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Thermodynamic Study on Mixed Monolayers of Butyl Eicosanedioate and Tetradecanoic Acid

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In order to clarify the behavior of mixed monolayers of butyl eicosanedioate and tetradecanoic acid, the surface pressure was measured as a function of mean area at various compositions and temperatures. Four types of phase transition were observed. By use of the thermodynamic treatment previously developed, the apparent molar entropy and energy changes associated with the phase transition were evaluated. It was concluded on thermodynamic considerations that the butyl eicosanedioate and tetradecanoic acid monolayers are immiscible in condensed states and their phase diagram has a two-dimensional eutectic point.

It seems valuable to relate the states of monolayers with the molecular structure of film-forming substances by the thermodynamic approach.[1,2)] It has been clarified through the study on mixed monolayers that the monolayer systems reveal the ideal,[3,4)] eutectic,[5)] azeotropic,[6–8)] and other behaviors,[9)] depending upon their molecular interactions. Now it seems useful to investigate the mixed monolayers of bipolar substances because they are expected to show a two-step transformation. While many works have been reported on the monolayer of dibasic substances since those of Adam *et al.*,[10–12)] they are insufficient to make clear the state of the monolayers.

In this paper, the system consisting of tetradecanoic acid and butyl eicosanedioate was employed and the state of monolayers was clarified thermodynamically. Butyl eicosanedioate is a bipolar substance which contains a long carbon chain between two relatively large polar groups.

Experimental

Tetradecanoic acid was purified by vacuum distillation and recrystallization from ether. Butyl eicosanedioate was synthesized by the Fischer method from 1-butanol and eicosanedioic acid (presented by the courtesy of Okamura Seiyu Co.), and its purity was checked by gas-liquid chromatography and elemental analysis. Benzene purified by the standard procedure was used as the spreading solvent. Monolayers were spread on 0.5 mol kg^{-1} sodium chloride solution which was prepared from twice distilled water and sodium chloride (Wako special grade) as done in the previous papers.[6–9)]

Surface pressure was measured by a Wilhelmy type electro-surface balance and automatically recorded on the chart paper. Temperature was kept constant within 0.1 K by circulating thermostated water. The surface pressure *vs.* area curve was reproducible within an experimental error.

Results and Discussion

The surface pressure of mixed monolayers consisting of butyl eicosanedioate and tetradecanoic acid was measured at various compositions and temperatures. The surface pressure π *vs.* surface area per monolayer molecule A curves of butyl eicosanedioate obtained at temperatures 290.7, 293.2, 295.7, and 298.2 K are shown in Fig. 1. It is seen that the π *vs.* A curves have two break points which represent phase transitions. The surface pressure of the second transition point decreases, while that of the first transition point increases, with increasing temperature. This is shown clearly in Fig. 2. Comparing these temperature dependences of the transition pressure π^{eq} with those of tetradecanoic acid, the first break point is found to correspond to the transformation from an expanded to a

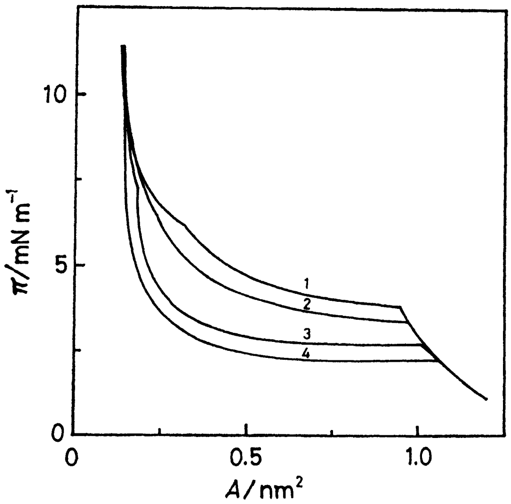

Fig. 1. Surface pressure π *vs.* mean area A curves of butyl eicosanedioate monolayer: (1) 298.2 K, (2) 295.7 K, (3) 293.2 K, (4) 290.7 K.

