

Spontaneous Formation of Gel Emulsions in Organic Solvents and Commercial Fuels Induced by a Novel Class of Amino Acid Derivatized Surfactants

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A novel class of amphiphiles, sodium *N*-(*n*-dodecyl-2-aminoethanoyl)-L-amino acidate, have been synthesized. These amphiphiles have been shown to form oil-in-water-type gel emulsions with a high internal-phase ratio in organic solvents as well as in commercial fuels simply by agitation. No heating and cooling cycle was required for the formation of gels. The amphiphiles also showed efficient phase-selective gelation in the presence of excess water. The minimum gelator concentrations for the amphiphiles in the solvents employed have been determined. The effects of the chain length of the hydrocarbon tail and the chirality of a representative amphiphile on its ability to promote gelation in a given organic solvent have been investigated. Also, the effect of acid and alkali on the gelation has been examined. The optical microscopic picture of the gel emulsion showed foamlike structures with oil compartments separated by the continuous aqueous phase. The mechanism of the formation of gel emulsions has been discussed.

Introduction

Low-molecular-mass organic gelators (LMOGs) have recently attracted tremendous attention because of their unique features and potential applications in the industry.¹ Therefore, the synthesis and properties of many LMOGs have been reported in the literature.² In fact, the discovery of almost all the LMOGs was accidental rather than design.³ These organogelators create three-dimensional network structures through self-association. The driving forces for gelation are (i) intermolecular hydrogen-bonding interactions that facilitate the formation of large aggregates and (ii) van der Waals interactions (e.g., π stacking and solvophobic effect) that bring the large aggregates close to each other. Since many aspects of gelation by LMOGs are poorly understood, the control of gelation phenomena induced by LMOGs and the design of new organic gelators are challenging works. Therefore, this may lead to an area of fascinating organic materials. Recently, Bhattacharya et al. have reported that *N*-lauroyl-L-alanine and related amphiphilic molecules act

as phase-selective gelators of oil/water mixtures.⁴ The gelation of hydrocarbon solvents has been attributed to intermolecular amide hydrogen bonding between amphiphilic molecules. The phase-selective gelation was achieved only by heating and cooling cycles of the mixture. In fact, most of these organic gelators need heating and cooling cycles to form gels. However, it should be noted that the heating process is a major disadvantage for many industrial applications of organogelators.

The formation of gel-like supermolecular structures can also occur in dilute solutions of surfactants.^{5–7} Surface-active, amphiphilic molecules, under suitable conditions, tend to assemble into large aggregates that may be connected to form network structures. Amphiphilic molecules can also form two-dimensional network structures at the air/water interface or at the interface of two immiscible liquids.^{8–10} Because of their ability to stabilize interfaces, surfactants have been used as emulsifiers, dispersing agents, and also as foam-forming additives. It has been found that some amphiphilic molecules strongly stabilize emulsions to form viscous gel-like materials in organic solvents.^{11–16} Under certain conditions, the highly

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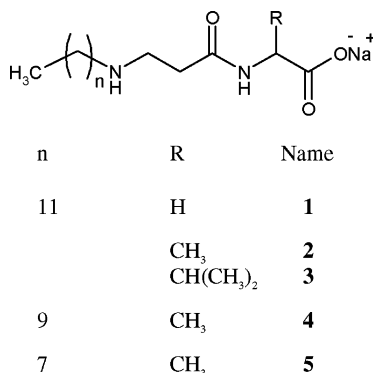


Figure 1. Chemical structures of amphiphiles 1–5.

concentrated emulsions are formed in either water-rich or oil-rich regions.^{11,12} The concentrated emulsions are called high-internal-phase-ratio (HIPR) emulsions. The HIPR emulsions contain more than 70% (v/v) of the internal phase. Because of the high viscosity and translucence characteristics, these are often called gel emulsions. The gel emulsions have found practical applications in cosmetics, aviation fuels, and emulsion explosives.^{17–19} It has been found that water-in-oil-type gel emulsions are spontaneously formed from oil-in-water (O/W) microemulsions or micellar solutions in a water/polyoxyethylene alkyl ether/oil system simply by heating the mixture.²⁰ It has been implicated in the studies reported in the literature that it is difficult to form gel emulsions by a simple agitation method,²¹ although researchers have been able to form HIPR emulsions by adding the dispersed phase gradually or mixing the system with glass balls or textile fabrics to enhance the local agitation.¹²

In the present work, we have synthesized a series of chiral amino acid derivatized surfactants, 1–5 (see Figure 1 for their molecular structures). These amphiphiles have several hydrogen-bonding sites and a hydrocarbon tail and are expected to act as potential gelators for organic solvents. Therefore, we have investigated their gelation properties in organic solvents and commercial fuels. The effect of hydrocarbon chain length on the gelation behavior has been studied. We have also examined the effect of chirality on the gelation properties.

