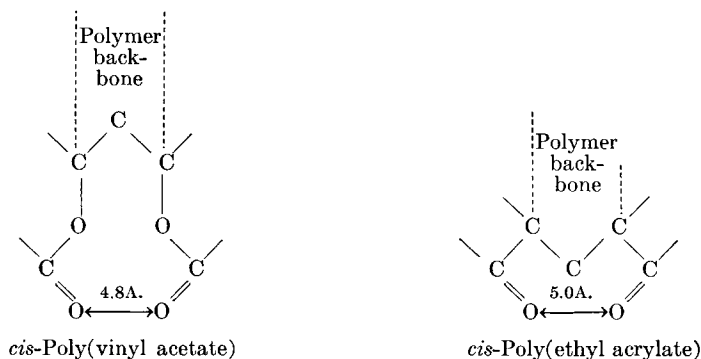


Figure 13.

possible to arrive at the energies involved in holding a polymer chain on the surface. In practical applications solid surfaces, no matter what their nature, have associated with them a certain number of adsorbed water molecules.²⁸ To this extent, then, film studies at the air-water interface can be related to the study of films on a solid substrate.

Existing evidence on monomolecular films of poly(vinyl acetate) and polyacrylates points out that these polymers exist in the *cis*-conformation at the interface.^{5,20} From the values derived for the limiting areas of these polymers from the present studies in conjunction with their bulk densities (PVAc, 1.19; PEA, 1.1),²⁹ their calculated film thicknesses are: PVAc, 4.5 Å. and PEA, 5.5 Å. These values are consistent with a polymer orientation in which the backbone of the polymer repeating unit lies flat at the interface. It will be pertinent to note in this connection that measurements of contact potential of PVAc on steel and platinum planar surfaces by Gottlieb³⁰ are consistent with a polymer orientation where both oxygen atoms of the polymer are in the plane of the surface with the intermediate carbon atom out of this surface. From a comparison of surface potential-surface coverage data for PVAc and octadecyl acetate it is also concluded that below the plateau coverage all of the acetate groups from the polymer are oriented in contact with the metal surface. By using the values for the covalent bond radii and bond angles,³¹ it is possible to calculate the distance between carbonyl groups consistent with a given conformation for *cis*-poly(vinyl acetate) and *cis*-poly(ethyl acrylate). These, as represented in Figure 13 are: $d(\text{PVAc}) = 4.8 \text{ \AA.}$ and $d(\text{PEA}) = 5.0 \text{ \AA.}$

It is assumed that among the various forces present at an interface, hydrogen bonding is the main interaction holding the polymer chain on the

surface. From the structure of the carbonyl group, $\text{C}=\ddot{\text{O}}:$, and that of the carbon-oxygen-carbon linkage, in an ester, one would expect that hydrogen bonding would take place preferentially with the carbonyl oxygen. This is indirectly supported by the higher dipole moment of compounds (such as acetone) containing a carbonyl group compared to those contain-

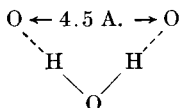


Fig. 14. Hydrogen bonding in water.

ing the $\text{C}-\text{O}-\text{C}$ group, such as ethyl ether.³² This is further supported by the higher hydrogen-bond energies involved in compounds containing the former group. From data on the $\text{H}-\text{O}$ bond distance in water and other bond radii,³¹ one may calculate the oxygen-oxygen separation in water where hydrogen bonding is involved. This turns out to be 4.5 Å. Comparing this with the carbonyl oxygen-oxygen separation in PVAc and PEA (Fig. 14), one notes that the distances are such that intrapolymer hydrogen bonding can take place without any molecular distortion.

One may also inquire into the possibility of interpolymer hydrogen bonding. This is governed primarily by the polymer structure and interchain distances in the film. At large separations this could not easily take place. At higher film compactness, however, the conditions would be more favorable.

In a typical pressure-area isotherm there are four points on the abscissa representing areas that are significant. These are: (1) A_0 , representing polymer segmental area obtained by the extrapolation of the linear region of the isotherm to zero pressure; (2) the segmental area, A_1 , representing the onset of the linear and the steepest region of the isotherm; (3) A_2 , the area where the linear region terminates; (4) A_3 , the area at which the vertical component of the interfacial interaction approximately equals the sum of the cohesive and adhesive force components holding the polymer on the surface. This is the collapse pressure. At this point the polymer film breaks and an overfilm develops. The word approximate is used in order to allow for any residual interactions between the molecules squeezed out and those on which they are superimposed. These areas and the corresponding film pressures are recorded in Table III.

Several interesting features become apparent from the data in Table III and the corresponding graphs.

(a) For equal pressures the values of A are all higher for PEA than those for PVAc.

