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ORIGINAL CONTRIBUTION

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Organogel from L-leucine-containing surfactant in nonpolar solvents

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Abstract Alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate formed organogel in nonpolar solvents. The gels exhibited thermally reversible sol–gel phase transitions. UV spectroscopic study suggested that dodecyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate forms reversed micelle-like aggregate at low concentration in a nonpolar solvent. Circular dichroism spectroscopy indicated that component molecules of the reversed micelle-like aggregate are cooperatively organized and result in chiral aggregate. The huge fibrous aggregate responsible for gelation was observed with transmission electron microscopy. The accumulation and rearrangement of reversed micelle-like aggregate resulted in the formation of huge fibrous aggregates. A gathering of numerous fibrous aggregates formed the three-dimensional network to immobilize the isotropic liquid.

Key words Gels – organogels – gelation – surfactant – amino acid

Introduction

It is known that aggregation of surfactant in nonpolar solvents containing a trace amount of water sometimes results in the formation of reversed micelles, in which the polar head groups form the interior water pool while the hydrophobic hydrocarbon moieties of surfactants are in contact with the apolar solvent [1]. However, even if reversed micellar aggregate is formed in nonpolar solvents, the solution is rarely transformed into physical gel. Recently, physical gels by low molecular weight compounds are of special interest for potential applications, e.g. environmentally as hardeners of spilled solvents or medically as drug-delivery systems. Although the reported low molecular weight gelators are frequently seemed to be nonionic surfactants [2–11], the gelation of dilute binary solutions of these gelators in nonaqueous solvents, to our knowledge, have never been discussed in connection with the formation of reversed micelle, except for the DMSO gel of sodium *bis*(2-ethylhexyl)sulfosuccinate in the presence of phenol [12]. It should be mentioned that hydrocarbon gels consisting of 99% of a hydrocarbon and small amounts of water and surfactant, ternary systems, are known and discussed from the standpoint of O/W microemulsion [13, 14]. Recently we encountered the unexpected gelation of nonpolar solvents in the presence of a small amount of alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate (from 0.2% to 3% by weight), which was derived from L-leucine. In this article we report on the gelation of nonpolar solvents by L-leucine-containing cationic surfactants. The striking characteristics of the present gel phenomenon is the fact that a small amount of alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate can cause physical gelation of nonpolar solvents.

Experimental

Materials

*Dodecyl (S)-2-ammonium-2-isobutylacetate p-toluenesulfonate (**7-L**)*

A mixture of 6.56 g (0.050 mmol) of L-leucine, 18.64 g (0.10 mol) of 1-dodecanol, and 11.40 g (0.060 mol) of

p-toluenesulfonic acid monohydrate in 120 ml of benzene was refluxed overnight by using a continuous Dean–Stark water separator. The resulting solution was evaporated and the residue was recrystallized from cyclohexane, followed by acetone to yield 19.78 g (84%) of dodecyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate. Elemental analysis: calculated for $C_{25}H_{45}NO_5S$, C 63.66, H 9.62, N 2.97; found, C 64.04, H 9.59, N 2.88.

Other alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate (**1–12**) were prepared from corresponding alcohols by a procedure similar to the one described above in the yield of 72–91%.

*Dodecyl (S)-2-ammonium-2-isopropylacetate p-toluenesulfonate (**13**)*

This compound was prepared from a mixture of 5.86 g (0.050 mmol) of L-valine, 27.95 g (0.15 mol) of 1-dodecanol, and 11.40 g (0.060 mol) of *p*-toluenesulfonic acid monohydrate in 100 ml of benzene by a procedure similar to the one described for **7-L**. The resulting solution was evaporated and the residue was recrystallized from hexane to yield 22.00 g (92%) of dodecyl (*S*)-2-ammonium-2-isopropylacetate *p*-toluenesulfonate. Elemental analysis: calculated for $C_{24}H_{43}NO_5S$, C 62.98, H 9.47, N 3.06; found, C 62.79, H 9.50, N 2.99.