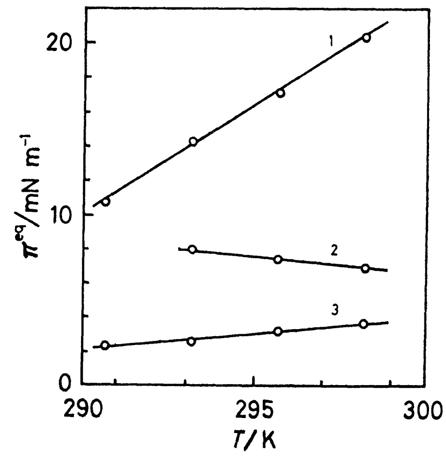

Fig. 2. Transition pressure π^{eq} *vs.* temperature curves: (1) tetradecanoic acid, (2) the second break point, (3) the first break point.

condensed film. On the other hand, the π^{eq} *vs.* T curve of the second break point has a negative slope greater than that of substrate with regard to the absolute value. This might suggest that the phase transition is accompanied by a positive entropy change, which leads us to the conclusion that the transformation takes place from the first condensed film (indicated by c(1,I)), in which both polar groups of butyl eicosanedioate molecule are in contact with the substrate, to the second condensed film (indicated by c(1,II)), in which one of them is in contact with the substrate.

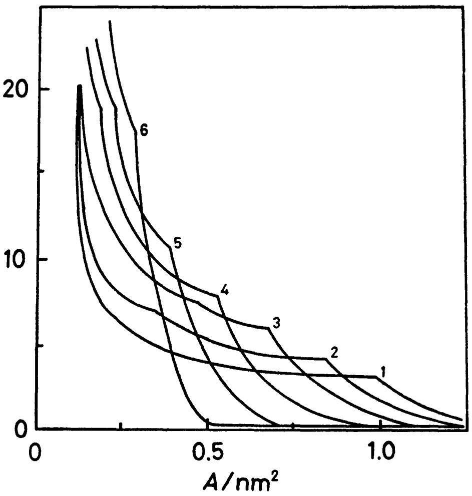

Fig. 3. Surface pressure π *vs.* mean area A curves of butyl eicosanedioate–tetradecanoic acid monolayers at 295.7 K: (1) $x_2^\pi=0$, (2) 0.2, (3) 0.4, (4) 0.6, (5) 0.8, (6) 1.

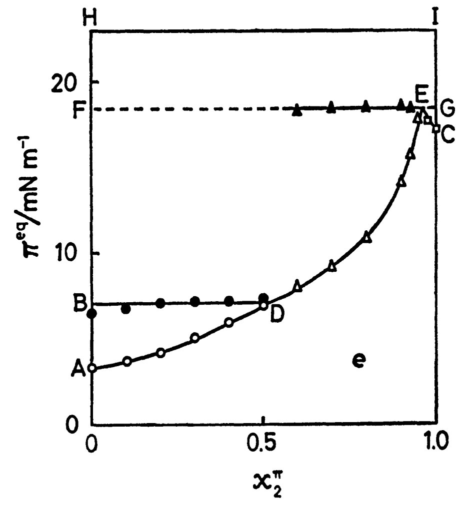

Fig. 4. Phase diagram of butyl eicosanedioate–tetradecanoic acid monolayer at 295.7 K.
Type of transition: ○, (e, c(1, I)); △, (e, c(1, II)); ●, (c(1, I), c(1, II)); □, (e, c(2)); ▲, (e, c(1, II) and c(2)).

The π *vs.* A curves of mixed monolayers obtained at various compositions at 295.7 K are shown in Fig. 3. These curves seem to have several kinds of break point. In Fig. 4, the surface pressure at the break point is plotted against the mole fraction of tetradecanoic acid defined by

$$x_2^\pi = n_2/(n_1+n_2), \tag{1}$$

where n_i is the number of moles of film-forming component i. It is seen that the first transition pressure of butyl eicosanedioate increases with addition of tetradecanoic acid (curve AE), whereas the second transition pressure remains approximately constant (curve BD). Similarly, the transition pressure of tetradecanoic acid increases with addition of butyl eicosanedioate (curve CE). These symmetrical π^{eq} *vs.* x_2^π curves appear to meet with each other at the point E which lies on the π^{eq} *vs.* x_2^π curve (curve FG) of the second break point observed in the concentration range from $x_2^\pi=0.50$ to 0.95. It is easily understood that the curves AE and CE express the equilibrium between expanded and condensed films.

