

The Flocculation of Veegum Suspension by Electrolytes

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Abstract The effect on the apparent viscosity of 2 wt. % Veegum suspensions of different types of electrolytes and of different electrolyte concentrations was studied. Measurements were made with a Brookfield Synchro-Lectric Viscometer, using No. 3 spindle at 30 R. P. M. at 24°C. As electrolyte concentration increased, the apparent viscosity was observed to increase to a maximum and then to decrease. Changes in viscosity were in general agreement with predicted results based on the Hofmeister sequence and the Schulze-Hardy rule. The observed electrolyte effect on the apparent viscosity was discussed in terms of the Verwey-Overbeek theory.

Introduction

Veegum^{1,2} is a clay with the composition of a complex hydrous magnesium aluminum silicate containing small amounts of other metal oxides. It is one of the most commonly utilized clay-type suspending or emulsifying agents for a wide range of pharmaceutical and cosmetic formulations. Although extensive research has been reported on the flocculation of the other clay-water systems because of its scientific and technical importance, few reports have appeared with regard to the flocculation of Veegum suspensions.

Vogt³ reported that the cation-exchange capacity of Veegum was about 87 meq. per 100 gm. of dried substance, and the pH could be changed from 9.55 to 8 by addition of NH_4Cl and to 6 with NaH_2PO_4 or $\text{NH}_4\text{H}_2\text{PO}_4$. He also described that the greatest sedimentation was observed in distilled water, but sedimentation was reduced by the addition of electrolytes and was lowest in the presence of NaH_2PO_4 . It was reported

that Veegum suspension in water was usually thickened by the addition of electrolytes.² The present paper has dealt with the rheological properties of Veegum suspensions flocculated by electrolytes. The flocculation was studied at various concentrations of mono-, di-, trivalent cations and anions.

Experimental Description

A. Preparation of the Sample

Sample Studied The sample studied was Veegum provided by the R. T. Vanderbilt Co., New York, New York. The composition of the sample was in weight percent:² SiO_2 (61.1), MgO (13.7), Al_2O_3 (9.3), TiO_2 (0.1), Fe_2O_3 (0.9), CaO (2.7), Na_2O (2.9), K_2O (0.3), CO_2 (1.8) and water of combination (7.2). It was oven dried at 50°C for 12 hours prior to use to remove nonbound moisture which might have been adsorbed by the material during storage.

Preparation of Veegum in Water Suspension

A 4 wt. % suspension was prepared in 500 gm.

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portions by adding 20 gm. of Veegum to 480 ml. of demineralized water, and by mixing for 10 minutes in a Waring Blender, Model No. 1120. The suspension was then weighed, and water lost by evaporation was replaced. The prepared gel was allowed to stand overnight for sufficient hydration to occur, and then used for the study. Veegum suspensions of 2 wt. % were used for all tests in this work.

Preparation of the Suspensions Containing a Final Concentration of Electrolyte Let the final concentration of an electrolyte be x wt. % clay and y equiv. /l. One hundred ml. of $2x$ wt. % clay was pipetted into the blender and 100 ml. of $2y$ equiv. /l. electrolyte was then added slowly with constant stirring at moderate speed for 3 minutes. By this means, high local concentrations of electrolyte were avoided in preparing the samples. The concentrations of electrolyte ranged from 0.001 to 5 equiv. /l.

B. Apparatus

The Brookfield Synchro-Lectric Viscometer is a commercial rotational viscometer. The instrument was powered by a General Electric synchronous induction-type motor, Model 5 SMY 20 J, to ensure constant speeds of rotation of the spindle, which was immersed in a test sample. As the motor rotated, the viscous drag of the sample on the spindle was shown as a deflection on the dial of the instrument with a 0—100 scale. When analyzing Newtonian materials, the absolute viscosity value was computed by the relation: viscosity (in CPS.) = Brookfield factor \times dial reading. In the case of non-Newtonian fluids, the results were only of comparative value, and the conditions of the test, such as R. P. M., spindle number, temperature, and time should be specified.

All tests in this study were made at 24°C, using a No. 3 spindle at 30 R. P. M. All viscosity readings were taken after 5 minutes rotation of

the spindle in test samples which had been allowed to stand for 12 hours in the bath at 24°C.

