

Surfactant Titration Technique: An Improved Approach for Determining Latex Adsorption Isotherm Endpoints

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Synopsis

A unique approach has been developed for determining surfactant titration end points via computer analysis utilizing nonlinear regression. This approach fits the data to an equation and then mathematically solves this equation to yield a reproducible endpoint. In this study, this computer program was utilized to interpret titration data for model acrylate, methacrylate, and styrene homopolymer and copolymer systems.

INTRODUCTION

Because many physical properties of latices are highly dependent upon the nature of polymer particle surfaces, it is extremely important to be able to characterize these surfaces. If polymer particles were homogeneous throughout, no special analysis would be necessary since the surface composition would then be identical to the bulk composition. However, non-uniform mixing frequently occurs during polymerization, resulting in the formation of heterogeneous particles (e.g., core/shell, compositional gradients) of unknown surface composition.

There are several techniques currently available for characterizing the surface morphology of polymeric films (ESCA, staining techniques utilizing electron microscopy); however, few techniques are available for characterizing the surface morphology of latex particles in the dispersed state. The only technique extensively utilized in the literature to characterize latex particle surfaces has been the surfactant titration technique of Maron et al.¹

The fundamental principle of the surfactant titration technique is that hydrophobic surfaces have the potential to adsorb large quantities of hydrophobic surfactant while hydrophilic surfaces will only adsorb small amounts of hydrophobic surfactant.^{2,3} The surfactant titration technique utilizes this principle to quantify the hydrophobicity/hydrophilicity of latex particle surfaces.

In actual practice, the utility of the surfactant titration technique is hindered by ambiguity in the endpoint determination.⁴ The objective of this study was to improve the titration technique by developing an automated procedure which reproducibly determines the mathematical endpoint. This method facilitates subtle comparisons by removing the ambiguity in endpoint determination. Using this new approach, the particle surface com-

positions of several model acrylate, methacrylate, and styrene homopolymer and copolymer systems were quantified.

EXPERIMENTAL

Preparation of Latex Dispersions

All polymerizations were carried out under a nitrogen atmosphere. The kettle water was heated to the reaction temperature of 81°C before addition of the initiator, ammonium persulfate (APS); this was followed by addition of polymer seed. The seed technique was similar to those described by Woods et al.⁵ The monomer emulsion was then fed into the reaction flask over a 3-h period (see Table I).

Because of the low surfactant level, the latices were synthesized at 23% solids. The mean particle size of the various latices ranged from 200 to 230 nm, as determined by a Coulter Nano-Sizer.

Method

A surfactant titration curve is obtained by plotting surface tension as a function of added surfactant titer for a known mass of polymer latex with a known particle size. In this study, surface tension measurements were made with a Sensa Dyne 5000 Bubble Tensiometer. The surfactant used in all titrations was commercial-grade sodium dodecyl benzene sulfonate diluted to 3% solids.

Figure 1 represents an ideal surfactant titration curve. The sharp break in the curve determines the end point which is defined as the amount of surfactant required to initiate micellization in the aqueous phase.¹ Unfortunately, in practice, end points in experimental titrations are much less obvious (see Fig. 2) and are often very difficult to reproducibly pick. Thus, a less ambiguous approach would greatly facilitate the analysis.

DISCUSSION

Computer Analysis of Surfactant Titration Data

The approach we have taken for endpoint determination is to utilize the nonlinear regression routine (NLIN) from the SAS (Statistical Analysis System) package.⁶ This procedure produces least-squares estimates of the

TABLE I
Charges for Latex Dispersions (g)

H ₂ O	2800
APS	4
Acrylic seed	10
Monomer emulsion	
H ₂ O	200
Sodium dodecyl benzene sulfonate	0.2
Monomer	900

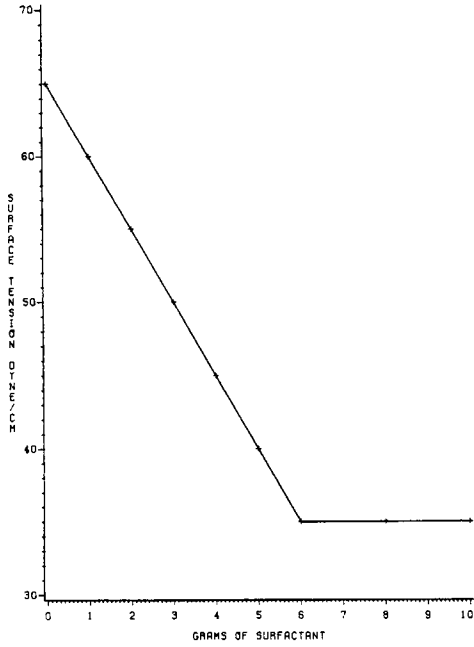


Fig. 1. Ideal surfactant titration curve.