Taking into account that the second transition pressure of mixed monolayer at low concentration is approximately equal to that of butyl eicosanedioate monolayer, it may be expected that the line BD in Fig. 4 represents the transformation from the first condensed film c(1,I) to the second condensed film c(1,II). This expectation is realized by consulting the temperature dependence of transition pressure. By measuring the surface pressure of mixed monolayers at 290.7, 293.2, and 298.2 K, the linear π^{eq} *vs.* T plots were obtained. As shown by the curve BD in Fig. 5, their slopes have about the same value. This result supports the above view.

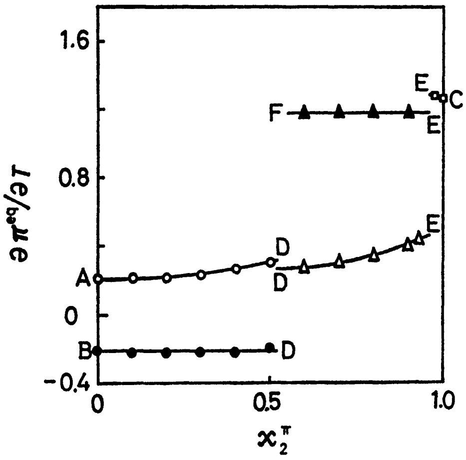

Fig. 5. $\partial\pi^{eq}/\partial T$ *vs.* x_2^π curves at 295.7 K.
Type of transition: ○, (e, c(1, I)); △, (e, c(1, II)); ●, (c(1, I), c(1, II)); □, (e, c(2)); ▲, (e, c(1, II) and c(2)).

Inspecting closely Fig. 4, on the other hand, the π^{eq} *vs.* x_2^π curve AE of the first break point seems to be divided into two parts at the point D where the curve is intersected by that of the second break point. This is substantiated by the fact that the value of $\partial\pi^{eq}/\partial T$ in Fig. 5 is discontinuous at that point. Thus we are led to the conclusion that the point D is the one where the condensed films c(1,I) and c(1,II) of butyl eicosanedioate and the expanded film, denoted by the letter e, composed of butyl eicosanedioate and tetradecanoic acid coexist in equilibrium at 295.7 K under atmospheric pressure. Now we may say that the curve AD represents the equilibrium between the films c(1,I) and e and the curve DE the equilibrium between the films c(1,II) and e.

Let us next consider the point E on Fig. 4. Consulting Figs. 4 and 5, we immediately notice that the values of the second transition pressure in the concentration range $x_2^{\pi}=0.50$ to 0.95 are on the straight line FG parallel to the abscissa and their derivatives with respect to temperature are nearly equal. Furthermore, the temperature dependences of the curves DE and CE are found to be significantly different. Taking into consideration that the curve DE refers to the equilibrium of the expanded phase e of mixed monolayer with the condensed phase c(1,II) of butyl eicosanedioate monolayer, therefore, we can assign the curve CE to the equilibrium of the expanded state e with the condensed phase c(2) of tetradecanoic acid monolayer. The above results lead us to the conclusion that the point E represents the state where the films c(1,II), c(2), and e coexist in equilibrium and is called a two-dimensional eutectic point.

Now it is possible to say that the areas ADB, BDEF, CEG, and HFGI in Fig. 4 are the heterogeneous regions composed of the condensed film c(1,I) and expanded film e, the condensed film c(1,II) and expanded film e, the condensed film c(2) and expanded film e, and the condensed films c(1,II) and c(2), respectively. It is needless to say that the area denoted by e is the stable region of expanded film e. Therefore, Fig. 4 can be regarded as a phase diagram of the mixed monolayer of butyl eicosanedioate and tetradecanoic acid at 295.7 K under atmospheric pressure.