Experimental Results

Viscosity Change with Electrolyte Concentrations

Monovalent Cation Effect Fig. 1 represents the variation of the viscosity as a function of 1-1 valent electrolyte concentrations for 2 wt. % Veegum suspension. Various concentrations of 1-1 valent electrolytes were used to study the effect of concentration of the monovalent cations on flocculation of the Veegum suspension. In Fig. 1, the following is observed:

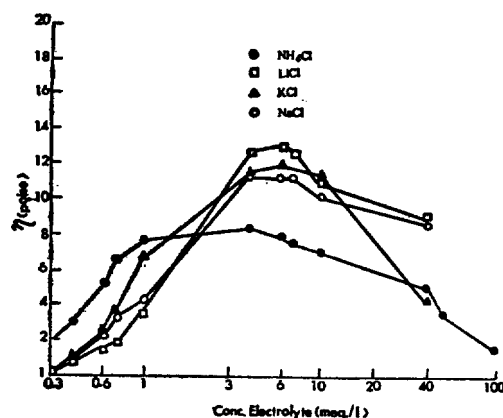


Fig. 1. Variation of the viscosity with 1-1 valent electrolyte concentration for 2 wt. % Veegum suspension.

1. The flocculation power of monovalent cations decreases slightly in the order of $\text{NH}_4 > \text{K} > \text{Na} > \text{Li}$ in the case of lower electrolyte concentration. This sequence of the monovalent cations is called the lyotropic series or Hofmeister series in colloid chemistry. The "flocculation value" is defined by the minimum concentration of an electrolyte to cause the flocculation of a certain sol in a given time. That is, the lower the flocculation value of an electrolyte, the greater

its flocculating power.

2. The viscosity increases to a maximum followed by a decrease as the concentration of a 1-1 valent electrolyte increases. Other investigators⁴ have also shown that the decrease in viscosity occurred regardless of the type of monovalent cations, the rotation time of the spindle, and the type of sample.

3. A viscosity maximum is observed in the samples which contain 4 to 10 meq. of a 1-1 valent electrolyte regardless of the type of monovalent cations.

Divalent Cation Effect Fig. 2 illustrates the effect of concentration of the divalent cation electrolytes on the viscosity of 2 wt. % Veegum suspension. Fig. 2 shows the following:

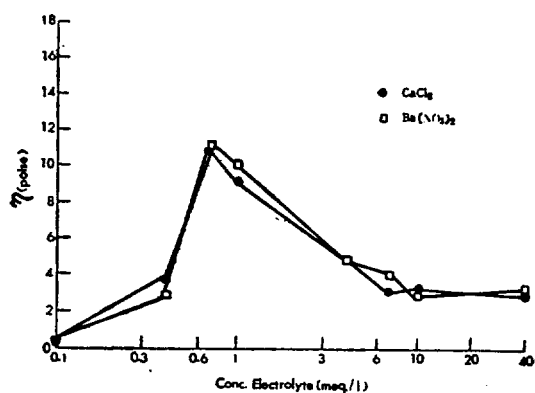


Fig. 2. Variation of the viscosity with 2-1 valent electrolyte concentration for 2 wt. % Veegum suspension.

1. The flocculating power of Ca^{++} and Ba^{++} , and the degree of flocculation at a given concentration of both cations are similar to each other. These are in agreement with the Schulze-Hardy rule and the Verwey-Overbeek theory, *i.e.*, the flocculation of clay suspension is not affected by the type of cations, but by the concentration and the charge of cations.

2. The apparent viscosity increases to a maximum followed by a decrease as the amount of the divalent cation electrolyte increases.

3. When concentrations higher than 10 meq./l. of the electrolytes were added, the viscosity remained fairly constant.

Anion Effect Fig. 3 illustrates the variation of the viscosity as a function of the concentration of three different types of anions for the Veegum suspension, *i.e.*, the salt-flocculation curves for KCl, KI and K_2SO_4 are shown. The result in Fig. 3 does not reveal any significant difference in the viscosity due to the three different types of anions. This indicates that Veegum suspension is not affected by anions, but by cations because of the fact that most clay particles are negatively charged.

