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Preparation and Properties of Lactic Acid-based Modified Carboxylic Surfactant

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Abstract — Acyl lactylates are a class of nitrogen-free surfactants derived from natural and bio-renewable resources by reacting lactic acid with fatty acid. Lactylates are well known in food industry and in personal care applications as they function as viscosity builders, emulsifiers, foam boosters, stabilizers and can also be used as secondary surfactants. In present work, we studied the synthesis methodology of stearyl lactylates (SL) using two different routes. SL was synthesized as condensation product of lactic acid with stearic acid by base-catalyzed direct esterification method under reduced pressure, while the other protocol involved the esterification of lactic acid using acid chloride as intermediate. The resulting products after subsequent purification were neutralized with alkali to prepare their sodium salts, sodium stearyl lactylates (SSL). The synthesized lactylates and their salts were characterized for their various performance properties such as surface tension, pH and hydrolysis rate, emulsifying power and wetting behavior in relation to conventional surfactant having same hydrophobic chain length, sodium stearate (SS).

Keywords : *Lactic acid, esterification, stearyl lactylates, performance properties.*

INTRODUCTION

Soap, essentially a surfactant having carboxylic surface active group, is one of the most versatile products of chemical industry. They show optimum properties when used under favorable conditions. They are generally non-toxic and biodegradable with excellent detergent property. However, their performance is dampened when used under mild acidic condition or in hard water. Heavy metal ion salts of soap are

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formed when used with hard water while there is liberation of free fatty acids on soap acidulation [1]. On both occasions the soap precipitates out because of low solubility of the resultant products in water. These shortcomings have triggered the need to synthesize new or modified carboxylic surfactants. Modification in soap implies injecting relatively hydrophilic group into the surface active part of the soap molecule. This group can be polyhydric alcohols, amino acids, hydroxy-carboxylic acids and many more [2-7].

Acyl lactylates are a class of nitrogen-free modified carboxylic surfactant obtained through the condensation of fatty acid with lactic acid (2-hydroxypropanoic acid) and neutralizing with a base. It was first developed by *Thompson* and *Buddemeyer* [8] of C. J. Patterson Company. They called this modified carboxylic surfactant as "lactylates". Acyl lactylates never exist as single definite product rather as a mixture of various derivatives of lactic acid and fatty acid with different number of lactic group per molecule of fatty acid. The fatty acid portion of the acyl lactylate is preferably that of a saturated fatty acid containing 16-22 C-atoms. Compounds having less than 16 C-atoms do not show appropriate functional properties and those above 22 are difficult to obtain. *Thompson* and *Buddemeyer* [9] have shown that the average number of lactic groups desired is between 1 to 3 and preferably 2-lactylates, whereas *Buddemeyer et al* [10] have shown that the lactylates with average number of lactic group less than one are more functional than those containing more than one lactic groups. They also discovered that the compound containing less than one lactic group in free acid form is having more stability.

The acyl lactylates are extensively used as food grade emulsifiers [11]. Bakery industry has been the major consumer of acyl lactylates where it is used as bread improver and dough conditioner [12]. But today their functional properties have been exploited for cosmetics [13-15] and pharmaceutical [16-19] applications. Sodium or calcium salts of acyl lactylates are preferred over free acid form for their emulsification and wetting properties and is been used to formulate hand and body creams, and hand lotion [20]. They also have been used in shaving creams and aerosols where gelling tendency of lactylates, when used with alcohol, is exploited [21]. The industry has seen continuous growth in the demands of lactylates and is forecasted to continue in far future also.

In this work, we have investigated two different strategies for synthesis of acyl lactylates. Of these, one synthesizes lactylates as condensation product of lactic acid with stearic acid by base-catalyzed direct esterification method under reduced pressure. Another method of esterification of lactic acid using acid chloride as intermediate was also studied. The resulting products after subsequent purification were neutralized with

alkali to prepare their sodium salts. These stearyl lactylates and their sodium salts synthesized were analyzed and compared with conventional surfactant, sodium stearate (SS) for their various performance and functional properties.

EXPERIMENTAL

Materials : Industrial grade stearic acid “Hydrite” was obtained from Godrej Soaps Ltd., Mumbai. Lactic acid (Assay- 87.5%, specific gravity at 25°C=1.22, heavy metal content < 1 ppm) was supplied by M. K. Traders, Mumbai. Other reagents and solvents were of analytical-grade, and purchased from S.D. Fine Chemicals Ltd., Mumbai. All materials were used as received unless otherwise stated. Water used for all analytical measurements was doubly distilled and purified by means of a Millipore (Billerica, MA) Milli-Q-Academic water purification system.

