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Scaling of the shear viscosity of the system polystyrene-cyclohexane in the critical region

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The shear viscosity of the system polystyrene-cyclohexane was measured along the isochores near the critical concentration. The value of the critical exponent for the shear viscosity ($\phi_\eta = 0.029 \pm 0.003$) is obtained by analyzing the results from the viewpoint of multiplicative renormalization of transport coefficients. In addition, it is shown that the shear viscosity satisfies scaling-law relations and the pseudospinodal generalization previously established for fluids and binary mixtures.

I. INTRODUCTION

In recent years the shear viscosity near the critical point has attracted an increasing amount of attention.[1] A number of studies have been conducted on fluids, binary mixtures, and three component systems, with the well-established universality and scaling-law relations.[2–5] Further extension of these concepts to a polymer solution in the critical region has been done only in the preliminary forms.[6]

In polymer solutions, the constituents are extremely different in size and in structure. Furthermore, a large deviation from simple scaling has been observed in coexistence-curve measurements at high molecular weight and the temperature range of simple scaling may depend on molecular weight.[7] For these reasons, polymer solutions are relevant systems for a test of universality and scaling-law relations.[6–8]

In this paper, the binary mixture polystyrene-cyclohexane over a wide range of the temperature-concentration diagram in the critical region was investigated by using a viscometric method. This system has been studied thoroughly by coexistence-curve measurement and light scattering measurement,[9,10] which enabled us to test universality and scaling-law relations using viscosity data. Experiments were made with a carefully fractionated polymer sample to minimize the effect of the molecular-weight distribution.

II. EXPERIMENTAL

Polystyrene (Pressure Chemical Company, Pittsburgh, PA) characterized by $M_w = 11 \times 10^4$ and $M_w/M_n < 1.06$, where M_w and M_n are the weight and number average molecular weight, respectively, was fractionated into five fractions by the fractional solution technique.[9] In the present study we used one of the fractions characterized by $M_w = 11 \times 10^4$ and $M_w/M_n < 1.02$. Reagent-grade cyclohexane was purified by passing it through a 1 m column of silica gel and was fractionally distilled over metal sodium in an atmosphere of dry nitrogen just before use. Preparation of the solution was performed in a dry box under dry nitrogen. We paid particular attention to avoid moisture in the air.

Since the coexistence curve and the pseudospinodal curve for the present system were determined several years ago,[9] we tried to test the purity of our sample by determining the coexistence curve. The results are shown in Fig. 1. The critical point ($T_c = 21.03_9$ °C, $\phi_c = 0.0825$) was established by phase-equilibrium measurements and the diameter, which is slightly away from the critical point

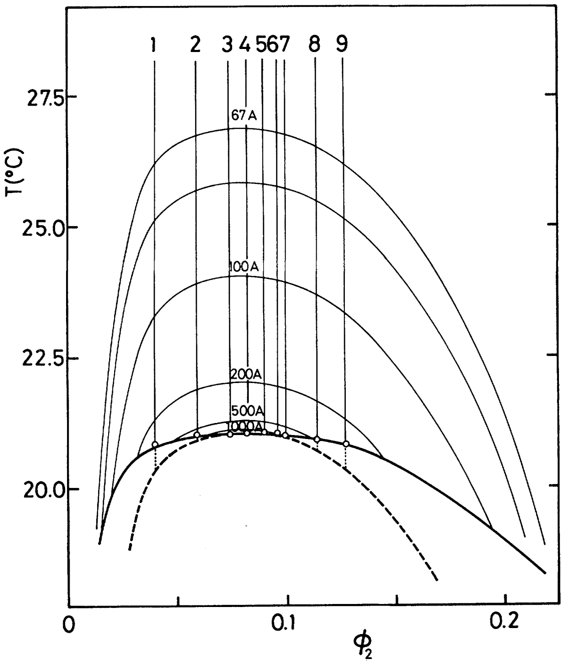

FIG. 1. Coexistence curve and pseudospinodal curve for the system polystyrene-cyclohexane. The solid and the dashed curves represent the coexistence curve with $\beta = 0.34$ and the pseudospinodal curve with $\beta^{\dagger} = 0.38$, respectively (after Ref. 9). Open circles represent the phase-separation temperatures for nine samples with different concentrations compiled in Table I. The straight lines of numbers 1–9 represent the paths of viscosity measurement along with the isochores. The curved lines with figures represent the isorange lines of correlation length.

