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Structure and Flow in Surfactant Solutions

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9. IMAE Spinnability of Viscoelastic Surfactant Solutions

Chapter 9

Spinnability of Viscoelastic Surfactant Solutions and Molecular Assembly Formation

Toyoko Imae

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

The spinnability was measured for aqueous viscoelastic solutions of cationic surfactants with aromatic salicylate counterion in the absence and presence of sodium salicylate. Aqueous solutions of alkyl- and oleyldimethylamine oxides also exhibited the characteristic spinnable behavior. The spinnability of these surfactant solutions was classified into the ductile failure type and the cohesive fracture failure type. The behavior was compared with that of spinnable polymer solutions. The spinnability is closely related to the viscoelasticity, that is, the plateau modulus or the dynamic (structural) relaxation. The assembly formation by surfactant molecules is discussed in connection with rheological properties of solutions.

When a rod in a liquid is pulled up at a constant rate, the liquid is stretched to form a thread. This rheological phenomenon is called the "spinnability", which is related to the Weissenberg effect. The spinnable liquids are generally non-Newtonian and viscoelastic, and the thread-forming property is characterized by the length of the liquid thread. The spinnability was reported for native and synthetic polymer solutions (1-5). It was suggested that the thread-forming state was described by the elastic deformation superposed on the viscous flow and that the spinnability was most remarkable when the drawing velocity coincided with the mechanical relaxation time in Maxwell's flow.

Similar characteristics were also observed for aqueous solutions of cationic surfactants with certain kinds of aromatic counterions such as salicylate (6). Such surfactants exhibited the strong viscoelasticity even in very dilute aqueous solutions. The micellar structure in the viscoelastic solutions and the mechanism for the inducement of the viscoelasticity are discussed in several works. Some investigators (7-9) confirm the formation of rodlike micelles in the viscoelastic solutions. It has been assumed that rodlike micelles build the three-dimensional network, where the contacts between micelles are constantly formed and broken (7). Later work indicates that the effect of micellar kinetics has to be taken into consideration at the same time

(10). The experimental data have also been explained by the formation of an entangled network of threadlike micelles and the breakdown-reformation of the network (11).

Since salicylate ions exhibit specific adsorption and penetration ability (12), the electric structure such as surface potential and electrical double layer, and as a result the micelle structure and their properties in a solution, may change remarkably. Therefore, the role of salicylate ions on micelle formation must be elucidated. It has been emphasized that the unique orientation of salicylate ions on the micellar surface is the crucial factor for inducing viscoelasticity, and two mechanisms have been proposed (13).

Dilute aqueous solutions of hexadecyl- and octadecyldimethylamine oxide (C16DAO, C18DAO) present iridescent colors at lower temperatures and are transparent at higher temperatures. It has been confirmed from microscopic observations that platelike assemblies and lamellar layers are constructed in the iridescent solutions (14,15). Rodlike micelles are formed in transparent solutions of C16DAO as well as of oleyldimethylamine oxide (ODAO) (16,17). Aqueous solutions of C16DAO and ODAO are viscoelastic (18), and the spinnability of aqueous ODAO solutions is especially remarkable.

Extract from the root of *Abelmoschus Manihot* is used to disperse paper fibers when Japanese paper is manufactured. It exhibits the remarkable viscoelasticity as well as sodium alginate, poly(ethylene oxide) (PEO), and sodium carboxymethylcellulose (NaCMC) which are also useful to disperse fibers (19). Although the spinnability phenomenon is known for these polymers, it is not necessarily discussed in relation to the viscoelasticity and the polymer structure in solutions.

In this work, the spinnability property is quantitatively investigated for aqueous solutions of tetradecyl- and hexadecyltrimethylammonium salicylates (C14TASal, C16TASal) in the absence and presence of sodium salicylate (NaSal) and is compared with that of CnDAO, ODAO and polymers described above. Moreover, the spinnability mechanism in dilute surfactant solutions is discussed. Such a mechanism has never clearly been identified and reported.

It may be noticed that aqueous C_nTASal solutions investigated here do not include any additive counterions like halides, since samples of C_nTASal were synthesized by counterions-substituting alkyltrimethylammonium halides with NaSal (20). Then the solution behavior of C_nTASal is partly different from that of alkyltrimethylammonium halides mixed with NaSal (20,21), because the specific adsorption and the penetration ability of salicylate ions are hindered by the adsorption of halide ions.

