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Abstract

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TWO-DIMENSIONAL PRESSURE AND THE ABILITY OF MONOLAYERS OF MIXTURES OF NORMAL AND SECONDARY HEXADECANOLS TO REDUCE WATER EVAPORATION

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In our previous works (^{1}), we described the properties of monolayers of certain technically available alcohols that could be used instead of normal hexadecanol (cetyl alcohol), which is commonly used to protect the water surface from evaporation (^{2,3}). Since technical synthetic alcohols are mixtures of substances of different structure and, above all, mixtures of primary and secondary alcohols (and also contain substances of other classes—aldehydes, ketones, unsaturated compounds), it seemed interesting to us to investigate the properties of monolayers of mixtures of individual substances of known structure. We chose mixtures of cetyl alcohol (imported sample, "pure" grade, m.p. 47.5-48°) and secondary hexadecanol of the structure CH_3—$(CH_2)_4$—CHOH—$(CH_2)_9$—CH_3 (m.p. 40.5-41°), obtained by us from the laboratory of A. D. Petrov (Institute of Organic Chemistry, Academy of Sciences of the USSR) and mentioned earlier (^{1}).

The two-dimensional pressure upon compression of monolayers of mixtures of two substances has been studied for *n*-long-chain fatty acids with isodextropimaric acid in (^{4}), for mixtures of arachidic acid with stearic acid and ethyl palmitate in (^{5}). Some other mixtures are mentioned in (^{6}). For mixtures of primary and secondary alcohols—especially together with data on their evaporation-protective properties—there appear to be no data.

The investigation of the curves of two-dimensional pressure versus area was carried out in the apparatus described earlier, with a trough, using a vertical balance consisting of a cover-glass plate suspended on a quartz spiral and a measuring microscope (^{7}). The equilibrium two-dimensional pressure and the kinetics of its increase were studied in the same apparatus, and also in an apparatus for measuring the protective properties of monolayers in reducing water evaporation, which is an apparatus of Baranaev (^{8}) improved by us; the apparatus was enlarged, provided with special control of the rate of gas (N_2) blowing and conditioning of its humidity, and also equipped with a vertical balance of the type indicated above for continuous monitoring of the two-dimensional pres-

Figure 1

Figure 1: Figure 1

sure of the monolayer. Measurements in all cases were carried out at 20 ± 0.5° on bidistillate distilled over alkaline permanganate.

Figure 1a shows the curves of the dependence of the two-dimensional pressure F on the area per molecule a, expressed both in $\mathring{\mathrm{A}}^2$ per molecule and in m^2/mg of substance, for mixtures of the above alcohols in different ratios.

It follows from the curves that the secondary alcohol forms a monolayer of the liquid-expanded type; its two-dimensional pressure (as for a number of other secondary alcohols considered by us elsewhere) begins to rise at large areas $a \approx 100\ \mathring{\mathrm{A}}^2$ and rises at point J only to the equilibrium value $F_e = 19.1$ dyn/cm at $a = 47\ \mathring{\mathrm{A}}^2$, and then remains constant as a result of the squeezing out of the monolayer molecules into microcrystallites. For cetyl alcohol, the F—a curve begins at $a = 22\ \mathring{\mathrm{A}}^2$ and, after a certain sloping section of the liquid-condensed type, rises steeply at $a \approx 20\ \mathring{\mathrm{A}}^2$ to $F > 50$ dyn/cm, exceeding the equilibrium $F_e = 46$ dyn/cm (for this sample of cetyl alcohol, containing impurities).

All mixtures of intermediate composition are characterized by a "lower" portion of the curve corresponding to the liquid-expanded state of the secondary alcohol-

···with a "horizontal" segment lying at a height $F = 19.1$ dyn/cm, corresponding to the expulsion of molecules of the secondary alcohol from the monolayer, and a "vertical" segment of compression of the monolayer of cetyl alcohol remaining on the water surface.

Fig. 1. a—curves of the dependence F—a for normal and secondary $(CH_3 - (CH_2)_4 - CHOH - (CH_2)_9 - CH_3)$ hexadecanols and their mixtures; b—curves of the dependence of the equilibrium surface pressure (F_e) and protective properties (K) on the composition of the mixture of normal and secondary hexadecanols.