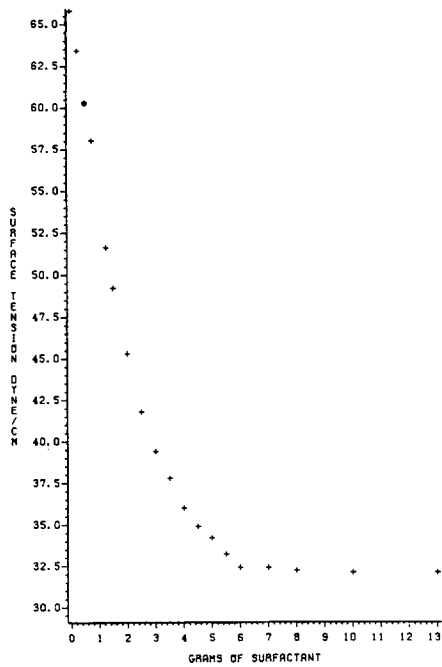


Fig. 2. Surfactant titration curve for PMMA at 23% solids.

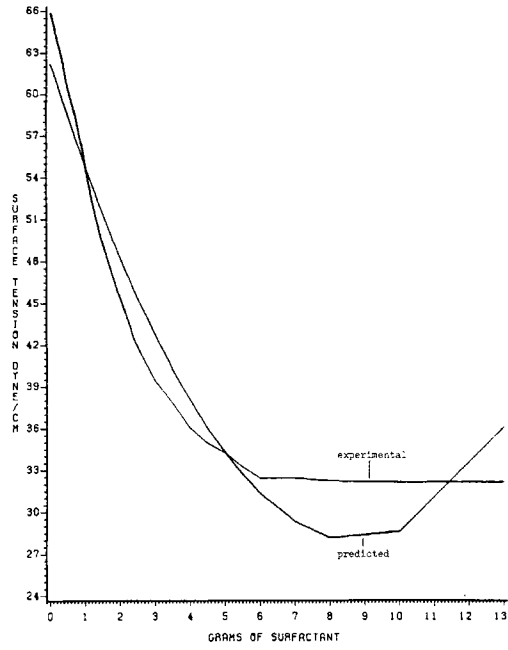


Fig. 3. Poor attempt to fit surfactant titration curve.

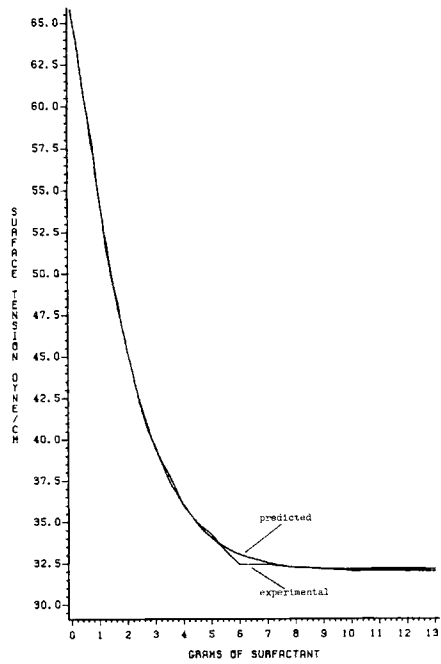


Fig. 4. Good fit of titration curve.

parameters of a nonlinear model to fit raw experimental data; the choice of a model is left to the user. In order to obtain a good fit of the experimental titration data, it is necessary to start with a good analytical model equation. Figure 3 illustrates the poor match obtained with the poor model equation $y = a_1x^2 + a_2x + a_3$. Figure 4 displays the significantly improved correlation resulting from our model. The calculated points in this figure were generated with the analytical expression

$$y = a_1 \exp(-a_2x^{a_4}) + a_3 \quad (1)$$

where a_1 , a_2 , a_3 , and a_4 are constant parameters which were varied by the NLIN routine to minimize differences between experimental points and points calculated with this equation. A plot of the residuals (Fig. 5) emphasizes how well this model fits the data (residuals are the difference between experimental and calculated points). For PMMA at 23% solids, all residuals are less than 1 dyn/cm.