Spinnability

Spinnability was measured on an apparatus constructed as previously reported (2). A rod in a test solution was driven up at a constant rate (20). The maximum thread length, namely, the drawing length was measured as a length from the rod to the surface of the solution. The drawing lengths at various immersion depths were extrapolated to the zero depth to obtain the intrinsic drawing length.

Figure 1 gives the schematic representation of the intrinsic drawing length L₀ as a function of drawing velocity v. The L₀ values increase linearly with v in some cases,

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Figure 1. Schematic representation of the variation of drawing length against drawing velocity (upper) and the drawing process (lower) for the type D and C spinnability. (Reproduced with permission from ref. 20. Copyright 1990 Verlag GmbH.)

while others decrease with v or are almost independent of v. Both cases are respectively characterized by a slope $\Delta Lo/\Delta v$ of the straight line and by a constant intrinsic drawing length L0, c at the finite drawing velocity.

The former (type D) spinnability is a kind of ductile failure (or capillary-ductile failure), which is observed for viscoelastic solutions with low viscosity (22). In this case, the liquid thread becomes thin with drawing until it breaks, as seen in the schematic representation in Figure 1. In the latter (type C) spinnability, the liquid thread keeps almost constant thickness during drawing and behaves like cohesive fracture failure, which occurs in rubber or gel elasticity (22).

A liquid thread in the type C spinnability is pulled back into the liquid reservoir, when it is broken, since the strong elasticity acts against the deformation caused by drawing up the rod. The liquid thread snaps at a position near the rod when the tension (retracting force) of a solution overcomes the adhesive force of the liquid thread to the rod. The tension may be approximately inversely proportional to the length of the liquid thread. If the liquid thread deforms more quickly than its maximum relaxation time, the thread is broken at a certain drawing length, regardless of the drawing velocity of the rod. Therefore, the constant drawing length can be related to the elasticity of a solution. On the other hand, it is reported that the shear modulus increases as the solute concentration increases (18). Hence the drawing length may become shorter with an increase in solute concentration. Such a relationship for the type C spinnability was confirmed by the present work (19,20).

Aqueous Solutions of Tetradecyl- and Hexadecyltrimethylammonium Salicylates

In aqueous solutions without NaSal, C14TASal molecules associate into elliptic or short rodlike micelles at temperatures below 25 $^{\circ}$ C (23). Since the external interference effect indicating the intermicellar correlation is strong at micelle concentrations above 10-3 g cm⁻³, short rodlike micelles may interact and pseudolink with each other. The linked micelles form the pseudonetwork structure, as shown in Figure 2a.

The absolute complex viscosity $|\eta *|$, the storage modulus G', and the loss modulus G" were measured as a function of angular frequency, and the zero shear viscosity η_0 the plateau modulus G_N, and the relaxation time τ were evaluated from experimental data (21). While the relaxation time is almost independent of micelle concentration, the zero shear viscosity and the plateau modulus increase at micelle concentrations above 10-3 g cm⁻³.

Type D spinnability is observed at 20-40 °C, where the $\Delta L_0/\Delta v$ values increase with increasing micelle concentration (20). The surfactant solutions at higher micelle concentrations provide type C behavior, and the $L_{0,c}$ values decrease gradually as the micelle concentrations are increased. The spinnability changes from type D to C at 4 x 10-2 g cm⁻³ micelle concentration and is strongest in the transitional region of type D to C. At the transition region, type D is observed at low drawing velocities, and type C is observed at high velocities.

When the micelle concentration is diluted, $C_{14}TASal$ micelles are short and few, and the intermicellar correlation is rather weak. Then the loose pseudonetwork composed of short rodlike micelles is formed in micellar solutions. Such structure

induces the type D spinnability. The type D spinnability is observed for solutions where the viscous flow overcomes the elastic deformation. The spinnability strengthens with increasing micelle concentration, owing to the increase in the amount of micelles and/or to the micellar growth. Then the pseudolinkages between micelles increase and tighten. Therefore, the elasticity becomes more operative. In solutions having a drawing length too long to measure by the apparatus in this work, the elasticity and the viscosity must be favorably balanced.