Experimental Section

Materials. All amino acids and alkylamines were obtained from SRL and used directly from the bottles. Acryloyl chloride (Aldrich) was used as received. Other reagents were all analytical grade and obtained locally. The solvents used in this work were all analytical grade (Merck) and were used without further purification. The commercial liquid kerosene and petrol were purchased from a local market.

Synthesis. *N*-(*n*-dodecyl-2-aminoethanoyl)-L-alaninate (**2**) was synthesized by Michael addition reaction of *n*-dodecylamine with 1 mol equiv of sodium *N*-acryloyl-L-alaninate in superdry methanol. The reaction mixture was stirred in the dark under nitrogen atmosphere for 72 h. After evaporation of the solvent, the excess amine was removed by washing with acetone. Isolated solid was recrystallized from the acetone/ethanol mixture (yield 93%).

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To prepare *N*-acryloyl-L-alaninate, L-alanine (1.46 g) was dissolved in 50 mL of a water/ethanol (8:2) mixture containing 1.05 g of NaHCO₃ and cooled to 5 °C. Acryloyl chloride (1.1 equiv) was then added in drops while maintaining the pH at around 9.0 by adding dilute NaOH solution. The reaction mixture was stirred for 2 h at room temperature. After evaporation of the organic solvent, the solution was acidified with 0.1 N HCl and the compound was extracted with ethyl acetate. It was isolated as a solid. Yield 74%; mp 130–135 °C. [α]_D²⁵ (c = 1 in methanol) = −63.0°. IR (KBr, cm^{−1}): 3313, 1737, 1652, 1603. ¹H NMR (200 MHz, CD₃OD) δ: 6.38 (dd, 1H), 6.24 (dd, 1H), 5.68 (dd, 1H), 4.47 (q, 1H), 1.43 (d, 3H). The corresponding sodium salt was prepared by stirring the compound with an equivalent amount of sodium methoxide in superdry methanol at 0–5 °C for 4 h. The solvent was evaporated, and the solid was purified by recrystallization from the acetone/ethanol mixture.

The other amphiphiles were prepared and identified in the same way as described above from the corresponding alkylamine and sodium *N*-acrylamidoamino acidate.

Amphiphile 1. mp 174–176 °C. IR (KBr, cm^{−1}): 1673, 1471, 1401. ¹H NMR (200 MHz, D₂O) δ: 3.66 (s, 2H), 2.85 (t, 2H), 2.55 (t, 2H), 2.5 (t, 2H), 1.19 (m, 18H), 0.78 (t, 3H). Elemental analysis (C₁₇H₃₃N₂O₃Na·2H₂O). Calcd: C, 54.82; H, 10.01; N, 7.52. Found: C, 52.19; H, 10.31; N, 7.06.

Amphiphile 2. mp 182–184 °C. [α]_D²⁵ (H₂O, 1%): −17°. IR (KBr, cm^{−1}): 1651, 1459, 1408. ¹H NMR (200 MHz, D₂O) δ: 4.06 (q, 1H), 2.89 (t, 2H), 2.67 (t, 2H), 2.47 (t, 2H), 1.25 (d, 3H), 1.21 (m, 18H), 0.77 (t, 3H). Elemental analysis (C₁₈H₃₅N₂O₃Na·2H₂O). Calcd: C, 55.9; H, 10.2; N, 7.25. Found: C, 59.32; H, 9.67; N, 7.45.

Amphiphile 3. mp 68–70 °C. [α]_D²⁵ (H₂O, 1%): −6.32°. IR (KBr, cm^{−1}): 1647, 1462, 1404. ¹H NMR (200 MHz, D₂O) δ: 3.9 (d, 1H), 2.67 (t, 2H), 2.37 (t, 2H), 2.22 (t, 2H), 1.96 (m, 1H), 1.04 (m, 18H), 0.64 (dd, 6H), 0.59 (t, 3H). Elemental analysis (C₂₀H₃₉N₂O₃Na·2H₂O). Calcd: C, 57.94; H, 10.45; N, 6.76. Found: C, 57.3; H, 10.81; N, 6.76.