The model expression [eq. (1)] was utilized throughout this paper to fit the experimental points for each system; however, the constants (a_1 , a_2 , a_3 , and a_4) were varied to produce a customized equation which predicted the observed curve for each system.

The end point of a surfactant titration curve is defined as the point of maximum change in direction of the curve. Angle must be used to monitor change in direction because slope is heavily dependent upon orientation.

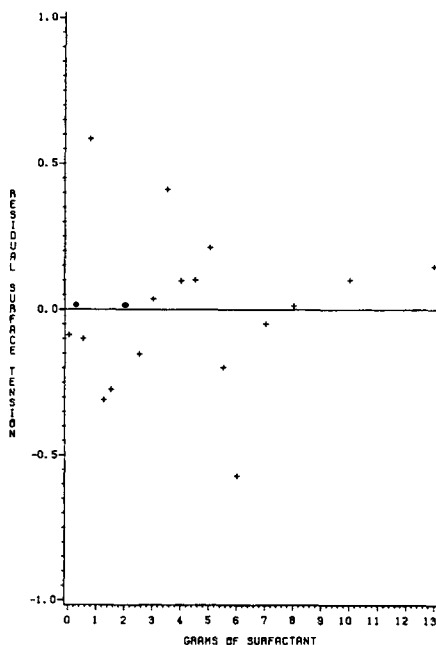


Fig. 5. Residuals from fit of PMMA titration curve.

The first derivative of the adsorption isotherm model equation (1) gives the slope of this curve:

$$\frac{dy}{dx} = -a_1 a_2 a_4 x^{a_4-1} \exp(-a_2 x^{a_4}) \quad (2)$$

The arctangent of eq. (2) describes the angle of a line tangent to the adsorption isotherm at any point:

$$\tan^{-1} \frac{dy}{dx} = \tan^{-1}[-a_1 a_2 a_4 x^{a_4-1} \exp(-a_2 x^{a_4})] \quad (3)$$

The first derivative of eq. 3 provides the change in angle and the second derivative gives the change in the change in angle of a line tangent to the isotherm:

$$\frac{d^2}{dx^2} \tan^{-1} \frac{dy}{dx} = A - BC \quad (4)$$

where

$$A = -\frac{a_1 a_2 a_4 [(a_4 - 1)(a_4 - 2)x^{a_4-3} - a_2 a_4 (2a_4 - 2)x^{2a_4-3}]}{\exp(a_2 x^{a_4}) + a_1^2 a_2^2 a_4^2 x^{2a_4-2} \exp(-a_2 x^{a_4})}$$

$$B = \frac{-a_1 a_2 a_4 [(a_4 - 1)(x^{a_4-2}) - (a_2 a_4)x^{2a_4-2}]}{[\exp(a_2 x^{a_4}) + a_1^2 a_2^2 a_4^2 x^{2a_4-2} \exp(-a_2 x^{a_4})]^2}$$

$$C = a_2 a_4 x^{a_4-1} \exp(a_2 x^{a_4}) + a_1^2 a_2^2 a_4^2 (2a_4 - 2)x^{2a_4-3} \exp(-a_2 x^{a_4})$$

$$- a_1^2 a_2^3 a_4^3 x^{3a_4-3} \exp(-a_2 x^{a_4})$$

The end point (point of maximum change in angle) is obtained by setting eq. (4) equal to zero and solving for x . This can be accomplished on a computer using a method of successive approximations. Figure 6 illustrates the surfactant titration curve for PMMA with the computer designated end point marked.

The computer approach for determining end points has several major advantages over picking end points by hand. First, it removes the subjectivity of determining breaks by hand (significantly improved reproducibility). Secondly, the computer conveniently provides plots of superimposed experimental and theoretical isotherms plus a plot of residuals which readily reveal human errors, poor curve fitting, or experimental anomalies. Finally, the computer approach drastically reduces the amount of time required for data analysis.