TABLE I. Characteristic of the sample and values of the Vogel parameter and ϕ_η. (PS is polystyrene.)

Sample				$\eta_{id}=A\exp[B/(T-C)]$				
PS—C_6H_{12}	ϕ_2	T_p (°C)	T_{sp} (°C)[a]	10^2A	B	C	ϕ_η	$\phi_{\eta,\mathrm{theor}}$
1	0.0405	20.77_0	20.31_9	5.78	1030	48.2	(0.029_5)	0.033_5 (Refs. 14, 15, and 17)
2	0.0593	20.98_8	20.91_0	11.05	840	87.4	0.029_5	
3	0.0741	21.03_5	21.02_9	38.45	431	162.1	0.029_3	
4	0.0827	21.04_0	21.03_0	40.83	460	160.3	0.029_2	
5	0.0899	21.03_5	21.01_9	55.44	394	175.5	0.029_0	
6	0.0959	21.02_5	20.98_5	68.03	368	182.5	0.029_1	
7	0.1000	21.00_5	20.94_3	77.32	353	187.2	0.029_4	
8	0.1143	21.91_8	20.69_5	90.04	369	190.3	0.029_3	
9	0.1271	20.82_3	20.27_9	151.56	289	209.5	(0.029_4)	

[a] Taken from the experimental data of Kojima *et al.* (Ref. 9). T_p and T_{sp} are the phase-separation temperature and pseudospinodal temperature, respectively.

($T_c=21.33_0$°C, $\phi_c=0.0825$) reported by Kuwahara *et al.*[9,10] It is noted that the critical concentrations in two laboratories are the same, though the slight difference between the critical temperatures will be attributed to different amounts of impurities in the samples studied by each laboratory. Therefore, we used the data of Kuwahara *et al.* in the data analysis of the viscosity taking into account the slight difference of the critical temperatures.

The kinetic viscosity η/ρ (ρ, density) was measured with a modified Ubbelohde viscometer. The viscometer was calibrated by comparing flow times of isobutyl alcohol. It was found that the kinetic-energy correction was also needed. Samples were prepared from the stock solution by adding appropriate amounts of cyclohexane by weight in the dry box. The samples were quickly prepared by filtering the solution into the viscometer, freezing, and subsequently sealing the viscometer with a torch under vacuum. The sealed viscometer was mounted on a rotary board and placed in a water bath along with a thermostat which provided constant temperature within 0.005 °C. A detailed description of the experimental procedures has been reported elsewhere.[5,11]

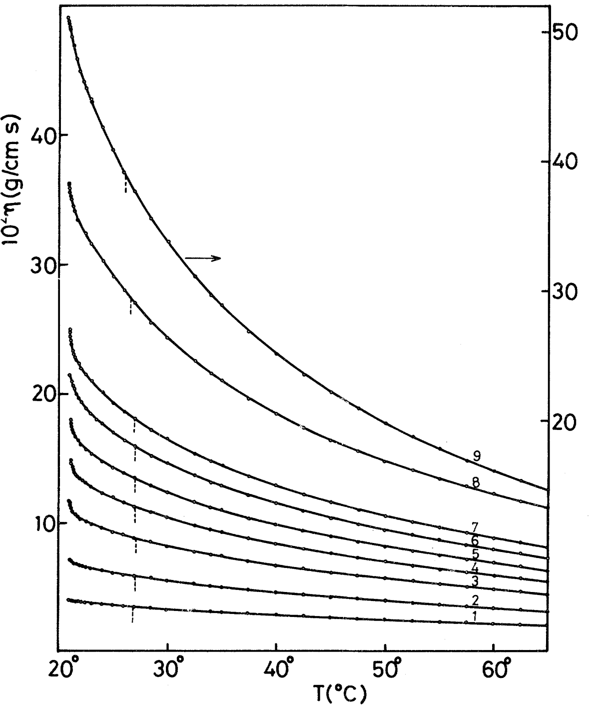

FIG. 2. Shear viscosity as a function of temperature at nine different concentrations are shown by numbers 1–9 in Table I. Simple power law of correlation length and osmotic compressibility is realized in the temperature range lower than the broken lines.