Amphiphile 4. mp 156–160 °C. [α]_D²⁵ (H₂O, 1%): −13.5°. IR (KBr, cm^{−1}): 1651, 1463, 1406. ¹H NMR (200 MHz, D₂O) δ: 3.9 (q, 1H), 2.93 (t, 2H), 2.66 (t, 2H), 2.59 (t, 2H), 1.1 (d, 3H), 1.08 (m, 14H), 0.62 (t, 3H). Elemental analysis (C₁₆H₃₁N₂O₃Na·2H₂O). Calcd: C, 53.61; H, 9.84; N, 7.81. Found: C, 53.88; H, 9.59; N, 7.91.

Amphiphile 5. mp 170–176 °C. [α]_D²⁵ (H₂O, 1%): −14.8°. IR (KBr, cm^{−1}): 1651, 1460, 1398. ¹H NMR (200 MHz, D₂O) δ: 3.9 (q, 1H), 3.07 (t, 2H), 2.8 (t, 2H), 2.47 (t, 2H), 1.1 (d, 3H), 1.05 (m, 10H), 0.61 (t, 3H).

Methods. ¹H NMR spectra were recorded on a Bruker SEM 200 instrument in CD₃OD/D₂O solvents. The IR spectra of solid samples were recorded with a Perkin-Elmer model 883 IR spectrometer using KBr as solvent. The optical rotation was measured with a Jasco P-1020 digital polarimeter. Melting points were determined with an Instind (Kolkata) melting point apparatus in open capillaries. The elemental analysis was carried out with a Perkin-Elmer 2400 Series II CHNS/O analyzer. The pH measurements were done with a Thermo Orion model 710A+ digital pH meter. For light micrographs, a drop of the appropriate solution was placed on a thoroughly cleaned glass plate and covered with a cover slip. The light micrographs were obtained from a Leica-DMRXP microscope. The images taken by a video camera were analyzed by Leica Qwin software.

Results and Discussion

Spontaneous Formation of Gel Emulsions. In the course of our studies on the gelation behavior of chiral *N*-acylamino acid amphiphiles, we accidentally discovered that sodium *N*-(*n*-dodecyl-2-aminoethanoyl)-L-alaninate (**2**) forms a highly viscous, semisolid mixture with hydrocarbon solvents in the presence of a small amount of water. The solidification took place just by gentle agitation of the mixture at room temperature. However, in the absence of water, neither agitation nor heating and cooling cycles induced gelation in hydrocarbon solvents. The amphiphile was also observed to solidify mineral oils, for example, commercial kerosene and petrol in the

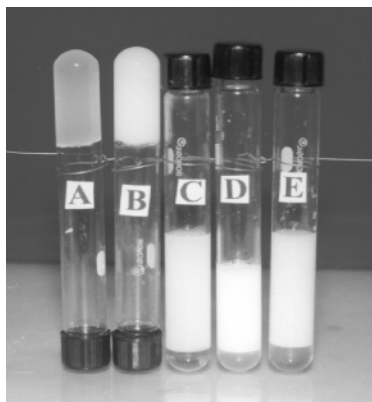


Figure 2. Test tubes containing gels: (A) *n*-heptane; (B) toluene; (C) *n*-heptane; (D) toluene; (E) petrol.

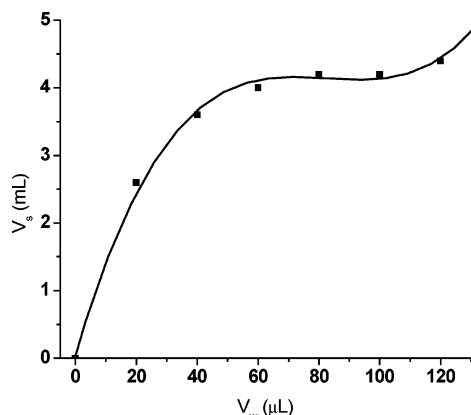


Figure 3. Plot of the volume of petroleum ether (V_s , milliliters) gelled as a function of the volume of water (V_w , milliliters).