(b) PVAc is more compressible than PEA. While PVAc can be compressed to 13 Å.² per repeating unit (A_2) without any break in the film, PEA can be compressed only to an area corresponding to 18 Å.² per repeating unit.

(c) Since in these polymers the segments are separated by a distance equal to $2a \cos 36^\circ = 2.5 \text{ Å.}$, where a is the $\text{C}-\text{C}$ bond distance, one would note from the above values for the segmental areas that while in a packed monolayer of poly(vinyl acetate) the chains approach each other to within 5 Å.,⁵ in poly(ethyl acrylate) the chain separation is 7 Å. This is no doubt related to the steric interaction of the bulky ethyl groups in the latter

TABLE III
 Film Areas and Pressures at Several Points of the Pressure–Area Isotherms
 for Poly(vinyl Acetate) and Poly(ethyl Acrylate)

Designation	Poly(vinyl acetate)				Poly(ethyl acrylate)			
	Area		Film pressure, dyne/cm.	Calcd. film thickness, A.	Area		Film pressure dyne/cm.	Calcd. film thickness, A.
	m. ² /mg.	A. ² /unit			m. ² /mg.	A. ² /unit		
A ₀	1.65	24	0 ^a	4.6	1.83	30	0 ^a	5.5
A ₁	1.14	16	12.5	6.3	1.34	22	12.7	8.0
A ₂	0.91	13	18.2	7.9	1.06	18	19.7	10.0
A ₃	0.40	6	25.8	9.6	0.88	15	22.0	22.0

^a Extrapolated.

polymer. To the extent that the calculated film thicknesses (based on bulk densities), corresponding to the areas A_1 , A_2 and A_3 , as in Table III, are approximate, they reflect, nonetheless, the degree to which the polymers coil upwards from an interface on which they are adsorbed.

Film balance data can also be used to estimate the bonding energy on the surface. The collapse pressures of poly(vinyl acetate) and poly(ethyl acrylate) are 26 and 22 dyne/cm., respectively; these are equivalent to 26 and 22 erg/cm.². Since the cohesive energy of polymer films is, by definition, a negative quantity, the total collapse energy will be slightly higher. Such values can be used in a comparative way to assess the relative "adhesion" of such polymers to surfaces. Values obtained for the adhesion energy of polymers to surfaces by such a technique are comparable to those obtained by wetting or adsorption. They are much lower than values obtained in dynamic stripping tests.

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Résumé

On a étudié le comportement d'un film monomoléculaire d'acétate de polyvinyle (PVAc), de polyacrylate d'éthyle (PEA) et de mélanges de ces polymères sur une variation du rapport de concentration de PEA sur PVAc allant de 0.088 à 11.301 en utilisant une balance à film du type Langmuir au-dessus d'un substrat aqueux constitué d'acide chlorhydrique 0.01*N*. On a observé une hystérèse dans le cycle compression-expansion pour PVAc. Une discussion de l'interaction polymère-polymère dans un film monomoléculaire mixte à l'interface est présenté. L'importance de cette interaction pour les films comprenant du PVAc et PEA a été déterminée en termes de déviations de la surface du film au départ du comportement idéal. Les résultats sont présentés graphiquement pour l'entière composition du film. Les données sur les surfaces du film de PVAc et de PEA sont discutées en termes d'orientation moléculaire de ces polymères à la surface. Un traitement thermodynamique à l'équilibre simple est appliqué à ces résultats sur les films monocouches mixtes. Les implications résultant de cette étude sont discutées.

Zusammenfassung

Das Verhalten von Polyvinylacetat (PVAc), Polyäthylacrylat (PEA) und von Mischungen dieser Polymeren im Bereich des Konzentrationsverhältnisses 0,088 bis 11,301 von PEA zu PVAc als monomolekulare Filme auf wässriger 0,01*N* HCl wurde mit einer Langmuir-Waage untersucht. Bei PVAc trat im Kompressions-Expansionszyklus Hysterese auf. Eine Diskussion der Polymer-Polymer-Wechselwirkung wurde bei Filmen aus PVAc und PEA aus der Abweichung des Filmflächenbedarfs vom idealen Verhalten bestimmt. Die Ergebnisse werden im gegebenen Bereich der Filmzusammensetzung graphisch dargestellt. Die Ergebnisse bezüglich des Flächenbedarfs der Filme aus PVAc und PEA werden an Hand der Molekülorientierung dieser Polymeren an der Oberfläche diskutiert. Eine einfache thermodynamische Behandlung der Ergebnisse an gemischten monomolekularen Schichten wird gegeben. Die Folgerungen aus dieser Untersuchung werden diskutiert.

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