Let us now consider to evaluate the apparent molar entropy change $\Delta s^{\gamma}(\alpha,\beta)$ associated with the transition from phase α to phase β. For a pure monolayer, we have the equation[1,13)]

$$\begin{aligned}\Delta s^{\gamma}(\alpha,\beta) &= \bar{s}_i^{\gamma,\beta}-\bar{s}_i^{\gamma,\alpha}\\ &= N_A(A^{\beta}-A^{\alpha})[(\partial\pi^{\mathrm{eq}}/\partial T)_p-(\partial\gamma^{\circ}/\partial T)_p],\\ &\qquad \mathrm{i}=1,2, \qquad (2)\end{aligned}$$

where s_i^{γ} is the apparent partial molar entropy of component i, γ° the surface tension of substrate, and N_A Avogadro's number. On the other hand, the apparent molar entropy of transition from the expanded phase of mixed monolayer to the condensed phase c(1,I), c(1,II), or c(2) is evaluated with the aid of the relation

$$\begin{aligned}\Delta s^{\gamma}(\mathrm{e},\beta) &= \bar{s}_i^{\gamma,\beta}-\bar{s}_i^{\gamma,\mathrm{e}}\\ &= N_A[A^{\beta}-A^{\mathrm{e}}-(\delta_{i2}-x_2^{\pi,\mathrm{e}})(\partial A^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}]\\ &\quad\times[(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_i^{\pi,\mathrm{e}}}-(\partial\gamma^{\circ}/\partial T)_p],\\ &\qquad \mathrm{i}=1,2, \qquad (3)\end{aligned}$$

where

$$\begin{aligned}\delta_{i2} &= 0, \quad \mathrm{i}=1\\ &= 1, \quad \mathrm{i}=2. \qquad (4)\end{aligned}$$

The value of Δs^{γ}(e,c(2)) may be calculated by making use of the value of $\partial\pi^{\mathrm{eq}}/\partial T$ given in Fig. 5 on the assumption that the area of tetradecanoic acid in the condensed film is replaced by the corresponding one of octadecanoic acid and the value of γ° is approximated by that of pure water. The values obtained are depicted as a function of $x_2^{\pi,\mathrm{e}}$ in Fig. 6. In evaluating Δs^{γ}(e,c(1,I)) and Δs^{γ}(e,c(1,II)), however, it is necessary to estimate the values of $A^{\mathrm{C(1,I)}}$ and $A^{\mathrm{C(1,II)}}$. With the aid of the thermodynamics, we can easily derive the equation which holds at the eutectic point E:

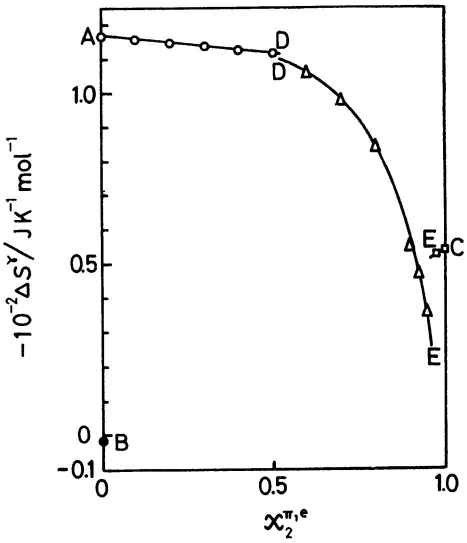

Fig. 6. Apparent molar entropy change Δs^{γ} *vs.* mole fraction of tetradecanoic acid $x_2^{\pi,\mathrm{e}}$ curves at 295.7 K. Type of transition: ○, (e, c(1, I)); △, (e, c(1, II)); ●, (c(1, I), c(1, II)); □, (e, c(2)).