presence of water. The semisolid mixtures formed in aliphatic hydrocarbon solvents are translucent, whereas those formed in aromatic and chlorinated hydrocarbon solvents are milky. In the presence of excess water, however, the gels in aliphatic hydrocarbon solvents also look milky. The solidification of the organic solvents induced by **2** was tested by the “stable to inversion of the test tube” method (see test tubes A and B in Figure 2). In a typical test, 0.3 mg of the amphiphile was first dissolved in a small amount (50 μL) of Milli-Q water and then the solvent was added gradually in steps of 100 μL by the use of a micropipet with gentle agitation of the mixture. However, addition of excess fuel results in breakdown of the gel completely to produce a clear solution of W/O microemulsion. The maximum volume of solvent gelled by a given amount of the amphiphile also depends on the amount of water. As can be seen in Figure 3, the volume of petroleum ether gelled increases with the increase of the volume of water and reaches a maximum at $\sim 95\%$ (v/v).

In hydrocarbon solvents including commercial fuels, the gels remained unchanged for several weeks to months. However, in chlorinated solvents, gels broke into a clear solution of microemulsion after a week or two. The gels do not break upon mechanical agitation and are thermostable. Unlike normal gels, no sharp melting point of the gels upon heating was observed. (The melting point was tested by putting an iron ball on the gel in a test tube placed in a water bath.) The gels completely broke to produce a clear solution when heated at a temperature above 70 $^{\circ}\text{C}$. However, no gelation of the solution took place upon cooling to room temperature or upon agitation.

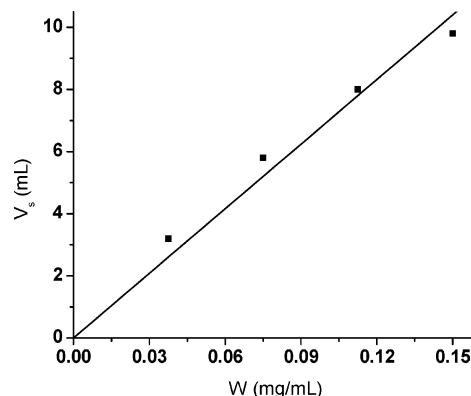


Figure 4. Plot of the volume of petroleum ether (V_s , milliliters) gelled as a function of the quantity (W , milligrams/milliliter) of **2**.

Table 1. Volume of *n*-Hexane Solvent Gelled by an Equimolar (0.78 μM) Quantity of Amphiphiles 1–5

solvent	V_s (mL)				
	1	2	3	4	5
<i>n</i> -hexane	2.2	2.4	2.8	2.2	1.5

The formation of gel was also found with amphiphile **3**, which has L-valine as its headgroup. To examine if chirality has any influence on the gelation mechanism, the achiral glycine derivative **1** was synthesized and gelation was studied. Amphiphile **1** also showed similar behavior. However, the maximum volumes of *n*-hexane solvent gelled by an equimolar (0.78 μmol) amount of each of the amphiphiles in the presence of 100 μL of water are different (see Table 1). To further examine the effect of chain length, we have performed the same studies with compounds **4** and **5**, which have hydrocarbon tail lengths shorter than that of **2**. The data in Table 1 suggest that the volume of solvent gelled by **4** is less than that of **2** and more than that of **5**. That is, the volume of *n*-hexane solvent that is dispersed in the gel decreases with the decrease in chain length of the hydrocarbon tail of the amphiphile. The order of the volumes of *n*-hexane for **1**, **2**, and **3** suggests that the volume of solvent gelled increases with the increase of hydrophobicity of the surfactant headgroup.

Phase-Selective Gelation. The phase-selective gelation of organic solvent is very important in view of its applications in oil extraction, disposal of crude oil, and water pollution control. Therefore, we have investigated the phase-selective gelation of the above-mentioned amphiphiles in water. The phase-selective gelation of **2** in water/oil mixtures has been demonstrated in Figure 2. As shown in test tubes C, D, and E, a clear separation of the aqueous and hydrocarbon gel layers can be observed in the solvents employed. However, it should be noted here that the gel layer above the aqueous layer is slightly less viscous compared to that obtained by the use of a small quantity of water, as discussed in the preceding section. To investigate the phase-selective gelation, 0.555 mg of the amphiphile was dissolved in 2 mL of water and the oil was added gradually in steps of 100 μL with gentle agitation at room temperature. The maximum volume of the solvent gelled was noted. However, it is interesting to note that addition of excess solvent destroys the gel, leaving separate layers of water and the solvent. The maximum volume of solvent that could be gelled linearly varies with the amount of compound taken, as shown by the representative plot of the volume of petroleum ether as a function of the amount of **2** (Figure 4).