Surfactant Adsorption Determination

Although surfactant titration results determine the amount of added surfactant required to initiate micellization, this information in itself is not sufficient to determine the amount of surfactant adsorbed onto the polymer

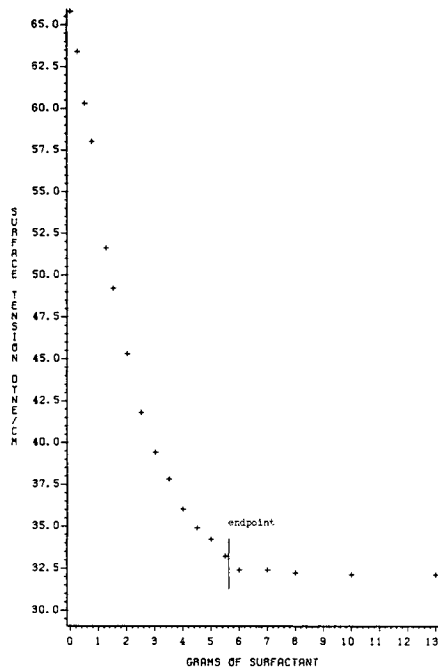


Fig. 6. Adsorption isotherm for PMMA at 23% solids with the computer-defined end point marked.

particles because the titration end point C is composed of two components: C_a , moles of surfactant adsorbed on polymer particles, and C_f moles of surfactant in the aqueous phase (1):

$$C = C_a + C_f \quad (5)$$

In order to ascertain the quantity of surfactant adsorbed per unit area of particle surface, it is necessary to determine the value of C_a . The problem of extracting C_a from C may be resolved by performing surfactant titrations at several different latex concentrations. Figure 7 illustrates surface tension curves for three different concentrations of PMMA. Obviously, less surfactant is required to reach the end point as the polymer concentration decreases. When the various end points are plotted as a function of polymer mass, as in Figure 8, they form a straight line.⁷ This line is described by

$$C = (C_a/m - I)m + I \quad (6)$$

where the variables are defined in the Appendix. The derivation of eq. (6) is also provided in the Appendix.

The sum of the slope ($C_a/m - I$) and intercept (I) of this line provides the value of C_a/m , the moles of surfactant adsorbed per gram of polymer. Although this quantity will be constant for a given latex, it is dependent upon particle size. Therefore, it is more conventional to express surfactant adsorption in terms of A_m , the surface area occupied by a molecule of sur-

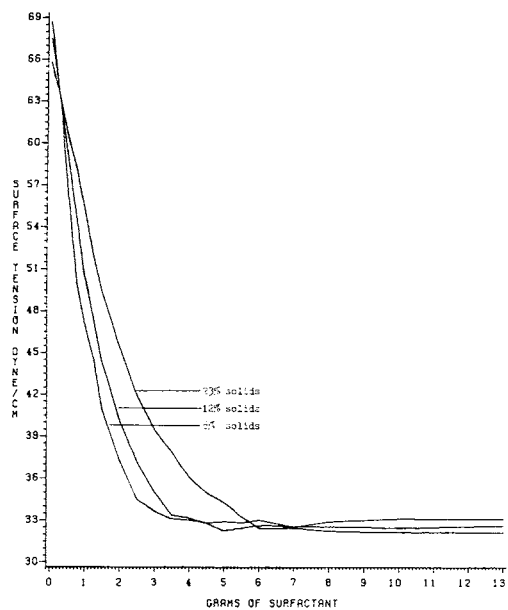


Fig. 7. Adsorption isotherms for PMMA as a function of latex solids.

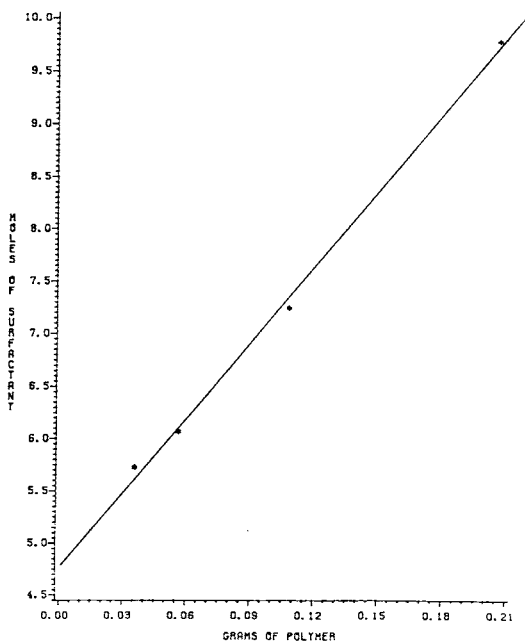


Fig. 8. Plot of c vs. m for PMMA utilizing end points from curves in Figure 7.