$$\begin{aligned}(\partial\pi^{\mathrm{eq}}/\partial T)_p^{\mathrm{FE}}-(\partial\gamma^{\circ}/\partial T)_p &= [x_1^{\pi,\mathrm{e}}\Delta s^{\gamma}(\mathrm{e},\mathrm{c}(1,\mathrm{II}))\\ &\quad+x_2^{\pi,\mathrm{e}}\Delta s^{\gamma}(\mathrm{e},\mathrm{c}(2))]/N_A[(x_1^{\pi,\mathrm{e}}A^{\mathrm{c(1,II)}}\\ &\quad+x_2^{\pi,\mathrm{e}}A^{\mathrm{c(2)}})-A^{\mathrm{e}}], \qquad (5)\end{aligned}$$

where the superscript FE on $(\partial\pi^{\mathrm{eq}}/\partial T)_{\mathrm{p}}$ means that its value is the extrapolated one of the curve FE to the point E in Fig. 5. Substituting Eq. 3 and rearranging the resulting equation, Eq. 5 is rewritten in the form

$$\begin{aligned}A^{\mathrm{c(1,II)}} &= A^{\mathrm{e}}+\{x_2^{\pi,\mathrm{e}}(A^{\mathrm{c(2)}}-A^{\mathrm{e}})[(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_i^{\pi,\mathrm{e}}}^{\mathrm{CE}}\\ &\quad-(\partial\pi^{\mathrm{eq}}/\partial T)_p^{\mathrm{FE}}]\\ &\quad+x_1^{\pi,\mathrm{e}}x_2^{\pi,\mathrm{e}}[(\partial A^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}^{\mathrm{DE}}(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_i^{\pi,\mathrm{e}}}^{\mathrm{DE}}\\ &\quad-(\partial A^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}^{\mathrm{CE}}(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_i^{\pi,\mathrm{e}}}^{\mathrm{CE}}]\}/x_1^{\pi,\mathrm{e}}[(\partial\pi^{\mathrm{eq}}/\partial T)_p^{\mathrm{FE}}\\ &\quad-(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_i^{\pi,\mathrm{e}}}^{\mathrm{DE}}]. \qquad (6)\end{aligned}$$

The superscripts CE and DE have the same meaning as FE concerning the respective curve. Thus the value of $A^{\mathrm{C(1,II)}}$ at the eutectic point can be estimated experimentally; $A^{\mathrm{C(1,II)}}=1.68\,A^{\mathrm{C(2)}}$ was obtained. By assuming the relation

$$A^{\mathrm{c(1,II)}}(\pi')/A^{\mathrm{c(2)}}(\pi') = A^{\mathrm{c(1,II)}}(\pi)/A^{\mathrm{c(2)}}(\pi), \qquad (7)$$

we can now evaluate Δs^{γ}(e,c(1,II)). The value obtained is also shown in Fig. 6.

Further, the following equation is proved to hold at the point D where the three phases e, c(1,I), and c(1,II) coexist in equilibrium:

$$\Delta s^{\gamma}(\mathrm{c}(1,\mathrm{I}),\mathrm{c}(1,\mathrm{II})) = \Delta s^{\gamma}(\mathrm{e},\mathrm{c}(1,\mathrm{II}))-\Delta s^{\gamma}(\mathrm{e},\mathrm{c}(1,\mathrm{I})). \qquad (8)$$

Substitution of Eqs. 2 and 3 into Eq. 8 and rearrangement yield the expression

$$\begin{aligned} A^{c(1,I)} = {} & A^{e}+\{(A^{c(1,II)}-A^{e})[(\partial\pi^{eq}/\partial T)^{ED}_{p,x_2^{\pi,e}}-(\partial\pi^{eq}/\partial T)^{BD}_{p}] \\ & -x_2^{\pi,c}[(\partial A^{e}/\partial x_2^{\pi,e})^{AD}_{T,p,\pi}(\partial\pi^{eq}/\partial T)^{AD}_{p,x_2^{\pi,e}} \\ & -(\partial A^{e}/\partial x_2^{\pi,e})^{ED}_{T,p,\pi}(\partial\pi^{eq}/\partial T)^{ED}_{p,x_2^{\pi,e}}]\}/[(\partial\pi^{eq}/\partial T)^{AD}_{p,x_2^{\pi,e}} \\ & -(\partial\pi^{eq}/\partial T)_{p}{}^{BD}]. \end{aligned} \tag{9}$$

Thus the value of $A^{C(1,I)}$ was estimated to be $1.86A^{C(2)}$. In a similar manner as above, we can evaluate the values of Δs^{γ}(e,c(1,I)) and Δs^{γ}(c(1,I), c(1,II)) by virtue of Eqs. 2 and 3. The results are also shown in Fig. 6.