At higher micelle concentrations, the contribution of the strong elasticity from the sufficiently developed pseudonetwork of micelles is superior to that of the viscosity and, therefore, type C spinnability appears. In this case the effective tension of the solution strengthens enough to pull the thread back into the solution and to break the thread. The drawing length thus becomes short, and the spinnability converts from the ductile failure to the cohesive fracture; that is, from the viscous response to the elastic deformation.

The pseudonetwork composed of pseudolinkages between short rods in which salicylate ions participate is formed even in aqueous C_{16} TASal solutions without NaSal (24). As the alkyl chain length of surfactant becomes longer, larger or longer rodlike micelles are formed. Hence the pseudonetwork is formed at lower micelle concentrations and will tighten. Such structure may induce the type C spinnability. In fact, type C behavior is predominant for aqueous C_{16} TASal solutions, when the aspect is compared with that of aqueous C_{14} TASal solutions (20).

The pseudonetwork in aqueous CnTASal solutions without NaSal is constituted by the pseudolinkages but not by the entanglement. These kinds of assembly structures are distinguished by the contrary angular dependence of static light scattering (23, 24). In the pseudolinkages, salicylate counterions penetrate into rodlike micelles and hydrogen-bond between counterions through water. This kind of network is indispensable for inducing strong spinnability and viscoelasticity, because such properties are not induced by only the entanglement. In this connection, semidilute solutions of entangled rodlike micelles of alkyltrimethylammonium halides and oligooxyethylene alkyl ethers exhibit strong viscosity but very low viscoelasticity (25,26).

Aqueous NaSal Solutions of Tetradecyl- and Hexadecyltrimethylammonium Salicylates

When 0-0.4 M NaSal is added into aqueous C14TASal solutions at a surfactant concentration of 1.6 x 10⁻² g cm⁻³, the type D behavior is observed at 15-35 $^{\circ}$ C (20). In Figure 3, rheological and light scattering results are compared as a function of ionic strength $C_0 + C_s$ for aqueous C_{14} TASal solutions at 25 °C (21,23,24), where C_0 and Cs are critical micelle concentration and salt concentration, respectively. Mapp is the apparent molecular weight (24) and U is the electrophoretic mobility. While the plateau modulus is independent of ionic strength, the zero shear viscosity, the relaxation time, and the ductile failure spinnability increase with addition of a small amount of NaSal, since the intermicellar correlation diminishes above ~ 0.001 M ionic strength and rodlike micelles lengthen. On further addition of NaSal, the zero shear viscosity and the spinnability decrease through a second maximum and a shoulder, respectively, at

(b) entangled rodlike micelles; (c) small micelles; (d) rodlike micelles; (e) lamellar layers; (f) super-network.

(f)

(e)

Figure 2. Structures of various assemblies. (a) Linked short rodlike micelles:

(d)



STRUCTURE AND FLOW IN SURFACTANT SOLUTIONS



Figure 3. Light scattering and rheological properties as a function of ionic strength for aqueous CnTASal solutions at 25 °C. Surfactant: a-d, C₁₄TASal; e-h, C₁₆TASal. Surfactant concentration (10⁻² g cm⁻³): a, 0.8; b, 0.8; c, 1.6; d, 1.6; e, 0.2; f, 0.055; g, 1; h, 0.2. Broken lines in a and e represent the contribution of external interference. (Reproduced with permission from ref. 23. Copyright 1992 American Chemical Society.)

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 ~ 0.1 M NaSal, where the micelle size is maximum. The spinnability disappears at higher ionic strength.

As seen in Figure 3, viscoelasticity and light scattering of aqueous $C_{16}TASal$ solutions behave as well as those of aqueous $C_{14}TASal$ solutions (20,21,24). The zero shear viscosity has two maxima, and the corresponding maximum around 0.1 M NaSal is also obtained for the relaxation time. The type C spinnability is observed at 25 and 35 °C, and the reciprocal $L_{0,c}$ values and the micelle size have a maximum at \sim 0.1 M NaSal.