*Dodecyl (S)-2-ammonium-2-(1-methylpropyl)acetate p-toluenesulfonate (**14**)*

This compound was prepared from a mixture of 3.30 g (0.025 mmol) of L-isoleucine, 9.32 g (0.050 mol) of 1-dodecanol, and 5.70 g (0.030 mol) of *p*-toluenesulfonic acid monohydrate in 100 ml of benzene by a procedure similar to the one described for **7-L**. The resulting solution was evaporated and the residue was recrystallized from hexane to yield 6.78 g (55%) of dodecyl (*S*)-2-ammonium-2-(1-methylpropyl)acetate *p*-toluenesulfonate. Elemental analysis: calculated for $C_{25}H_{45}NO_5S$, C 63.66, H 9.62, N 2.97; found, C 63.51, H 9.44, N 2.96.

*Dodecyl (S)-2-ammonium-2-benzylacetate p-toluenesulfonate (**15**)*

The refluxing of a mixture of 4.13 g (0.025 mmol) of L-phenylalanine, 13.98 g (0.075 mol) of 1-dodecanol, and 5.70 g (0.030 mol) of *p*-toluenesulfonic acid monohydrate in 100 ml of benzene by using a continuous Dean–Stark water separator gave dodecyl (*S*)-2-ammonium-2-benzylacetate *p*-toluenesulfonate. Recrystallization from hexane yielded 11.06 g (88%). Elemental analysis: calculated for $C_{28}H_{43}NO_5S$, C 66.50, H 8.57, N 2.77; found, C 66.63, H 8.39, N 2.91.

*Dodecyl (S)-2-ammonium-2-(2-dodecyloxycarbonylethyl) acetate p-toluenesulfonate (**16**)*

This compound was prepared from a mixture of 3.68 g (0.025 mmol) of L-glutamic acid, 18.60 g (0.10 mol) of 1-dodecanol, and 5.70 g (0.030 mol) of *p*-toluenesulfonic acid monohydrate in 100 ml of benzene by the similar procedure described for **7-L**. The resulting solution was evaporated and the residue was recrystallized from hexane to yield 15.00 g (91%) of dodecyl (*S*)-2-ammonium-2-(2-dodecyloxycarbonylethyl)-acetate *p*-toluenesulfonate. Elemental analysis: calculated for $C_{36}H_{65}NO_7S$, C 65.92, H 9.99, N 2.14; found, C 66.37, H 10.01, N 2.00.

*Dodecyl (S)-2-ammonium-2-isobutylacetate benzenesulfonate (**17**)*

This compound was prepared from a mixture of 1.31 g (0.010 mmol) of L-leucine, 3.73 g (0.10 mol) of 1-dodecanol, and 2.11 g (0.012 mol) of benzenesulfonic acid monohydrate in 100 ml of benzene by the similar procedure described for **7-L**. Recrystallized from cyclohexane yielded 4.43 g (97%) of dodecyl (*S*)-2-ammonium-2-isobutylacetate benzenesulfonate. Elemental analysis: calculated for $C_{24}H_{43}NO_5S$, C 62.99, H 9.47, N 3.06; found, C 62.61, H 9.77, N 2.78.

*Dodecyl (S)-2-ammonium-2-isobutylacetate benzoate (**18**)*

A solution of 1.00 g (2.12 mmol) of **7-L** in 30 ml of chloroform was treated with 10 ml of aqueous solution containing 0.225 g (2.12 mmol) of Na_2CO_3 in separatory funnel. The chloroform layer was washed with water, dried with $MgSO_4$, and evaporated. The residue was dissolved in 10 ml of acetone and then 0.27 g (2.12 mmol) of benzoic acid was added. The resulting solution was evaporated and recrystallized from a mixed solvent of acetone and hexane to yield 0.45 g (51%) of dodecyl (*S*)-2-ammonium-2-isobutylacetate benzoate. Elemental analysis: calculated for $C_{25}H_{43}NO_4$, C 71.22, H 10.28, N 3.32; found, C 71.06, H 10.57, N 3.34.

*Dodecyl (S)-2-ammonium-2-isobutylacetate 4-methylbenzoate (**19**)*

This compound was prepared from 2.00 g (4.24 mmol) of **7-L**, 0.45 g (4.24 mmol) of Na_2CO_3, and 0.577 g (4.24 mmol) of 4-methylbenzoic acid by a method similar to the one described for **18**. The resulting solution was evaporated and recrystallized from a mixed solvent of

acetone and hexane to yield 0.45 g (24%) of dodecyl (*S*)-2-ammonium-2-isobutylacetate 4-methylbenzoate. Elemental analysis: calculated for $C_{26}H_{45}NO_4$, C 71.68, H 10.41, N 3.22; found, C 71.99, H 10.81, N 3.04.