It is seen from Fig. 6 that the apparent molar entropy change Δs^{γ}(e,c(1,I)) of butyl eicosanedioate monolayer has an appreciably large negative value as compared with the corresponding one Δs^{γ}(e,c(2)) of tetradecanoic acid monolayer. The value of Δs^{γ}(c(1,I), c(1,II)) is found to be small but definitely positive. These results are compatible with the view that butyl eicosanedioate is a bipolar molecule of which the hydrocarbon chain is long enough to take a bent conformation in the first condensed film. Further, Fig. 6 reveals that the apparent molar entropy change associated with the transformation of component i from expanded to condensed film increases with decreasing $x_1^{\pi,e}$. In cases of the mixed monolayers of tetradecanoic acid with pentadecanoic acid and ethyl heptadecanoate which form homogeneous condensed phases, we have observed that the corresponding apparent partial molar entropy changes of these film-forming substances are approximately constant over the whole range of concentrations.⁶⁾ Therefore it is supported by the above results that butyl eicosanedioate and tetradecanoic acid are immiscible in the condensed state.

Now let us evaluate the apparent molar energy changes $\Delta u^{\gamma}(\alpha,\beta)$ and $\Delta u^{\gamma}(e,\beta)$ related, respectively, to $\Delta s^{\gamma}(\alpha,\beta)$ and $\Delta s^{\gamma}(e,\beta)$ (Eqs. 2 and 3) by the expressions⁶⁾

$$\Delta u^{r}(\alpha,\beta) = -(\pi^{eq}-\gamma^{0})N_{A}(A^{\beta}-A^{\alpha}) + T\Delta s^{r}(\alpha,\beta), \quad i = 1, 2 \tag{10}$$

and

$$\begin{aligned} \Delta u^{r}(e,\beta) = {} & -(\pi^{eq}-\gamma^{0})N_{A}[A^{\beta}-A^{e}-(\delta_{i2}-x_2^{\pi,e}) \\ & \times(\partial A^{e}/\partial x_2^{\pi,e})_{T,p,\pi}] + T\Delta s^{r}(e,\beta), \quad i = 1, 2 \end{aligned} \tag{11}$$

where we have neglected contribution of the apparent molar volume change. Evidently they can be calculated by making use of the experimental results. The numerical values are shown in Fig. 7. It is observed, as expected, that the values of apparent molar energy of transition deviate from the straight line connecting the values of Δu^{γ} for the pure components. Comparing with Fig. 6, we notice that the Δu^{γ} vs. $x_2^{\pi,e}$ and Δs^{γ} vs. $x_2^{\pi,e}$ curves behave similarly except that the value of Δu^{γ}(c(1,I), c(1,II)) is negative while that of Δs^{γ}(c(1,I), c(1,II)) is positive. It is of importance to note that the value of Δu^{γ}(c(1,I), c(1,II)) is responsible for the difference between Δu^{γ}(e,c(1,I)) and Δu^{γ}(e,c(1,II)) at the discontinuous point D.

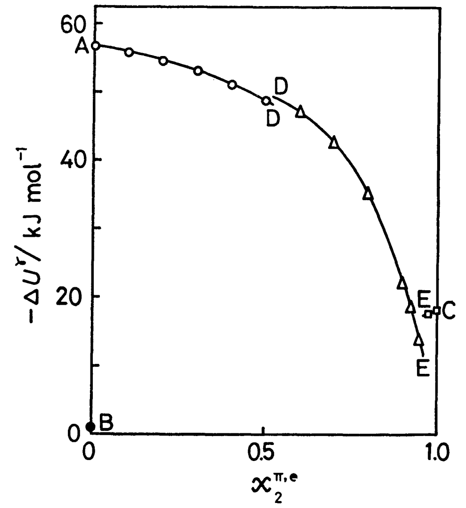

Fig. 7. Δu^{γ} *vs.* $x_2^{\pi,e}$ curves for butyl eicosanedioate–tetradecanoic acid system at 295.7 K.
Type of transition: ○, (e, c(1, I)); △, (e, c(1, II)); ●, (c(1, I), c(1, II)); □, (e, c(2)).

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