Electrophoretic light scattering is a useful method for examining the surface potential and the charge of colloidal particles, which are essential for the stability of particles in a medium. Electrophoretic mobility examination indicates that CnTASal micelles in water exhibit a positive, low net surface charge, as seen in Figure 3, suggesting the specific adsorption and penetration of salicylate ions to micelles (23, 24). With addition of NaSal, the net charge of micelles is converted from positive to negative through neutral at ~ 0.1 M NaSal. This indicates that the specific adsorption and the penetration of salicylate ions dominate the micelle size and the solution behavior such as spinnability and viscoelasticity. The added NaSal not only promotes the specific adsorption and penetration but also decreases the electric double layer. Thus, 0.1 M NaSal must be enough to reach to the zero thickness double layer.

Since addition of a small amount of NaSal stimulates the growth of rodlike micelles by the salting-out effect, the rheological character, spinnability and viscoelasticity, is slightly emphasized. Accompaning the increase of viscosity, the spinnability tends to be type D rather than type C and becomes stronger. The further addition of NaSal partly destroys the intermicellar correlation and the pseudolinkages in the pseudonetwork, owing to the electric shielding effect. As a result, the rheological character diminishes at NaSal concentrations above the first extreme.

The addition of excess NaSal promotes the specific adsorption of salicylate counterion at the Stern layer of the micelle surface and their penetration into micelles. This results in rodlike micelles with zero net surface charge at ~ 0.1 M NaSal and, therefore, the elongation and the entanglement of rodlike micelles in the semidilute region progress because of the diminution of electrostatic repulsion in the micelles. Then the rheological behavior again increases slightly. The pseudonetwork in semidilute solutions is constituted by the entanglement and a small fraction of pseudolinkages. While the pseudonetwork composed of the pseudolinkages presents rather elastic rheological character, the pseudonetwork by the entanglement has more viscous character.

Above 0.1M NaSal, the negative net charge of a micelle increases due to the excess adsorption and the penetration of salicylate ions. Therefore, the micelle size diminishes because of the electrostatic repulsion in "anionic" micelles, until small micelles with a negative charge are formed around 1 M NaSal. Simultaneously, the rheological behavior decreases and disappears with the diminution and the disappearance of entanglement and pseudolinkages. Since simple salts such as sodium halides generally tend only to increase micelle size, the destruction of the micelles by 1 M NaSal is unusual. The remarkable effect of NaSal may be attributed to the superior ability of NaSal to change water structure. Schematic models of typical micellar structures are illustrated in Figures 2a-2d.

Aqueous NaCl Solutions of Alkyl- and Oleyldimethylamine Oxides

While aqueous $C_{14}DAO$ solutions at 25 °C present no spinnability even in the presence of 0.2 M NaCl, the type D spinnability is observed on addition of HCl for solutions with 0.2 M NaCl (18). The $\Delta L_0/\Delta v$ values have a maximum at Ca/C ratio of \sim 0.3, where Ca and C are mole concentrations of HCl and $C_{14}DAO$, respectively. For aqueous $C_{16}DAO$ solutions without salt, the type C spinnability is observed at 20 and 25 °C, and the type D is at 35 - 45 °C. The $L_{0,c}$ and $\Delta L_0/\Delta v$ values increase with the initial increase of surfactant concentration. Aqueous ODAO solutions with and without NaCl present only the type D spinnability. Whereas the $\Delta L_0/\Delta v$ values are independent of low NaCl concentrations, they increase above 0.1 M NaCl.

When a moderate amount of HCl is added, $C_n DAO$ molecules with charge make pairs with noncharged molecules, and rodlike micelles grow and entangle (16). This strengthens the type D spinnability. At higher Ca/C ratios, the micelle size decreases by the electrostatic repulsion between charged surfactants in a micelle, and the spinnability weakens.

The viscoelastic behavior of dilute solutions of $C_{16}DAO$ without salt at 35 °C and ODAO at 25 °C is similar to that of dilute nonlinked polymer solutions; and that of concentrated solutions is like that of entangled polymer solutions (18). The G' and G" values increase with surfactant concentration. Moreover, the values increase sharply with angular frequency ω and there is even a small peak in a G"- ω plot for a concentrated solution. This aspect is consistent with rodlike micelles being formed in dilute surfactant solutions and entangling each other at high surfactant concentrations. Then the spinnability is affected by the surfactant concentration.