*Dodecyl (S)-2-ammonium-2-isobutylacetate chloride (**20**)*

A solution of 2.00 g (4.24 mmol) of **7-L** in 50 ml of chloroform was treated with 20 ml of aqueous solution containing 0.45 g (4.24 mmol) of Na_2CO_3 in separatory funnel. The chloroform layer was washed with water, dried with $MgSO_4$, and evaporated. The residue was dissolved in 20 ml of acetone and then 0.35 ml (4.24 mmol) of 12 M HCl was added. The resulting solution was cooled to give 1.20 g (85%) of dodecyl (*S*)-2-ammonium-2-isobutylacetate chloride. Elemental analysis: calculated for $C_{18}H_{38}NO_2Cl$, C 64.35, H 11.40, N 4.17; found, C 64.24, H 11.42, N 4.16.

Method

Organic liquids used for gelation testing were hexane, cyclohexane, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, ethyl acetate, acetone, 2-butanone, cyclohexanone, chloroform, tetrachloromethane, tetrahydrofuran, 1,4-dioxane, pyridine, benzene, toluene, chlorobenzene, nitrobenzene, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, dimethyl sulfoxide, kerosene, light oil, heavy oil, silicone oil, salad oil, and soybean oil. A typical procedure for gelation testing is as follows: a weighed sample was mixed with an organic liquid (2 ml) in a test tube with screw cap (inside diameter; 14 mm) and the mixture was heated until the solid was dissolved. The resulting solution was cooled at 25 °C for 2 h and then the gelation was checked visually. When upon inversion there was no fluid running down the walls of the tube, we judged it "gel". When the samples caused gelation, we evaluated quantitatively the gelation ability by critical gel concentrations (cgc) which are the minimum concentrations of gelling materials necessary for gelation at 25 °C. The unit of cgc is $g\,l^{-1}$ (gelator/liquid).

Sample preparation for transmission electron microscopy

For transmission electron microscope (TEM), surfactant **12** was dissolved in hexane at the cgc (2 $g\,l^{-1}$) and a droplet of the gel was put on a collodion-and carbon-coated grid (copper, 400 mesh). The solvent was removed off by keeping at room temperature for 2 h, followed by pumping in vacuo overnight. To negatively stain, the sample was exposed to vapor of osmium tetroxide (2 wt% methanol solution) for 10 h.

Table 1 Gelation test of surfactant **7-L** in various solvents and critical gel concentrations at 25 °C[a)]

Solvent	Aspect
Hexane	16
Octane	5
Decane	2
Dodecane	1
Cyclohexane	Crystallization
Methanol	Solution
Ethanol	Solution
1-Propanol	Solution
2-Propanol	Solution
1-Butanol	Solution
Ethyl acetate	Crystallization
Acetone	Crystallization
2-Butanone	Solution
Cyclohexanone	Solution
Chloroform	Solution
Tetrachloromethane	Solution
Tetrahydrofuran	Solution
1,4-Dioxane	Solution
Pyridine	Solution
Benzene	Solution
Toluene	Solution
Chlorobenzene	Solution
Nitrobenzene	Solution
N,*N*-dimethylformamide	Solution
N,*N*-dimethylacetamide	Solution
Dimethyl sulfoxide	Solution
Kerosene	8
Light oil	9
Heavy oil	Gel-like
Silicone oil	2
Salad oil	8
Soybean oil	3

[a)] Values mean the critical gel concentration, whose unit is $g\,l^{-1}$ (surfactant/solvent).

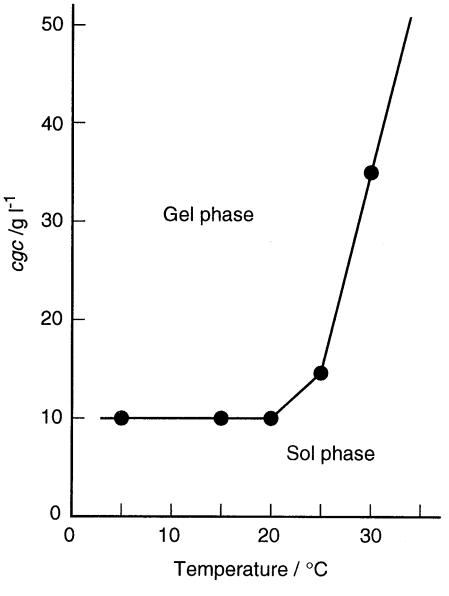
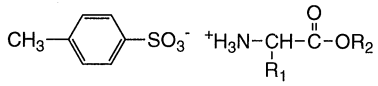