For the purpose of comparison with the theory, the measured kinetic viscosity has been multiplied by the density. The values of the density were calculated from the density of cyclohexane and of polystyrene[12] and compared with the existing data.[13] Viscosity measurements were carried out over the temperature range of T_p (phase-separation temperature) ~65 °C along the isochores for nine samples with different concentrations as shown in Fig. 1 and Table I. The viscosity data as a function of temperature are shown in Fig. 2.

III. DATA ANALYSIS

The very complicated problem of the critical behavior of transport coefficients has been widely studied. The recent refinement of mode-mode coupling theory[14–16] and the success of renormalization-group theory[17,18] have enabled the critical exponent z_η (i.e., ϕ_η) for the shear viscosity to be examined more rigorously. The theories predict that the shear viscosity along with the critical isochore may be written as

$$\eta=\hat{\eta}(q_D\xi)^{z_\eta}=\hat{\eta}(q_D\xi_0)^{z_\eta}t^{-\phi_\eta}\,, \tag{1}$$

with $\phi_\eta=+z_\eta\nu$, where q_D is a microscopic cutoff wave number, $\xi=\xi_0 t^{-\nu}$ is the correlation length, and t is given by (T/T_c-1). $\hat{\eta}$ is the critical amplitude for the diverging shear viscosity near critical point, which can be identified as the bare (background) viscosity η_{id}, where the correction to $\hat{\eta}$ of order t has been omitted.

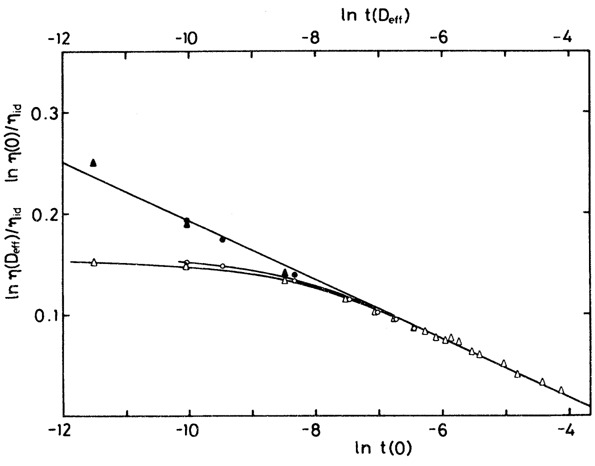

FIG. 3. Plot of $\ln\eta/\eta_{id}$ vs $\ln t$ for the system polystyrene-cyclohexane ($\phi_2=0.0827$). △, our original data; ○, our data corrected for a lowering of the critical temperature; ▲, our data corrected for nonlinear effect after Oxtoby; ●, our data corrected for nonlinear effect taking into account $T_c(D_{\text{eff}})$.

From mode-mode coupling theory the critical exponent ϕ_η is found to be 0.033_5 using the self-consistent approximation[14,15] and 0.043 with vertex correction,[16] while the renormalization-group theory predicts ϕ_η to be 0.033_5 in an ϵ expansion to first order[17] and 0.040 in an ϵ expansion to second order for the dimensionality $d=3$.[18] A common feature of all these theories is that the shear viscosity shows a weak anomaly in the critical region and that the renormalization of its anomalous part is of a multiplicative rather than of an additive type.[19]

On the experimental side, Eq. (1) has been confirmed by a critical reexamination of the existing viscosity data[3,4] and a shear viscosity measurement in a large temperature range.[20] However, it is important to note that Eq. (1) is only the first approximation and, in general, the existence of the correction term is predicted theoretically, though fortunately it has not been needed to account for the behavior of the shear viscosity in many binary critical mixtures.[3,4]

In interpreting viscosity data, much of the ambiguity is due to different methods of subtracting η_{id}. It is natural that a systematic procedure should be developed for the evaluation of η_{id}. To gain some insight into the problem we used two different equations to represent η_{id}.