The arrangement of the curves in the lower part corresponds mainly to the additive relation of the areas of the two alcohols at each F, taken from the curves of the individual alcohols, as is seen from Table 1.

Table 1

Additivity of the areas of mixtures of alcohols from the lower portions of the F—a curves (in $\mathring{\mathrm{A}}^2$)

F, dyn/cm	Individual alcohols $a_{\text{norm.}}$	Individual alcohols $a_{\text{sec.}}$	Alcohol ratio—normal/secondary 4 : 1 a_{add}	Alcohol ratio—normal/secondary 4 : 1 a_{exp}	Alcohol ratio—normal/secondary 1 : 1 a_{add}	Alcohol ratio—normal/secondary 1 : 1 a_{exp}	Alcohol ratio—normal/secondary 1 : 4 a_{add}	Alcohol ratio—normal/secondary 1 : 4 a_{exp}
4.0	21.0	72.0	31.2	30.3	46.5	48.6	61.8	60.0
14.0	20.2	52.0	26.9	26.8	36.1	37.5	45.6	44.4
19.1	20.0	47.0	25.4	25.0	33.5	33.5	41.6	40.0

The length of the "horizontal" segment of the F—a curve, corresponding to the expulsion of the secondary alcohol, is obtained from the difference between the area of the break point J and the area A', found by extrapolating the "vertical" segment of the F—a curve to the abscissa $F = 19.1$ dyn/cm (Table 2).

From the data of Table 2 it follows that the secondary alcohol is not expelled completely on the horizontal segment of the F—a curve; approximately 4% of the amount of secondary alcohol taken remains in the monolayer.

The values $a_{IA'}$, found by extrapolation, and a_{II}, calculated for normal (cetyl) alcohol, as well as the relative increase in area relative to the area of cetyl alcohol, are shown in Table 3, where b is the molar content of normal alcohol in the mixture.

From the data of Table 3 it is seen that, on average, 6.5 mole % of secondary alcohol by···

with respect to the normal alcohol is retained in it upon compression up to the beginning of the "vertical"branch of the F—a curve. This, evidently, corresponds to the two-dimensional solubility of the secondary alcohol in the normal alcohol at $F = 19.1$ dyn/cm. This is also confirmed by the fact that the compressibility of the monolayer of the mixture on the branch $F > 19.1$ dyn/cm is higher than the compressibility of a monolayer of normal alcohol alone (Table 3). At the same time, the very high compressibility in the 1 : 4 mixture and the decrease in the area attributable to cetyl alcohol at $F = 50$ dyn/cm make it possible to suppose that part of the cetyl alcohol is in turn squeezed out, dissolving in crystals of the secondary alcohol.

Table 2

Fraction of squeezed-out and remaining molecules of secondary alcohol, calculated from the horizontal portions of the $F - a$ curves

Ratio of alcohols normal / secondary	a_J, Å^2	$a_I A'$, Å^2	Fraction of squeezed-out molecules of secondary alcohol $\frac{a_J - a_I A'}{47} \cdot 100$	Fraction of unsqueezed molecules of secondary alcohol, %
4 : 1	25.0	17.4	16.15	3.85
1 : 1	33.5	12.5	44.75	5.25
1 : 4	40.0	4.5	75.7	4.3

Of interest is the kinetics of spreading of the monolayer $F(\tau)$ from the bulk phase and the influence on it of the secondary alcohol. The experiments were carried out both at a constant perimeter of the polycrystalline layer of the solid phase—alcohol (deposited on a glass rod by immersion in a melt of the alcohol followed by solidification)—and when a large number of crystallites were deposited on the water surface. It was found that the long "induction" period on the $F(\tau)$ curve, associated with the gradual condensation of the two-dimensional vapor of cetyl alcohol, is regularly shortened as the content of secondary alcohol in the mixture is increased. This corresponds to the fact that the areas at small F increase with increasing secondary-alcohol content (Fig. 1a). From the $F(\tau)$ curve in Fig. 2, obtained when crystallites of the 1 : 1 mixture were deposited, it is seen that at first F rises almost instantaneously to 19.1 dyn/cm, which is the equilibrium value for the secondary alcohol, then for a long time ($\sim$ 20 min.) rises to 19.5 dyn/cm, and only after this increases more rapidly to $F_e = 44$ dyn/cm—the equilibrium value for this mixture. This kinetic curve corresponds to the $F - a$ curve in Fig. 1a for the same mixture. It shows that initially the secondary alcohol spreads rapidly, but then almost all of it is gradually displaced from the monolayer into bulk microcrystallites by the more surface-active normal alcohol. In the final monolayer about 6% of secondary alcohol is probably retained. In general form, the kinetic curve for spontaneous spreading reproduces the curve for ordinary compression of the monolayer with all its phase transitions ([9]).