factant. A_m is inversely proportional to C_a/m and is constant for a given surface composition^{2,8}

$$A_m = \frac{6m}{(N_a)(C_a)(PS)} \quad (7)$$

where N_a is Avogadro's number and PS is the particle size of the latex. For latexes with hydrophobic particle surfaces, A_m will be small; i.e., only a small area will be assigned to each surfactant molecule because of the large number of surfactant molecules. Conversely, A_m is large for hydrophilic surfaces since relatively few surfactant molecules are absorbed on this type of surface.

A SAS routine is utilized to perform a linear least-squares fit of the plot of C vs. m (the values of C and m are dictated by the titration end point and latex concentration). The slope ($C_a/m - I$) and intercept (I) [defined in eq. (6)] are then manipulated via eq. (7) to solve for A_m .

RESULTS AND CONCLUSIONS

The model homopolymer and copolymer systems characterized for particle surface morphology in this study are described in Table II. In our study, particle size was intentionally held relatively constant to minimize effects other than those of polymer composition. In theory, this is not necessary as the A_m value is independent of particle size [the calculation of A_m takes into account the particle size of the system [see eq. (7)]}.

In copolymer systems, A_m varies linearly with surface composition (8). Therefore, by using homopolymer results as reference points and performing surfactant titrations on copolymers, it is possible to determine the surface composition of the copolymers.

Figures 9 and 10 show the variation in A_m with changes in polymer composition for BA/MMA and Sty/MMA copolymer systems. In both systems, the A_m values vary essentially in a linear fashion with increasing bulk MMA concentration. Thus, despite hydrophilic/hydrophobic differences between MMA and BA or Sty, a particle of uniform polymer composition is formed. This result indicates that polymer composition at the particle surface is representative of the bulk composition for these copolymers; i.e., BA/MMA and Sty/MMA systems copolymerize to form homogeneous particles.

Although there exists some differences between the A_m value reported here for pSty (81 Å²/molecule) and that reported in the literature (53 Å²/molecule)^(2,8), differences in A_m values for identical compositions are not without precedent. Paxton² and Okubo et al.⁸ set A_m for PMMA equal to 131 and 133 Å²/molecule, respectively. However, Piirma and Chen³ report an A_m value of 152 Å²/molecule for PMMA. This latter value closely agrees with our value of 156 Å²/molecule for PMMA. We speculate that these differences in A_m are the result of synthetic differences in polymer preparation. For example, our polymer latices were synthesized with significantly higher molar levels of persulfate and at a higher temperature than the latices of Okubo et al. This processing difference should result in pol-

TABLE II
Physical Properties of Dispersions

Composition	% solids	Brookfield viscosity 60 rpm	pH	Nano-Sizer particle size (nm)	Standing monomer	A_m ($\text{\AA}^2/\text{molecule}$)
100 Sty	23.0	4.5	2.3	228	—	81
100 BA	22.9	3.1	2.5	206	—	84
100 MMA	23.0	3.1	2.6	221	—	156
75 BA/25 MMA	23.2	7.3	2.7	210	1.0	98
52 BA/48 MMA	23.2	5.5	3.1	213	—	111
25 BA/75 MMA	22.3	5.8	2.9	217	0.1	144
67 Sty/33 MMA	23.2	4.4	2.8	214	0.8	108
33 Sty/67 MMA	23.1	5.9	2.5	206	0.5	129