It is known that the temperature dependence of the viscosity of nearly all pure and multicomponent liquids can be adequately represented by the Arrhenius equation. However, for the present system this equation does not hold except for a very narrow range of temperatures. Using this equation, we obtained a significant critical region which was not consistent with the results obtained by other independent experiments.[7,9,10] Therefore we used the Vogel equation[21]

$$\eta_{id}=A\exp[B/(T-C)]\ , \tag{2}$$

where A, B, and C are constants independent of temperature. Equation (2) has been successfully applied to represent the behavior of the viscosity of the polymer solution in which large systematic deviations from the simple Arrhenius equation were observed.[22,23]

As an alternative method we can use the equation expanded as a series of increasing powers of t,

$$\hat{\eta}=\eta_0+\sum_{i\geq 1}\eta_i t^i\ , \tag{3}$$

since the amplitude $\hat{\eta}$ is expected to be an analytical function of t. Although Eq. (3) with four parameters is equivalent to the Vogel equation, we did not adopt Eq. (3) in the present analysis.

As it is known that physical quantities such as correlation length and osmotic isothermal compressibility in this system[9,10] diverge in a simple power law in the temperature region lower than the broken lines in Fig. 2, we took into account this point in the evaluation of η_{id}. Fittings to the Vogel equation and Eq. (3) have been done by using the program system, "Statistical Analysis by Least Squares"[24] (SALS). The Vogel parameters obtained were also compiled in Table I.

IV. RESULTS AND DISCUSSIONS

In order to test the power-law relation of Eq. (1), the plot of $\ln\eta(D_{\text{eff}})/\eta_{id}$ vs $\ln t(0)$ for sample 4 ($\phi_2=0.0827$) is shown in Fig. 3. Figure 3 shows that $\ln\eta/\eta_{id}$ at first increases linearly and then starts to level off as one approaches the critical point, while Eq. (1) suggests a straight line of slope $-\phi_\eta$ in the same plot along with the critical isochore. Such a leveling off of shear viscosity has been mainly attributed to the nonlinear effect in the measurement of the capillary method.[5,25] Depending on the type of viscometer used and on the correlation length of the system, the effect can become very important, especially in the present polymer solution.

According to Oxtoby, the nonlinear effect $\Delta(\lambda)$ is expressed as a function of λ ($=\eta\xi^3 D/k_BT$, where D is the magnitude of the shear gradient),

$$\Delta(\lambda)=[\eta(0)-\eta(\lambda)]/\eta(0)\ ,$$

which should be a universal function of λ, independent of q_D. On the other hand, Onuki *et al.*[26] have found a lowering of the critical temperature $T_c(D)$ in the presence of shear flow, which has been observed on the experiments for the critical mixtures aniline-cyclohexane[27] and polydimethylsiloxane-diethyl carbonate.[28] For the present system $\Delta T=T_c(D_{\text{eff}})-T_c(0)$, in which D_{eff} is the effective average value in terms of the experimentally known $D_{\max}$, is estimated as -0.010 K in an ϵ expansion to the second order. In Fig. 3 the closed triangles represent the points after the correction of the nonlinear shear-gradient effect, while the closed circles represent the corresponding points after the correction of the nonlinear shear-gradient effect taking into account $T_c(D_{\text{eff}})$. It is noted that data points after the correction of this effect are in reasonable agreement with the prediction of Eq. (1). The critical exponent corrected for $\Delta(\lambda_{\text{eff}})$ and $T_c(D_{\text{eff}})$ is represented by $\phi_\eta=0.029\pm0.003$ and is in good agreement with $\phi_\eta=0.033_5$ in the first order, but is in disagreement with

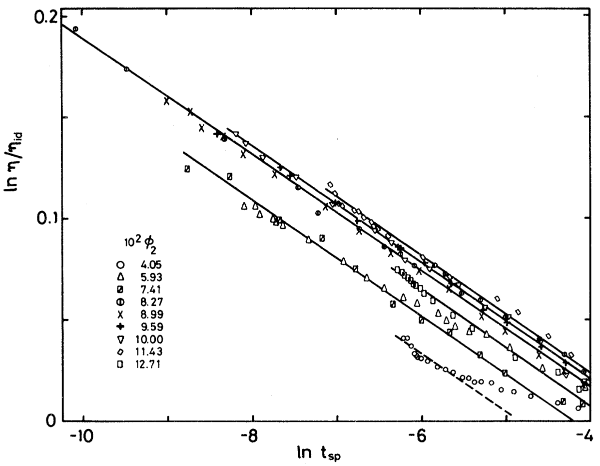

FIG. 4. Plot of $\ln\eta/\eta_{id}$ vs $\ln t_{sp}$ for the system polystyrene-cyclohexane. ϕ_2 is the volume fraction of polystyrene.