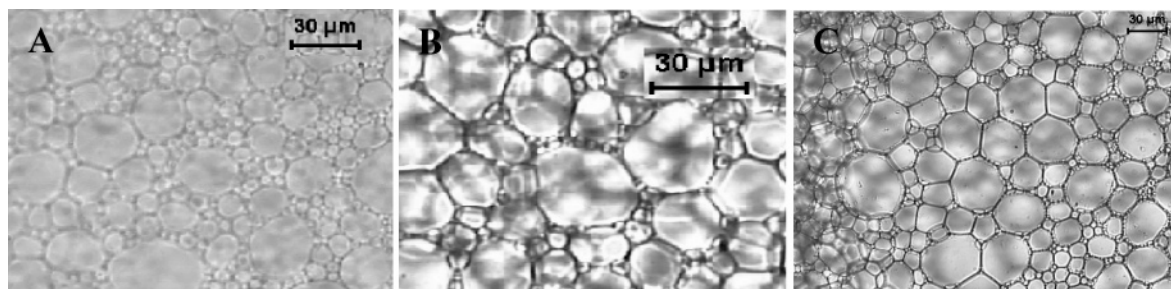


Figure 5. Optical micrographs of the gels formed in (A) *n*-heptane, (B) toluene, and (C) tetrachloromethane.

Table 2. Minimum Gelator Concentrations (MGCs, mg L⁻¹) of Amphiphiles 1–5 in Various Solvents

solvent	MGC (mg L ⁻¹)				
	1	2	3	4	5
<i>n</i> -hexane	33	36	34	38	47
<i>n</i> -heptane	34	31	39	34	42
isooctane	40	42	44	46	55
cyclohexane	44	36	36	38	42
petroleum ether(40-60)	37	31	34	34	42
petrol	48	50	54	53	57
kerosene	44	43	42	46	53
benzene	37	36	36	38	39
toluene	48	45	43	46	48
<i>o</i> -xylene	44	44	43	46	50
<i>m</i> -xylene	34	35	34	39	47
chloroform	48	39	48	42	47
tetrachloromethane	40	35	34	38	45

To compare the abilities to form gel emulsions, we have calculated the minimum gelator concentrations (MGCs, in milligrams per liter) of all the amphiphiles necessary for gelation of various organic solvents at room temperature ($\sim 28^\circ\text{C}$). (The MGC values were calculated as described in ref 2a. Though the MGC values are strictly defined for normal gels, we have used the same to compare the abilities of the amphiphiles to form the gel emulsions.) The values are listed in Table 2. The MGC values are less in aliphatic hydrocarbon solvents as compared to those in aromatic hydrocarbon solvents. Further, in aliphatic hydrocarbon solvents, the MGC value decreases with an increase in the chain length of the solvent. However, the lowest MGC value can be observed only in petroleum ether solvent.

The results in Table 2 also indicate that the MGC values of **1**, **2**, and **3** slightly differ from each other. This might be due to the differences in hydrophobicity of the amino acid moieties, and the chirality seems to have no significant role in the formation of gel emulsions. The order of MGC values of amphiphiles **2**, **4**, and **5** in any given solvent indicates that the increase of the chain length of the hydrocarbon tail enhances the ability to form gel emulsions, as discussed before. This is consistent with the mechanism proposed for the formation of gel emulsions, as the formation of bilayer lamellar self-assemblies in water depends on the chain length of the hydrocarbon tail of amphiphiles.

Effect of Acid and Alkali. Each of the amphiphiles described above has an acidic and a basic functional group. Therefore, the ionization state of the amphiphiles may have an effect on the gelation behavior in a given solvent. To examine this, we have studied the effect of acid and alkali on the gelation behavior of the amphiphiles in petroleum ether. The gels could not be prepared when neutral or acidic (0.1 N HCl, pH 2) water was used for gelation. However, in the presence of 0.1 M NaOH, gelation was observed and the MGC value was equal to that in pure water. (It should be noted here that upon dissolution