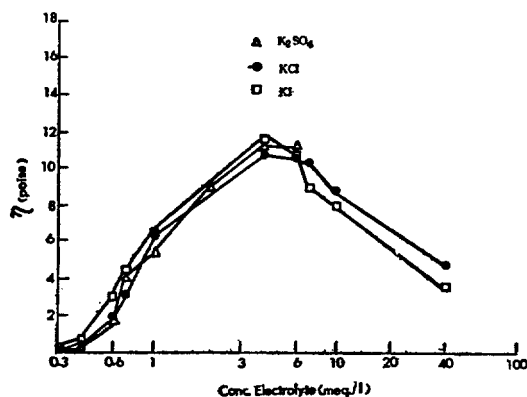


Fig. 3. Variation of the viscosity with KCl, KI and K_2SO_4 concentration for 2 wt. % Veegum suspension.

Effect of Cation Valence In Fig. 4, the variation of the viscosities with 1-1, 2-1, and 3-1 valent electrolyte concentrations for the Veegum suspension is shown. NaCl, CaCl_2 and AlCl_3 were used for the comparison of the effect of cation valence on flocculation of the Veegum suspension. Fig. 4 shows the following:

1. The flocculating power of the three cations (Na^+ , Ca^{++} and Al^{+++}) of different charge follows the Schulze-Hardy rule over the range of low electrolyte-concentrations.

2. A maximum viscosity is observed at 1 meq./l. for both CaCl_2 and AlCl_3 . In the case

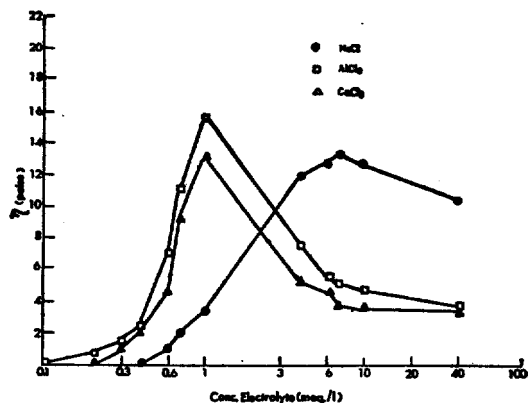


Fig. 4. Variation of the viscosity with 1-1, 2-1, and 3-1 valent electrolyte concentration for 2 wt. % Veegum suspension.

of NaCl, a maximum viscosity is observed at 7 meq./l.

3. The degree of flocculation caused by the three cations at a given high concentration of electrolyte decreases in the order of $\text{Na}^+ > \text{Al}^{+++} > \text{Ca}^{++}$.

Other investigators claimed that the initial viscosity decreased when small amounts of NaCl, KCl, BaCl_2 and LaCl_3 were added to clay suspension. In most cases, however, they used low concentration of clay suspension such as 0.025 wt. %.⁴ As mentioned previously, we used 2 wt. % Veegum suspension, and the viscosity was invariably increased upon the addition of electrolytes. (See Fig. 1 to 4.)

Analysis and Discussion

Verwey and Overbeek's Theory Lyophobic colloids are characterized by the fact that their stability (peptization and flocculation), rheological properties, light-scattering and other physical properties are mainly determined by the electric double layer surrounding the particles.⁵ Theory of the interaction of the electric double layers

was offered by Verwey and Overbeek in relation to the stability of lyophobic colloids.⁶ They concluded that the stability must be associated with an increase in the free energy leading to a repulsion between the particles. The repulsive potential calculated from consideration of the free energy for certain special cases has been combined with London-van der Waals attractive potential calculated by Hamaker⁷ to obtain net interparticle energy as a function of particle distance.

Verwey and Overbeek derived the following equation for the repulsion potential V_R between two electric double-layers, utilizing the theories of both Gouy and Stern, mainly Gouy's view because of its more simple mathematical treatment:

$$V_R = \left(\frac{64nkT}{\kappa} \right) \gamma^2 \exp(-2\kappa d) \quad (1)$$

$$\left. \begin{aligned} \gamma &= \frac{\exp(z/2) - 1}{\exp(z/2) + 1} \\ z &= \frac{Ve\phi_0}{kT} \\ \kappa &= \left(\frac{8\pi ne^2 V^2}{\epsilon kT} \right)^{1/2} \end{aligned} \right\} \quad (2)$$

It was assumed that no changes in surface potential or double-layer charge occurred. This relation is often a good approximation for large values of d in comparison to $1/\kappa$ (i. e., $\kappa d \gg 1$). Here,

n local ionic concentration in number of ions/cm³ (i. e., normality $\times 10^{-3} \times$ Avogadro's number)

kT Boltzmann's constant \times absolute temperature

ϕ_0 surface potential

V valence of ion (number)

e elementary charge 4.77×10^{-10} e. s. u.