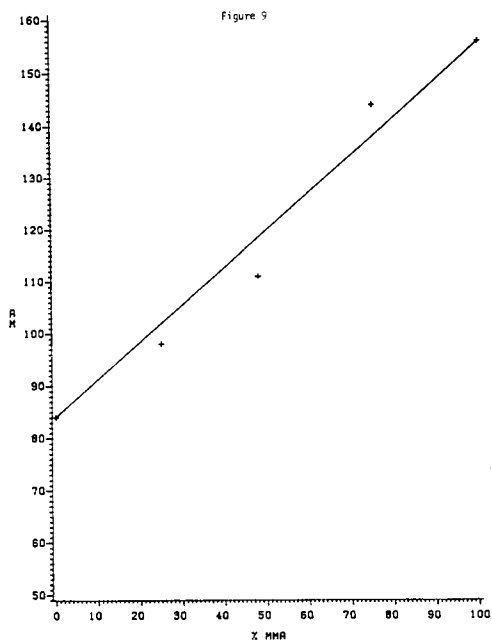


Fig. 9. A_m vs. % MMA for BA/MMA copolymers.

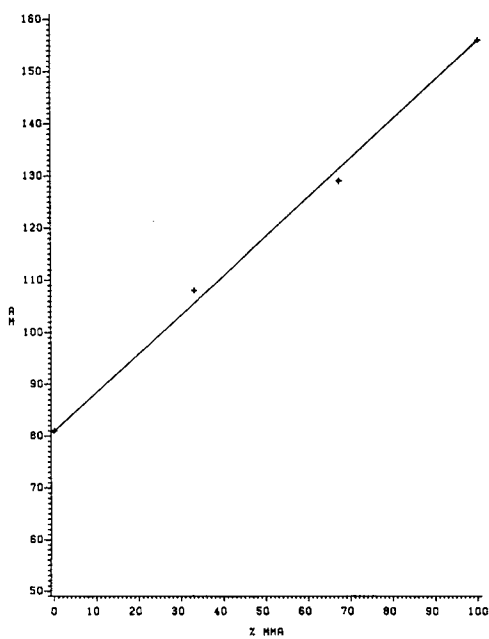


Fig. 10. A_m vs. % MMA for Sty/MMA copolymers.

mer particles with enriched sulfate endgroups relative to the particles of Okubo et al. We speculate that the increased presence of hydrophilic, negatively charged sulfate endgroups decreases surfactant adsorption, thereby raising A_m values of our polymers. These differences in A_m values for homopolymers emphasize the need for appropriate controls prior to drawing conclusions about the hydrophilicity of a particular latex.

I would like to thank A. B. Brown for his initiation of this project and his guidance through its development. I would also like to thank F. J. Parkhill for his constant encouragement and his helpful suggestions.

APPENDIX

$$C_f = \frac{\text{mol free soap}}{\text{g soln}}$$

$$C_f = \frac{(\text{mol free soap})}{(\text{g H}_2\text{O} + \text{g free soap})} \frac{(\text{g H}_2\text{O} + \text{g free soap})}{\text{g soln}}$$

$$C_f = I \frac{(\text{g H}_2\text{O} + \text{g free soap})}{\text{g soln}} \quad (\text{A})$$

But

$$1 = \frac{\text{g H}_2\text{O} + \text{g free soap} + \text{g bound soap} + \text{g polymer}}{\text{g soln}}$$

$$\frac{\text{g H}_2\text{O} + \text{g free soap}}{\text{g soln}} = 1 - \left(\frac{\text{g bound soap} + \text{g polymer}}{\text{g soln}} \right)$$

$$\frac{\text{g H}_2\text{O} + \text{g free soap}}{\text{g soln}} = 1 - \frac{\text{g polymer}}{\text{g soln}}$$

[assume (g bound soap/g soln) is insignificant relative to g polymer/g soln],

$$\frac{\text{g H}_2\text{O} + \text{g free soap}}{\text{g soln}} = 1 - m$$

Substituting into eq. (A)

$$C_f = I(1 - m),$$

$$C = C_a + C_f \quad [\text{eq. (2)}]$$

$$C = \left(\frac{C_a}{m} \right) m + I(1 - m)$$

Thus,

$$C = \left(\frac{C_a}{m} - I \right) m + I \quad [\text{eq. (4)}]$$

where C = mol surfactant added at end point/g solution, C_a = mol surfactant adsorbed on particles/g solution, C_f = mol surfactant in aqueous phase at end point/g solution, I = mol surfactant required to form micelles/(g surfactant + g H₂O), m = g polymer/g solution, and A_m = surface area (Å²/molecule of surfactant).

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