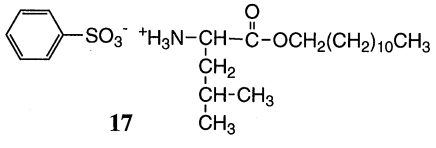
Fig. 1 Sol–gel phase diagram; the cgc of **7-L** vs. temperature in hexane

Scheme



1-16

	Starting material	R_1	R_2
1	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_4CH_2$
2	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_6CH_2$
3	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_7CH_2$
4	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_8CH_2$
5	L-leucine	$(CH_3)_2CHCH_2$	$(CH_3)_2CHCH_2CH_2CH_2CH(CH_3)CH_2CH_2$
6	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_9CH_2$
7-L	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{10}CH_2$
7-D	D-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{10}CH_2$
8	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{11}CH_2$
9	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{12}CH_2$
10	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{13}CH_2$
11	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{14}CH_2$
12	L-leucine	$(CH_3)_2CHCH_2$	$CH_3(CH_2)_{16}CH_2$
13	L-valine	$(CH_3)_2CH$	$CH_3(CH_2)_{10}CH_2$
14	L-isoleucine	$CH_3CH_2CH(CH_3)$	$CH_3(CH_2)_{10}CH_2$
15	L-phenylalanine	$PhCH_2$	$CH_3(CH_2)_{10}CH_2$
16	L-glutamic acid	$CH_3(CH_2)_{10}CH_2OCOCH_2CH_2$	$CH_3(CH_2)_{10}CH_2$



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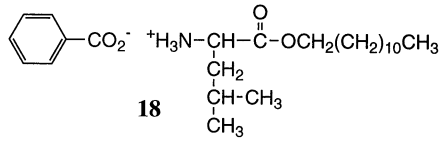

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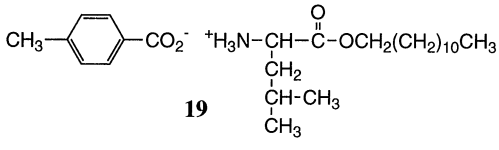

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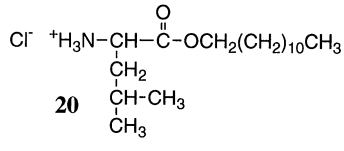

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Results and discussion

Formation of physical gel

Results for gelation test with surfactant **7-L** in various solvents are summarized in Table 1. Transparent physical gels were formed when a mixture of **7-L** and nonpolar solvents were heated to form a homogeneous fluid and then allowed to cool at 25 °C. The surfactant **7-L** was able to gel with hexane, octane, decane, dodecane, kerosene, light oil, silicone oil, salad oil, and soybean oil; all the gels exhibited thermally reversible sol–gel phase transition. In Fig. 1 the cgc of **7-L** necessary for gelation of hexane is

plotted vs. temperature. The phase above curve is the gel phase whereas the phase below curve is the sol. The sol–gel process depends on temperature, since the cgc increases with increasing the tempereature. At temperature above 35 °C, the gelation of hexane does not occur even by a large amount of **7-L**. The cgc of **7-L**, the amounts necessary to harden 1000 ml of liquid, are 16 g for hexane, 5 g for octane, 2 g for decane, 1 g for dodecane, 8 g for kerosene, 9 g for light oil, 2 g for silicone oil, 8 g for salad oil, and 3 g for soybean oil.

Structurally resembled surfactants, **1–20**, were prepared and the gelling ability was studied. Results of gelation test in hexane are summarized in Table 2. With respect to the *p*-toluenesulfonic acid salt leucine-containing surfactants (**1–12**), gel was not formed when the alkyl chain is shorter than 10 (surfactant **4**) to 8 carbons (surfactant **3**). This means that the hydrophobicity of the alkyl chains play an important role in the gelation. The cgc values of alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate (**4**, **6–12**) are plotted against carbon number of their alkyl chain R_2 (Fig. 2). It is clear that the cgc values against silicone oil is almost constant; on the contrary, those against hexane depend on alkyl chain length. The cgc in hexane seems to follow irregularly odd–even rule. It should be mentioned that **7-DL** prepared from a racemate D, L-leucine did not exhibit gel-forming ability, though dodecyl (*R*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate (**7-D**) from D-leucine revealed the same gel behavior as compared to **7-L**. The surfactants **13–16**, which have L-valine, L-isoleucine, L-phenylalanine, and L-glutamic acid residue, resulted in crystallization, but not gelation.