The addition of NaCl enhances the growth and the entanglement of rodlike ODAO micelles but shields the intermicellar interaction (17). The spinnability and the viscoelasticity are not strongly affected by the addition of NaCl below 0.1 M as a result of the compensation between these two opposite effects. On the other hand, the growth and the entanglement of micelles are remarkable above 0.1 M NaCl, and, therefore, the spinnability and the viscoelasticity increase.

Aqueous solutions of $C_{16}DAO$ and $C_{18}DAO$ without salt at room temperature present iridescence at 0.3 - 2 wt % surfactant concentrations. Optical and electron microscopic observation confirmed the formation of platelike assemblies and lamellar layers (14,15), as shown in Figure 2e. Such solutions exhibit rheological behavior different from that of rodlike micelles (18). For aqueous $C_{16}DAO$ solutions at 20 °C, which exhibit type C spinnability, the frequency dependence of G' and G" is small, and the G" values are larger than the G' values. The viscoelastic behavior of aqueous $C_{18}DAO$ solutions without salt at 25 °C is very similar to that of $C_{16}DAO$ at 20 °C. Long-range structure exists in the iridescent solutions, and such structure has a relaxation time longer than the experimental time scale. Therefore, the stretched solutions produce the large stress by the elastic force, but the relaxation of the elasticity by flow may not act there.

Polymers

Extract from the root of *Abelmoschus manihot* is a polysaccaride that is composed of rhammose and galacturonate (19). The extract in water is viscoelastic, since polymer chains form junctions. The major component of a brown seaweed, sodium alginate, is a linear copolymer of L-guluronate and β -D-mannuronate. Sodium alginate forms intermolecular linkages mediated by cations in aqueous medium. PEO chains form helical structures in water and interact through hydrogen bonding between polymer and water. Moderately substituted NaCMC molecules are joined by noncovalent linkages in a relatively concentrated solution and result in chain-bundles. Such junction formation between polymers should be related to their viscoelastic properties.

Aqueous solutions of extract from the root of *Abelmoschus manihot* and PEO exhibit type D spinnability as well as those of sodium alginate at low concentrations (19). On the other hand, type C spinnability is observed for aqueous solutions of sodium alginate at high concentrations and for NaCMC. The $\Delta L_0/\Delta v$ or reciprocal $L_{0,c}$ values always increase with increasing polymer concentration. The $\Delta L_0/\Delta v$ is the reciprocal deformation rate of a thread when the thread is broken, and it corresponds to the relaxation time. It can be interpreted that the relaxation time of aqueous PEO solutions increases with concentration (27). This is consistent with the concentration dependence of the $\Delta L_0/\Delta v$ values.

The $L_{0,c}$ value reflects the elastic modulus of the solution and may decrease with increasing modulus. The reciprocal $L_{0,c}$ and the dynamic modulus for aqueous sodium alginate solutions at high concentrations increase with concentration (18,19). It is found that the dynamic modulus of aqueous NaCMC solutions increases with increasing concentration (28). These results support the explanation described above.

Cryo transmission electron microscopic observation was carried out (29). Network images were observed for both sodium alginate and PEO solutions. The network is not homogeneous and the thick network domains segregate from the thin network domains, as seen in Figure 2f. The segregation produces a "super-network" structure. Then the characteristics of viscoelastic and spinnable solutions are due to the super-network structure based on the pseudonetwork formation.

It is suggested in many investigations that the high-order structure constructed by intermolecular interactions participates in the viscous property and the elastic response of polymer solutions. Parts of polymer chains form the linkages to constitute a junction zone. The network consists of junction zones and free residues of polymer chains. The junction-rich and free-residue-rich domains result in thick and thin networks, respectively. The segregated network domains form a supernetwork. Such three- dimensional network structures leads to viscoelastic behavior with long lifetime processes, where motions of networks relax with long relaxation times.

The difference between the type C and D spinnability may depend on life time, and the amount and strength of junctions among polymers. The type D spinnability appears for polymers with few or weak junction linkages, because the solution can easily deform and flow, allowing the stress to be dissipated. The type C spinnability is superior to polymers largely linked through the interaction, since the structure brings the elastic response. Thus the solution does not flow, and the stress is maintained.