ϵ dielectric constant of the medium

d half-distance between surfaces

$1/\kappa$ is known as Debye characteristic length, and is an approximate measure of the thickness

of the electric double-layer.

Eq. (1) for V_R is a useful equation as it confirms the facts that V_R for large distances declines exponentially, and the more rapidly, the smaller $1/\kappa$. Eq. (1) was used by Verwey and Overbeek for the explanation of a simple flocculation.

From Eq. (2) one can predict the effect of electrolytes on the configuration of an electric double-layer: the higher the concentration and the higher the valence of the ions of opposite sign, the more the double-layer will be compressed. This result will be important in the explanation of the Schulze-Hardy rule.

London-van der Waals attractive potential calculated by Hamaker is given by the equation

$$V_A = -\frac{\pi q^2 \lambda}{48} \left[\frac{1}{d^2} + \frac{1}{(d+\Delta)^2} - \frac{2}{\left(d + \frac{\Delta}{2}\right)^2} \right] \quad (3)$$

According to Eq. (3) for V_A , we may assume that London-van der Waals attractive potential is approximately independent of the electrolyte added, since the equation does not contain terms involving the concentration or valence of the ions of opposite sign. In Eq. (3), d is the half-distance between two parallel plates, Δ is the thickness of the plate and λ is a factor involved in the London formula. From the relation of the quantities q and λ , V_A can be expressed by the following formula:

$$V_A = -\frac{A}{48\pi} \left(\frac{1}{d^2} + \frac{1}{(d+\Delta)^2} - \frac{2}{\left(d + \frac{\Delta}{2}\right)^2} \right) \quad (4)$$

in which A is approximately equal to 10^{-12} .

Thus, one may see that the net interaction energy between particles is mainly governed by V_R . The net interaction-energy curves, or "potential curves of interaction", which involves both the repulsive and attractive energies, can be translated in terms of sol stability and flocculation by the following consideration:⁶ Two

particles may approach each other in a relative distance at which the deep minimum in the potential energy occurs, and become associated because of the prevailing attraction. The following three cases will appear:

1. In the case of very low electrolyte concentrations, where the particle separation is very large, the flocculation process is so retarded by the appreciable long-range repulsion that it may take a very long time before flocculation is perceptible in the sol (stable sol). (Fig. 5)
2. At intermediate concentrations of electrolytes (Fig. 6), the flocculation process is slowed down by the long-range repulsion (slow flocculation).
3. On the other hand, in the case of a high

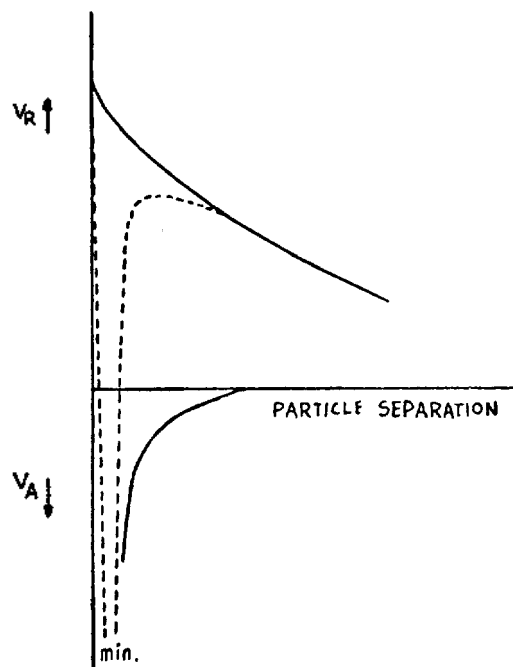


Fig. 5. Net interaction energy as a function of particle separation at low electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that the potential barrier is very high.