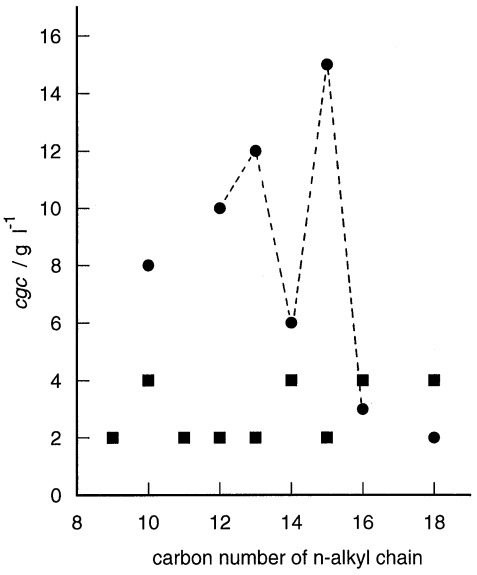

Fig. 2 Plot of cgc against carbon number of alkyl chain (R_1) (●) in hexane, (■) in silicone oil

Table 2 Gelation test of surfactants **1–20** in hexane at 25 °C

Surfactant	Aspect
1	Crystallization
2	Crystallization
3	Crystallization
4	Gelation
5	Crystallization
6	Crystallization
7-L	Gelation
7-D	Gelation
7-DL	Crystallization
8	Gelation
9	Gelation
10	Gelation
11	Gelation
12	Gelation
13	Crystallization
14	Crystallization
15	Crystallization
16	Crystallization
17	Gelation
18	Crystallization
19	Crystallization
20	Crystallization

The counter acid of surfactants also influences gelation. The benzoic acid salt (**18**), 4-methylbenzoic acid salt (**19**), and hydrochloric acid salt (**20**) of dodecyl (*S*)-2-ammonium-2-isobutylacetate have no gelling ability, while the benzenesulfonic acid salt (**17**) possesses the ability similar to *p*-toluenesulfonic acid salt (**7-L**). At the present time, we have not determined why **7-L** containing L-leucine gels with nonpolar solvents while the surfactants **13–16** do not, why the salts of arylsulfonic acids cause gelation while those of arylcarboxylic acids and hydrogen chloride do not. A reasonable hypothesis is that the steric bulkiness of isobutyl group in **7-L** is casually preferable to the formation of C–H $\cdots\pi$ interaction for molecular aggregate and the difference in the acidity of the acids may take part in building up aggregate through electrostatic interaction (Fig. 4).

Molecular aggregation in nonpolar solvent

It is reasonable to assume that surfactant **7-L** forms reversed micelle-like aggregate in nonpolar solvents. If reversed micelle-like aggregate should be formed, a change in emission spectra from toluenesulfonate lumophores of **7-L** would be observed. On this assumption, we studied molecular aggregation behavior of **7-L** in hexane. Emission spectrum of the solution of **7-L** at 5.0×10^{-6} M, excited at

265 nm, exhibited λ_{max}302 nm attributed to the fluorescence of monomeric **7-L**. At the concentration of 1.0×10^{-5} M, a new peak appeared at 288 nm in addition to the peak of λ_{max}302 nm. The new peak at 288 nm indicates that **7-L** formed molecular aggregate and the toluenesulfonate lumophores of **7-L** located in the more apolar microenvironment. The peak of λ_{max}302 nm almost disappeared in the large peak of λ_{max}288 nm at the concentration of 5.0×10^{-5} M. From the emission spectroscopic observation we concluded that **7-L** forms reversed micelle-like aggregate in hexane and the critical concentration for aggregation is ca. 1.0×10^{-5} M. Considering the fact that the cgc of **7-L** necessary to harden 1000 ml of hexane was 16 g (3.4×10^{-2} M), it is assumed that the smallest aggregate units, reversed micelle-like aggregate, interact with each other through noncovalent interaction and grow up the huge aggregate responsible for gelation. It can be said that the preferable steric bulkiness of isobutyl group in **7-L** is at least one of the essential factors for gelation, because the surfactants **13–16**, which are L-valine, L-isoleucine, L-phenylalanine, and L-glutamic acid derivatives can form reversed micelle-like aggregates in nonpolar solvents like **7-L**, but not gels.