Dehydration of lactic acid :

Lactic acid (LA) was analyzed for total and free acidity using method reported by *Fetzer and Jones* [22]. The sample was found to contain total acidity of 545 ± 0.5 and free acidity of 471 ± 0.3 . The 100% pure LA have an acidity of about 623 which when compared to total acidity of sample LA, indicated the presence of substantial amount of volatile matter in the sample. However, LA was required to be dehydrated completely for its advantage of faster esterification rate in anhydrous form. Dehydration of acid was accomplished through vacuum application. In the process requisite amount of LA was taken in a flask fitted with a glass by-pass, further connected to a KSW-6 Diaphragm type vacuum pump. The flask was heated on a magnetic stirrer hot plate under reduced pressure of about 150 mm Hg with precaution to limit the heating temperature below 85°C. Almost complete dehydration was achieved after 90 min of continued heating as signified by total acidity of 625 ± 0.5 of LA sample.

Preparation of alkanoyl lactylate :

Base-catalyzed Direct Esterification Method (DEM) — The product, stearyl lactylate (SL), was prepared by base-catalyzed direct esterification as reported by *Chaudhary and Qadri* [23] under vacuum in a glass reactor. Initially, stearic acid (0.2 mol) was taken into the reactor and heated initially to 60°C to bring it in molten form without applying vacuum. At this temperature, after ensuring entire amount is in liquid form dehydrated lactic acid (DLA) was added slowly but continuously over a period of 10 min. The amount of DLA was taken as 1.2 equivalent of LA (on free acidity basis) per equivalent of fatty acid. Vacuum was started and maintained at 150 mm Hg while reaction temperature was gradually raised to 120°C. As soon as the reaction

temperature was reached sodium carbonate (0.6 equivalent of fatty acid), a weak base which acts as a catalytic action promoter was added to the mixture. The course of the reaction was monitored by TLC as well as free acidity determination at regular interval. Heating was continued till acid value drops down and reaches to constant free acidity in the reaction mixture. The resulting solid product, SL was cooled to room temperature and volatile components were removed under reduced pressure to prevent local heating.

Esterification using Acid Chloride as Intermediate (ACM) — To the cold DLA (0.1 mol), stearoyl chloride (0.105 mol) dissolved in 80 mL ethyl acetate was added dropwise over a period of 30 min with gradual increase in temperature to 70°C. The reaction mixture was stirred at constant temperature for next one hour. Vacuum was then applied to remove the HCl gas liberated and maintained till the bubbling ceased. The resultant product, SL was subjected to refrigeration for 10 hours and then washed thoroughly with warm distilled water and dried in vacuum desiccator.

Preparation of sodium-salts of stearoyl lactylate

To the alcoholic solution of the lactylate, prepared by dissolving SL (0.1 mol) in 300 mL of methanol, the calculated amount of alcoholic caustic soda was added slowly drop by drop to the phenolphthalein indicator end point. The reaction mixture was heated at 60°C further for 15 min and then cooled to room temperature. Methanol was removed under reduced pressure. The product was given two successive warm water washings to ensure removal of excess alkali. The reaction product, sodium stearoyl lactylate (SSL) was then crystallized at 5°C and dried in vacua.

Analytical Methods

Acid value, Saponification value, Iodine value and Titre of the lactylates were determined according to AOCS Method Cd 3d-63, AOCS Method Cd 3-25, AOCS Method Cd 1b-87 and AOCS Cc 12-59, respectively [24].

The molecular weight of SSL was determined by preparative gel-permeation chromatography (GPC) using a low molecular weight polystyrene standard according to method reported by Law [25].

The performance and functional properties of the surfactants were evaluated by carrying out following tests :

Hydrolysis rate — Acyl lactylates being salt of weak acid and strong alkali shows tendency to hydrolyze in aqueous solution. As a result, hydroxyl ions and free acids exist in aqueous solution in equilibrium. The percentage hydrolysis extent was determined as hydroxyl ions concentration in relation to the molar concentration of

the sodium salt of surfactant and was calculated using following expression :

$$\text{Percent hydrolysis} = [\text{OH}^-] \times 100/\text{N}$$

where $[\text{OH}^-]$ – Hydroxyl ion concentration, N – concentration of solution mol/dm³.