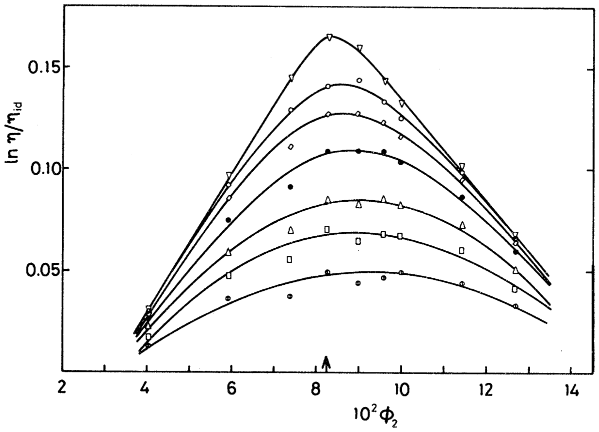

FIG. 5. Plot of $\ln\eta/\eta_{id}$ vs ϕ_2 for the system polystyrene-cyclohexane: $T-T_{sp,max}=0.02°$ (▽), 0.05° (○), 0.10° (◇), 0.20° (●), 0.50° (△), 1.00° (□), 2.00° (ø).

$\phi_\eta=0.040$ in the second order.

Since η/η_{id} and $\xi^\dagger$ along the noncritical isochore would diverge on the spinodal curve introduced by Benedek,[29] the following extension of Eq. (1) has been proposed[4–6]:

$$\eta=\hat{\eta}(q_D\xi^\dagger)^{z_\eta}=\hat{\eta}(q_D\xi_0)^{z_\eta}t_{sp}^{-\phi_\eta} \tag{1'}$$

where $t_{sp}=T/T_{sp}-1$. Straight lines of slope $-\phi_\eta$ are obtained in plots of $\ln\eta/\eta_{id}$ vs $\ln t$, as shown in Fig. 4. All the exponent values obtained are listed in Table I. These exponents are also consistent with the $\phi_\eta=0.033_5$ in the first order. Such a result agrees well with the hypothesis of universality, irrespective of the particular system under examination.

It is worthwhile to attempt a more general test of the homogeneity and scaling laws with the viscosity data. According to the initial approach of Green and coworkers,[30,31] the scaling relation of Eq. (1) takes a form[4,6]