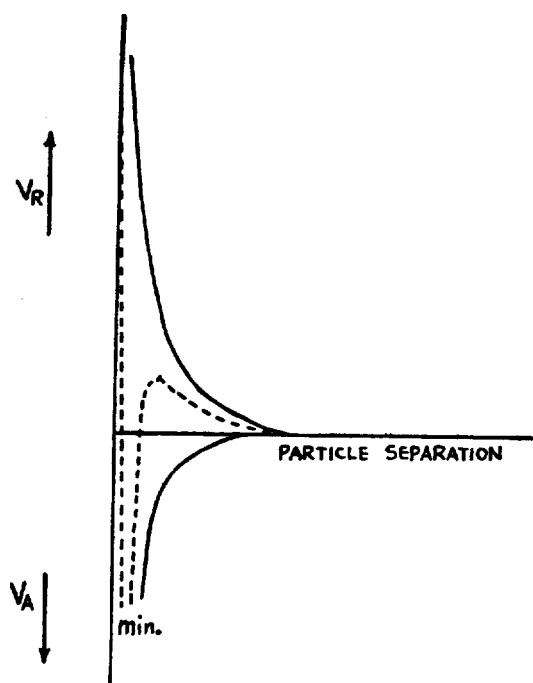


Fig. 6. Net interaction energy as a function of particle separation at intermediate electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that the potential barrier is remarkably reduced.

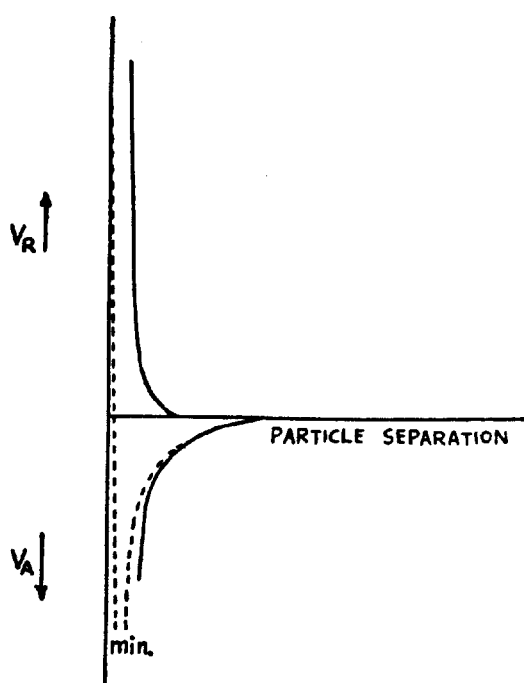


Fig. 7. Net interaction energy as a function of particle separation at high electrolyte concentration. V_R and V_A are represented by full curves whereas the sum of the two is expressed by a dotted curve. Note that there is no potential barrier.

electrolyte concentration the potential curve shows no repulsion at any particle distance (Fig. 7), and particle flocculation occurs at a maximum rate (fast flocculation).

A large portion of the potential curve above the distance coordinate, or a large energy barrier, reduces the rate at which the sol particles associate by "jumping over the barrier." When the potential barrier becomes smaller, the rate of flocculation increases, and in the absence of a barrier, the rate is maximal. The height of the barrier is determined by the magnitude and range of the double-layer repulsion energy. The addition of electrolytes causes a compression of the double layer (a decrease in $1/\kappa$) and,

therefore, a reduction of the range of repulsion and a reduction of the height of the energy barrier in the interaction curve. Since the compression of the double layer is determined by the concentration and valence of ions of opposite sign, the stability theory is able to explain the Schulze-Hardy rule (see Eq. (2)).