of the compounds the pH of water increased to 12.) This can be connected to the partition constant of the species present in water. Since the pK_a 's of the carboxylic acid and secondary amine group are around 5 and 10, respectively, the amphiphiles are expected to be present in the zwitterionic form in this pH range. However, upon acidification ($\text{pH} < 2$), the zwitterions transform into the corresponding ammonium salt and in the presence of base ($\text{pH} > 12$) the compound is converted to the carboxylate salt. Since the effective charge of the zwitterions is zero, it has poor solubility in water as well as in organic solvents. The failure to form gel by the cationic form of the amphiphiles in excess water may be due to the very low partition constant as compared to that of the corresponding carboxylate salt. At low pH, the headgroup of the amphiphile has, because of hydrogen bonding, strong interactions resulting in a high solubility in water. However, it should be noted that the concentrated aqueous solutions of the ammonium salt of the amphiphiles (i.e., in the presence of a small quantity of water) do induce gelation.

Optical Microscopy. To examine the microstructures of the gel emulsions, we have taken optical microscopic pictures of the gels formed by **2**. Parts A, B, and C of Figure 5 respectively show the micrographs of the gels formed in *n*-heptane, toluene, and tetrachloromethane. These micrographs exhibit network structures. Although the connected polygonal networks are mostly hexagonal in shape, other shapes including squares and pentagons can also be identified. The average diameter of the compartments is $\sim 20\text{--}30\ \mu\text{m}$. Similar network structures were also seen in the case of aromatic hydrocarbon solvents (not shown here). The optical micrographs clearly show that this gel system owes its features to different phenomena than those found in the traditional gel systems. The gels look like frozen macroemulsions consisting of polyhedral hydrocarbon cells separated by a continuous, flat, aqueous surfactant film. It seems that the initially formed macroemulsion droplets creamed due to the density difference between the droplets and the bulk liquid resulting in the formation of a viscous creamed layer. The quaternary system of 2-butanol/sodium dodecyl sulfate/water/*n*-hexane has been reported to form similar emulsion gels.²² Schurtenberger et al. and others have also reported water-induced aggregation of lecithin molecules into flexible cylindrical reverse micelles which subsequently formed a network of entangled micelles.²³ Solans et al. have reported similar network structures for W/O-type gel emulsions for neutral tetraethylene glycol dodecyl ether surfactant in decane solvent.²¹

As reported in the literature,^{11,24–26} stable concentrated emulsions with a high volume fraction (ϕ) ($0.9069 < \phi <$

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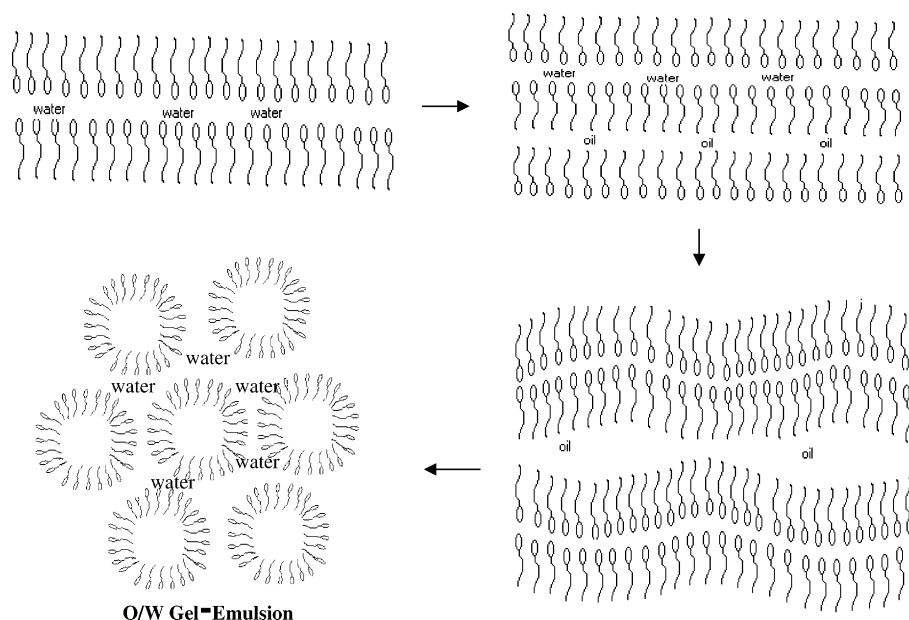


Figure 6. Schematic presentation of the mechanism of gel-emulsion formation.