Table 3

Relative increase in area relative to the area of cetyl alcohol and compressibility of mixed monolayers

Ratio of alcohols normal / secondary	$a_I A'$, Å^2	a_{II}, Å^2	$\frac{a_I A' - a_{II}}{47 \cdot b} \cdot 100$	$\chi = \left(-\frac{1}{a}\frac{\partial a}{\partial F}\right)$
1 : 0	–	20.0	–	1.5
4 : 1	17.4	16.0	3.75	3.9

Ratio of alcohols normal / secondary	$a_I A'$, Å^2	a_{II}, Å^2	$\frac{a_I A' - a_{II}}{47 \cdot b} \cdot 100$	$\chi = \left(-\frac{1}{a}\frac{\partial a}{\partial F}\right)$
1 : 1	12.5	10.0	10.6	7.0
1 : 4	4.5	4.0	5.3	18.0

Figure 1b shows the curves of the equilibrium two-dimensional pressure F_e and of the protective properties of the monolayer K as functions of the composition of the alcohol mixture. The value

$$K = \frac{Q_0 - Q}{Q_0}\,\%$$

indicates the relative decrease in the evaporation of water per unit time in the presence of the monolayer, Q, compared with evaporation under the same conditions from a pure water surface, Q_0. It follows from the curves that both F_e and K remain at approximately the same level, corresponding to the normal alcohol, up to a content of secondary alcohol in the mixture of no more

50–60% and then rapidly fall: F to 19.1 dyn/cm, and K to 0%, corresponding to the individual secondary alcohol.

From these data it follows that the protective properties of monolayers formed from mixtures of normal (cetyl) alcohol and the secondary alcohol used here are determined by the monolayer of normal alcohol, which displaces the secondary alcohol into microcrystals from the monolayer; i.e., this secondary alcohol itself in fact has no protective properties in the mixture. High protective properties are inherent in the densely packed condensed monolayer of normal cetyl alcohol. Small amounts of secondary alcohol ($<$ 6–7%) retained in the monolayer of the normal alcohol at high F_e do not noticeably reduce the protective properties; at the same time, their positive role in the mixture may probably consist in accelerating the spreading of the monolayer of normal cetyl alcohol. At large amounts of secondary alcohol ($>$ 50%), the equilibrium F_e and the protective properties decrease; evidently, the normal alcohol can no longer displace all the secondary alcohol from the monolayer, owing to its low concentration in the bulk phase of the alcohol mixture. Its excess relative to 7% in the mixture displaced from the monolayer by the normal alcohol would probably play the role of ballast in the protective properties and, upon considerable accumulation on the surface of the body of water, could even exert an adverse effect on the life of the body of water and hinder further spreading of the cetyl alcohol.

Fig. 2. $F - \tau$ dependence curves for a mixture of normal and secondary hexadecanols (1 : 1)

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As is seen from Fig. 1a, the formation of a condensed, densely packed monolayer of normal (cetyl) alcohol corresponds to an area of 0.5 m^2/mg (or 2 mg/m^2). This is the minimal theoretical amount necessary to ensure the protective properties of the monolayer on a smooth surface of a body of water (without taking into account losses of alcohol under practical conditions). In the case of mixtures of composition 4 : 1, 1 : 1, and 1 : 4, respectively, the areas of the condensed region, expressed in m^2/mg, shift to ~ 0.40, 0.27, and 0.18 m^2/mg at $F = 40$ dyn/cm. This clearly shows that only at such coverages of the surface of a body of water, i.e., considerably smaller than for normal (cetyl) alcohol alone, could a monolayer of the mixture provide protective properties. In this connection, the method of obtaining $F - a$ curves for mixtures of various surface-active substances (in particular, for technical products) can serve as a quantitative method for determining the fraction of substances forming a condensed monolayer, necessary (but not always sufficient) for ensuring protective properties.

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