For plate-shaped particles oriented parallel to each other, the London-van der Waals potential for the relevant distance region can be represented by a d^{-2} law. Combining this with the approximate Eq. (1) for the repulsion potential, Verwey and Overbeek derived the following criterion for the transition between flocculating and stable sols:

$$z = \frac{107e^3 k^5 T^5 \gamma^4}{A^2 (Ve)^6} \quad (5)$$

Thus, they found for the flocculating concentration c (in millimoles per liter) of a V - V valent electrolyte at room temperature,

$$c = 8 \cdot 10^{-22} \frac{\gamma^4}{A^2 V^6} \quad (6)$$

As for $z/2 < 1$ we obtain an even simpler equation relating V and c at incipient flocculation:

$$\gamma = \frac{1 + \frac{z}{2} + \dots - 1}{1 + \frac{z}{2} + \dots + 1} \approx \frac{z}{4} = \frac{Ve\phi_0}{4kT}$$

Hence, they found instead of Eq. (6)

$$c = \frac{10^{-22}}{32A^2 V^2} \left(\frac{e\phi_0}{kT} \right)^4$$

and they obtained the very simple result that the flocculating concentration is approximately proportional to the fourth power of the double-layer potential:

$$c = \text{constant} \cdot \frac{1}{V^2} \phi_0^4 \quad (7)$$

For larger values of ϕ_0 , however, especially for valences higher than 1, γ^4 approaches unity, and, therefore, the flocculation value is no longer very sensitive to the double-layer potential. This leads to a very simple limiting law which relates the influence of the valency of the electrolyte to the flocculation concentration. According to Eq. (6), if γ^4 approaches unity, the flocculating concentration of electrolytes is merely proportional to V^{-6} . Thus Verwey and Overbeek found in this case that the amounts of 1-1 valent, 2-2 valent and 3-3 valent electrolytes required to flocculate a lyophobic sol or suspension are in a ratio

$$1 : (1/2)^6 : (1/3)^6 \text{ or } 100 : 1.6 : 0.13.$$

This result of the approximate theory stands in very good agreement with colloid chemical experience as formulated long time ago in the well-known Schulze-Hardy rule. Good agreement between the theory and experiment has been found with sols containing asymmetric particles, *e. g.*, with the sodium montmorillonite clays by Kahn.⁴

Effect of Monovalent Cations In *Fig. 1*, one sees that the flocculating power of monovalent cations in low concentrations follows the sequence of the Hofmeister series in the order of $\text{NH}_4 > \text{K} > \text{Na} > \text{Li}$. Monovalent cation effect on the flocculation of lyophobic sols cannot be predicted from the Overbeek and Verwey theory, since the theory only involves the concentration and valence of ions of charge opposite to that of the particle surface. The concentration at which viscosity maximum occurs does not follow the Hofmeister series, and is variable dependent on the type of cation, sample, and the time at which viscosity readings are taken. This shows the fact that although these cations are all monovalent, their rates of ion exchange are different. The viscosity drop at very high concentrations can not be explained by the Verwey-Overbeek theory.

Effect of Polyvalent Cations *Fig. 2* shows that both Ca^{++} and Ba^{++} have nearly the same effect on the rheological property of Veegum suspension. This fact is predicted from the Schulze-Hardy rule or the Verwey-Overbeek theory, since those cations are divalent. It is a well-known rule of colloid chemistry that ions of higher valence preferentially replace those of lower valence in electric double-layer. In the case of the Veegum system, it is probable that sodium in the double-layer of the particle will be replaced mainly by calcium or aluminum ions to form calcium or aluminum Veegum.

Fig. 4 shows that the flocculating power of cations follows well the Schulze-Hardy rule, which states that the flocculating power of electrolytes is predominantly governed by the valence rather than type of those ions with a charge opposite to that of the particle. The results of the flocculation do not, however, fit quantitatively into the Verwey-Overbeek theory, which predicts flocculation values in the ratio of $1:(1/2)^6:(1/3)^6$ for mono-, di- and trivalent cations. It may be due to the two factors, the high concentration (2 wt. %) of Veegum suspension in our case and the effect of cation exchange which might occur in our system, since the two factors are not considered in the Verwey-Overbeek theory.

Effect of Anions Fig. 3 shows that anions Cl^- , I^- , and SO_4^{2-} show no effect on the rheological property of Veegum suspensions. This is due to the fact that the Veegum particles are negatively charged, and only the counter ions (cations) with a charge opposite to that of the particle can affect the configuration of the electric double layer, thereby affecting the rheological properties and other physical properties of lyophobic colloids. Negative ions which have charge as those on the particle will have nearly no effect.

Since the edges of Veegum particles have

positive charges, some degree of anion exchange capacity is expected. However, because of the small area of edge surface compared to that of face surface, the effect of anions should be negligible, and no effect of anions was observed in our results

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