Figure 4. Schematic representation of the variation of dynamic modulus against angular frequency. (a) Gel-like; (b)Maxwell-like, (c)polymer-like viscoelasticity. --- G''.

Conclusions

Some types of molecular assembly structures composed of surfactant molecules are formed in aqueous solutions of CnTASal and CnDAO. Such structures confer viscoelastic and spinnable properties on aqueous surfactant solutions. Then the spinnability depends on the strength of such structures or on the balance between the elasticity and the viscosity in which the structures result, with respect to the analogy of viscoelastic polymer solutions and of concentrated dispersions.

Three types of viscoelasticity illustrated in Figure 4 are observed in aqueous solutions of surfactants and polymers examined here. The storage modulus G' and the loss modulus G" in the gel-like viscoelasticity are almost independent of or slightly dependent on angular frequency ω . In the Maxwell-like viscoelasticity, the G' values increase at low frequencies and reach the plateau at high frequencies, while the G" values have a maximum. Both the G' and G" values in the polymer-like viscoelasticity increase with the initial slopes of 2 and 1, respectively, in a double logarithmic plot.

The types of viscoelasticity are listed in Table I for aqueous solutions of surfactants and polymers and compared with the types of spinnability and the assembly structures, which are drawn in Figures 1 and 2. The ductile failure spinnability can be connected with the Maxwell-like and the polymer-like viscoelasticity, and the cohesive fracture failure spinnability is connected with the gel-like viscoelasticity. The former is observed for entangled rodlike micelles in semidilute solutions and polymers with the super-network structure, and the latter is observed for linked rodlike micelles and lamellar layers.

Nakagawa (4) concluded that the relaxation time was comparable with the spinning time. This means that the spinnability depends on the dynamic relaxation of a solution. In fact, the spinnability for aqueous CnTASal solutions at 25 °C behaves similarly to the relaxation time, as seen in Figure 3. The relation of uniaxial elongation to the spinning process of the fiber was reported. When the Maxwell liquid is elongated at a constant velocity, the stress σ at the time t is described by

Table I. Rheological Characteristics and Assembly Structure of Aqueous Solutions of Surfactants and Polymers (14-21,23,24,29)

Solute	solvent	T, C 1	с, s 0-2gcm-3 п	pin- visco- nability elasticity	assembly structure
C ₁₄ TASal	water	25	0.8-3.2	D Maxwell+gel	linked short rodlike micelle
	water	25	10	C gel	linked short rodlike micelle
	1-4mMNaSal	25	1.6	D Maxwell	
	0.02-0.2MNaSal	25	1.6	D polymer	entangled rodlike micelle
	>0.3MNaSal	25	1.6	no no	small micelle
C14DAO 0.2MNaCl,Ca/C=0-1			5	D polymer	rodlike micelle
C ₁₆ DAO	water	20	1-3	C gel	platelike assembly lamellar layer
	water	35	1-3	D polymer	rodlike micelle
C ₁₈ DAO	water	25	0.5-3	C gel	platelike assembly lamellar layer
ODAO	water	25	0.45-6	D polymer	rodlike micelle
02.1.0	0-2MNaCl	25	0.9	D polymer	rodlike micelle
Abelmosch Manihot	us water	15-3	5 0.03-0.0	08 D	about of south -
PEO	water	15-2	5 6-12	D polymer	super-network
sodium alg	ginate water	25	1	D polymer	a langeringer B
.03	water	25	2-5	D polymer+gel	super-network
	water	25	7,10	C gel	
NaCMC	water	15-25	5 2-3	C gel	

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where B and C are constants (30). It is recognized that the stress reaches a maximum at the relaxation time τ . Therefore, with solutions exhibiting type D spinnability, the elongated thread is broken at the relaxation time τ . In the type C spinnability, where the elastic modulus is very strong, the maximum value of the stress is so high that the stress by the elongation is larger than the cohesion force of the thread, and the thread is pulled back elastically into the solution reservoir.

Acknowledgments

This article is dedicated to the memory of Yasuo Imae who died in July, 1993.

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