1.0) of the dispersed phase can be obtained under three conditions. First, when the emulsion is strongly polydispersed, second, under the influence of a centrifugal field, and third, by the use of suitable surfactants. Indeed, Lissant²⁴ and Nixon and Beerbower²⁶ have reported emulsions with ϕ values as high as 0.99. These authors have given importance on the nature of surfactants to explain the properties of the emulsions. However, Princen has given a geometrical description of the emulsion instead of explaining why these structures are stable in some cases and not in others.¹² In the case of monodisperse emulsions, Ostwald's phase volume theory suggests that the maximum value of ϕ that can be reached is 0.7405, which corresponds to the volume fraction of a hexagonal close packing of undistorted spheres.²⁷ However, when ϕ exceeds this value, the droplets get deformed and thin, flat films of the continuous phase are formed at the junction of the droplets. The optical micrographs (Figure 5), which exhibit typical foamlike structures, are very similar to that observed by Princen et al. for O/W-type emulsions.²⁸ Therefore, Princen's theoretical model^{29,30} can be used to describe the structural features of the direct emulsions. According to Princen,¹² each film is always under two opposing forces. One is the compressive pressure of the film, and the other is a disjoining pressure that is developed within the film as a result of repulsive forces between the approaching film surfaces, which counteracts the first so that equilibrium is maintained. With the increase of ϕ , the compressive forces increase and a point is reached when the disjoining forces can no longer balance the former ones and the emulsion breaks down or inverts. The dependence of ϕ on the compressive pressure has been discussed by Princen elsewhere.¹²

The specific structure giving the gel properties can be understood from the optical microscopic pictures, which look very similar to bimolecular layers in biomembranes. The bimolecular layers in biomembranes consist of two lipid layers tail-to-tail. In contrast, in the present case, the two layers of the amphiphile are head-to-head because it separates oil compartments from the continuous phase of the water. A three-layer amphiphile arrangement, two tail-to-tail and one head-to-head, would be necessary if oil compartments were separated by the continuous water phase. Our preliminary studies on the aggregation behavior of the amphiphiles in water have shown the formation of lamellar bilayer structures above a critical aggregation concentration.³¹ The Fourier transform infrared (FT-IR) spectral data have suggested that the bilayer structure is stabilized by the amide–amide and amine–carboxylate intermolecular hydrogen bonding between neighboring amphiphile molecules in the aggregate. The formation of the emulsion is, in fact, a result of the high spreading power of the lamellar liquid crystal. Figure 6 shows the proposed schematic change in shape of the flexible bilayer self-assemblies of the amphiphiles during the spontaneous formation of gel emulsions. The water molecules are spontaneously taken up by the layers of amphiphilic molecules during the formation of lamellar liquid crystal structures. The oil is trapped between two flexible amphiphile bilayers, resulting in the formation of micro-oil domains. Since the amphiphile bilayers are flexible, the microdomains are quickly connected to and disconnected from each other.

Conclusion

In summary, a novel class of amphiphiles, sodium *N*-(*n*-dodecyl-2-aminoethanoyl)-L-amino acidate, have been synthesized. We have shown that the amino acid derivatized surfactants induce the formation of O/W-type gel emulsions with a high internal volume percentage (up to 95%) of organic solvents and commercial fuels. Like traditional gels, the gel emulsions also show stability to mechanical agitation and are thermostable. The pictures showing the formation of highly viscous solutions due to the water-induced aggregation of the surfactants into

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emulsion gels have been presented. The optical micrographs have confirmed the foamlike structures of the emulsion gels. The properties of the gel emulsions follow Princen's theoretical model. The ability to induce gelation decreases with a decrease in the chain length of the hydrocarbon tail of the amphiphiles and the straight chain hydrocarbon solvents. The hydrophobicity of the surfactant headgroup also influences the gelation process. However, the chirality of the amphiphiles seems to play no role in the formation of gel emulsions. We have demonstrated the highly effective formation of phase-selective gel emulsions in hydrocarbon solvents and in commercial fuels by the surfactants. Only the anionic and cationic forms of the amphiphiles are able to promote the formation of

gel emulsions when the water content of the mixture is low. However, in the presence of excess water, only the anionic form of the amphiphiles forms gel emulsions. The amphiphiles may have potential use in the storage of fuels, in oil extraction, and in the disposal of crude oil spills.

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