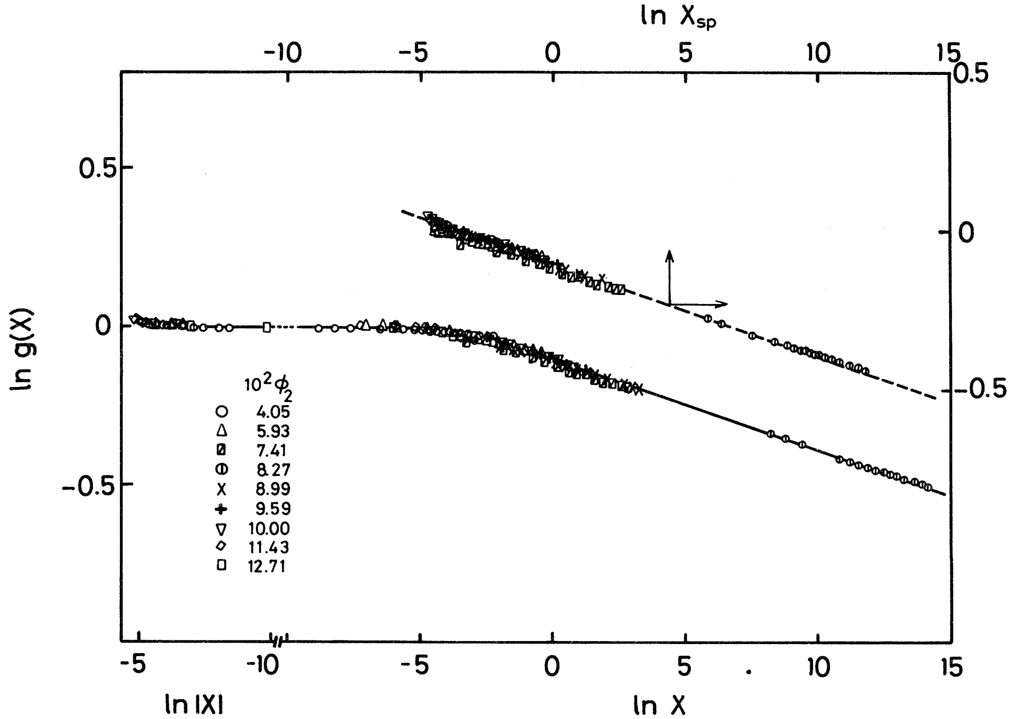

FIG. 6. Scaling plots of the shear viscosity as a function of X for the system polystyrene-cyclohexane. The solid line corresponds to $X=t/|\Delta\phi_2^*|^{1/\beta}$, the dashed line to $X_{sp}=t_{sp}/|\Delta\phi_2^*|^{1/\beta^\dagger}$, and the absolute values of X to the negative values of X.

$$(\phi_2/\phi_{2_c})^{-\phi_\eta/2\nu}\cdot\eta=\eta_{id}\,|\,\Delta\phi_2^*\,|^{-\phi_\eta/\beta}\cdot g(X)\;,$$
$$X=t/\,|\,\Delta\phi_2^*\,|^{1/\beta}\;, \tag{4}$$

where $\Delta\phi_2^*=(\phi_2''-\phi_2')/2\phi_{2_c}$ and ϕ_{2_c} is the volume fraction at the critical concentration. ϕ_2' and ϕ_2'' represent the dilute and the concentrated volume fractions on the coexistence curve, respectively. β is the critical exponent of the coexistence curve $\Delta\phi_2^*=B(-t)^\beta$. A factor $(\phi_2/\phi_{2_c})^{-\phi_\eta/2\nu}$ has been introduced in Eq. (4) in order to account for a small asymmetry in $\ln\eta/\eta_{id}$, which manifests itself in a shift of the peaks in Fig. 5. In regard to this point, it is noted that the factor was omitted in the earlier data analysis for binary critical mixtures[4] because of the symmetry in the plot of $\ln\eta/\eta_{id}$ vs x_2 (mole fraction), though the factor was contained to generally hold in the scaling equation. Therefore, the earlier analysis was equivalent to the data analysis without correction terms by Calmetts.[3,32] Such an asymmetric feature has also been observed in other independent measurements for polymer solutions near the critical point.[7,10]

The function $g(X)$ has a universal asymptotic behavior, i.e.,

$$\lim_{X\to\infty} g(X)=X^{-\phi_\eta}$$
and
$$\lim_{X\to 0_\pm} g(X)=1\;, \tag{5}$$

in the range of $-1/B^{1/\beta}\leq X<\infty$. The subscripts + and − are referred to as $T>T_c$ and $T<T_c$, respectively. The results applied to the present system are shown in Fig. 6. It should be noted that the analysis presented here is applicable to all temperatures above and below the critical temperature, even polymer solutions. Figure 6 demonstrates that the reduced shear viscosity data can be represented by a single-valued function $g(X)$ of the scaling parameter X.

Finally, it is remarkable that a simple scaling plot can be obtained when $t_{\text{sp}}/\,|\,\Delta\phi_2(\text{sp})^*\,|^{1/\beta^\dagger}$ is used instead of $t/\,|\,\Delta\phi_2^*\,|^{1/\beta}$ as X, as shown by the broken line in Fig. 6, where

$$\Delta\phi_2(\text{sp})^*=(\phi_2''-\phi_2')_{\text{spinodal}}/2\phi_2^{\max}(\text{sp})$$

and $\beta^\dagger$ is the critical exponent of the pseudospinodal curve $\Delta\phi_2(\text{sp})^*=B^\dagger(-t_{\text{sp}})^{\beta^\dagger}$. The plot may be considered as a natural result from the proposed pseudospinodal generalization previously established.[4,6] In fact, Fig. 4 suggests that such a scaled plot will be obtained already by changing only the shift factors on the horizontal axis which reflect on $(q_D\xi_0)^{z_\eta}$ in Eq. (1).

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