From CD spectroscopic results

A regular π–π stacking of toluenesulfonate moieties was detected by circular dichroism (CD) spectroscopic measurements. The CD spectra of gel (10 mM) for **7-L** and **7-D** in hexane are shown in Fig. 3. The CD spectrum for gel of **7-L** at 0 °C exhibited a markedly strong peak for toluenesulfonate chromophore: $[\theta]_{205} = +1.68 \times 10^5$ cm^2 dmol^{-1}. The corresponding value for **7-D** is $[\theta]_{205} = -1.51 \times 10^5$ cm^2 dmol^{-1}. These strong peaks decreased with increasing temperature and almost disappeared at 45 °C as the gel was transformed to sol. The disappearance of the CD signal in the sol led us to conclude that the strong induced CD band originates from a chiral structure of gel-aggregate, but not from a chiral conformation of **7-L** itself. Since such a much-enhanced CD is derived from exciton coupling among the organized chromophore [15], it is thought that the molecules of **7-L** or **7-D** in gels are cooperatively stacked helically with the toluenesulfonate chromophores regularly orienting one

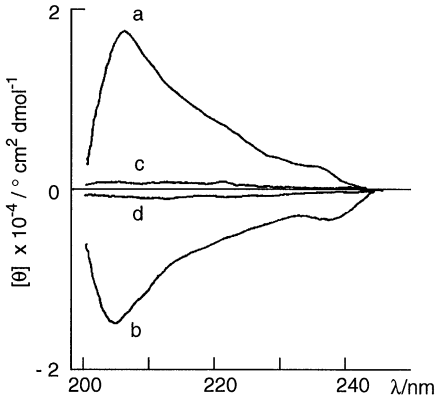

Fig. 3 CD spectra of **7-L** and **7-D** in hexane, (a) gel of **7-L** at 0 °C, (b) gel of **7-D** at 0 °C, (c) sol of **7-L** at 45 °C, (d) sol of **7-D** at 45 °C

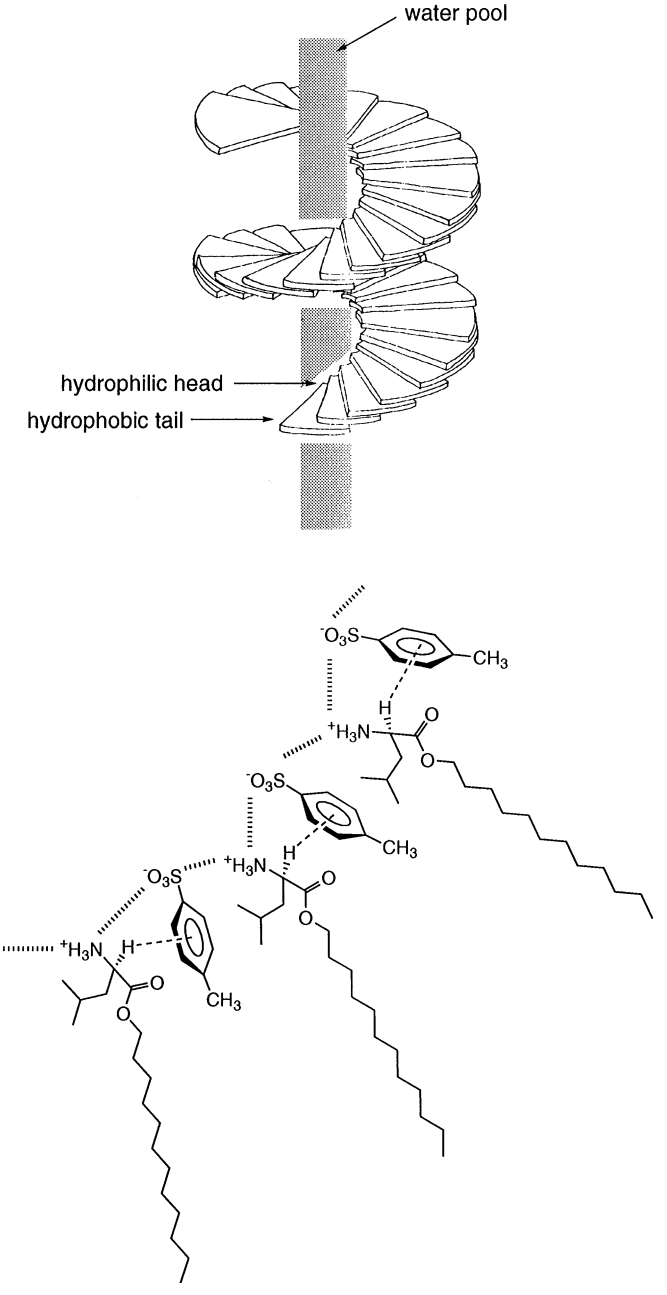

Fig. 4 A possible stacking model for CD-active aggregate

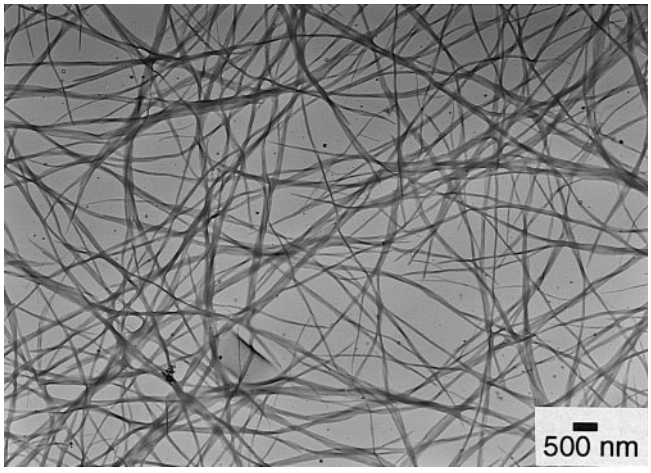

Fig. 5 Transmission electron micrograph for hexane gel of **12**. Magnification: ×6000

another. A possible stacking model of **7-L**, as one would expect from CD spectroscopic results, is illustrated in Fig. 4. The molecules of **7-L** or **7-D** turn the polar head group to the inside of rod-like aggregate, where a trace amount of water in solvent forms water pool, and may be stacking by repetition of helical twist. In fact, the water content in hexane and silicone oil was found by the Karl-Fisher's method to be 48 $mg\,l^{-1}$ and 114 $mg\,l^{-1}$, respectively. However, the helicence, right-handed or left-handed, is unclear at this time.

Transmission electron microscopic observation

When gels are formed by low molecular compounds, images of aggregates can be observed with electron microscope [3, 4, 8–11]; because self-aggregation of molecules is indispensible for physical gelation at least. The TEM of gel formed by **12** in hexane, negatively stained by osmic acid, is shown in Fig. 5. The image in Fig. 5 shows many juxtaposed fibrous aggregates whose diameters are ca. 20–200 nm. As yet, helical aggregates, as expected from CD spectroscopic results, are not observed with TEM. This suggests that the fibrous aggregate observed in the TEM does not represent the virtual CD-active helical unit illustrated in Fig. 4. Considering the fact that the width of the fibrous aggregates in the TEM (20–200 nm) are considerably large compared to the molecular length of **12** (ca. 4 nm) estimated from space-filling molecular model, the huge fibrous aggregates in the TEM seem to be built up via the process of accumulation and rearrangement of reversed micelle-like aggregate as the smallest units. It can be assumed that a gathering of numerous fibrous aggregates observed in Fig. 5 forms the three-dimensional network to immobilize the isotropic liquid, and finally causes physical gelation.

Conclusions

Alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate, having alkyl chain length more than 10 carbons, can gel with various saturated hydrocarbons, mineral oils, and edible oils at the low concentrations (from 0.2% to 3% by weight). The gelation behavior is limited to L-leucine-containing salts, and gel is not formed when L-leucine is replaced by D, L-leucine, L-valine, L-isoleucine, L-phenylalanine, and L-glutamic acid. The formed gels are transparent and the transition between the gel phase and the isotropic fluid is thermally reversible. Alkyl (*S*)-2-ammonium-2-isobutylacetate *p*-toluenesulfonate form the reversed micelle-like aggregate in hexane at very low concentrations. CD spectra suggest that the molecules in gel are cooperatively stacked helically with the toluenesulfonate chromophores regularly orienting one another. The image of many juxtaposed fibrous aggregates responsible for gelation is observed with TEM.

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