The pH of the aqueous solutions of surfactants was measured using ‘Bio-lab’ pH meter BL-501 equipped with glass electrode to accuracy of 0.01 at $60 \pm 1^\circ\text{C}$.

Emulsifying power – Emulsifying power of the aqueous solutions of products was determined for water/liquid paraffin system. Aqueous solutions of the products and reference sample SS of different concentrations were prepared. 20 ml of aqueous solution of product was taken in a 100 ml stoppered graduated measuring cylinder and 20 ml of paraffin was poured into it from the side of the wall. The entire cylinder was kept in the water bath maintained at $60 \pm 1^\circ\text{C}$. After sufficient time the cylinder containing solution was turned upside down for a total 30 times at the rate of 1 turn per 2 seconds. The time of separation of aqueous phase for 20 ml was noted.

Surface tension – Surface tensions of aqueous solutions were measured using Du Nouy Tensiometer model no. 63 according to ASTM D1331-56 method.

Wetting power – Wetting efficacy of the surfactants was evaluated by the canvas disc method at $60 \pm 1^\circ\text{C}$ for 0.1% solution in distilled water.

RESULTS AND DISCUSSION

The properties of stearic acid were analyzed as follows : acid value (mg KOH/g) = 197.3; iodine value (g I₂/100 g) = 1.14; saponification value (mg KOH/g) = 198; Titre (°C) = 66.8.

Effect of esterification methods : Base-catalyzed direct esterification reaction (DEM) between stearic acid and lactic acid was carried out at temperature 120°C, pressure 150 mm Hg and stirring speed 500 rpm. The progress of esterification reaction is shown in Fig. 1 where the initial rate of reaction was rapid as indicated by exponential decrease in acid value and the reaction approaches to completion within 60 min. DEM reaction is very susceptible towards oxidation. There was immediate color change as soon as the reaction mixture was exposed to atmosphere while drawing the samples for analysis. Therefore, it is extremely necessary to employ high vacuum during reaction. In another lactylate synthesis ACM route, stearyl chloride was used as intermediate rather using stearic acid as such. The chlorine atom attached to stearyl group is much better electrophile than the hydroxyl group of fatty acid and thus, the reaction of stearyl chloride with lactic acid is faster as seen in Fig. 1. However, the product obtained from this route showed lesser average degree of polymerization

TABLE 1.

Analysis of Stearoyl Lactylates and their sodium salts obtained via different routes.

Sample	Melting Point	Acid Value	Saponification Value	Average Molecular Weight (g/mol)	Average Degree of Polymerization	Solubility
SS	243–248	–	–	–	–	Soluble
SL (DEM*)	47–51	125.27	267.98	–	–	Dispersible
SL (ACM#)	50–53	146.84	262.12	–	–	Dispersible
SSL (DEM*)	–	0.00	132.06	424.86	1.34	Dispersible
SSL (ACM#)	–	10.26	136.82	410.09	1.16	Dispersible

*DEM- Base-catalyzed, Direct Esterification Method

#ACM- Acid Chloride Intermediate, Esterification Method

when compared with the product obtained by former route (Table-1). The main reason for this can be attributed to depolymerization of lactic acid during the course of reaction as reported by *Buddemeyer et al* [10].

pH and hydrolysis extent : pH : concentration curve (Fig. 3) was constructed, and hydroxyl ion activity was calculated and represented in terms of hydrolysis extent (Fig. 4). Initially when the concentration of aqueous solutions was low, the lactylate shows greater degree of hydrolysis compared to stearate. However at higher concentrations the increase in pH and consequently the rate of hydrolysis for stearate was found to be greater than the prepared lactylates. In general, the concentration of hydroxyl ion ranges from 0.001 to 0.0001 N for the less dilute solutions of the higher soaps, the upper limits is exceeded by several folds, and in the more dilute solutions the concentration may fall beneath the lower value. In our experimentation, hydroxyl ion concentrations obtained in aqueous solutions were calculated in the range of 7.3×10^{-8} to 1.05×10^{-6} mol/dm³. The lactylates prepared via two different routes when compared with each other showed distinct difference in hydrolysis extent, but for pH a narrow intermediate range was obtained. Percent hydrolysis for lactylate from DEM is very much higher than lactylate from ACM. However, the curves constructed for these two products shows analogous nature. The difference in their hydrolysis extent can be attributed to free acidity associated with lactylate prepared by ACM.

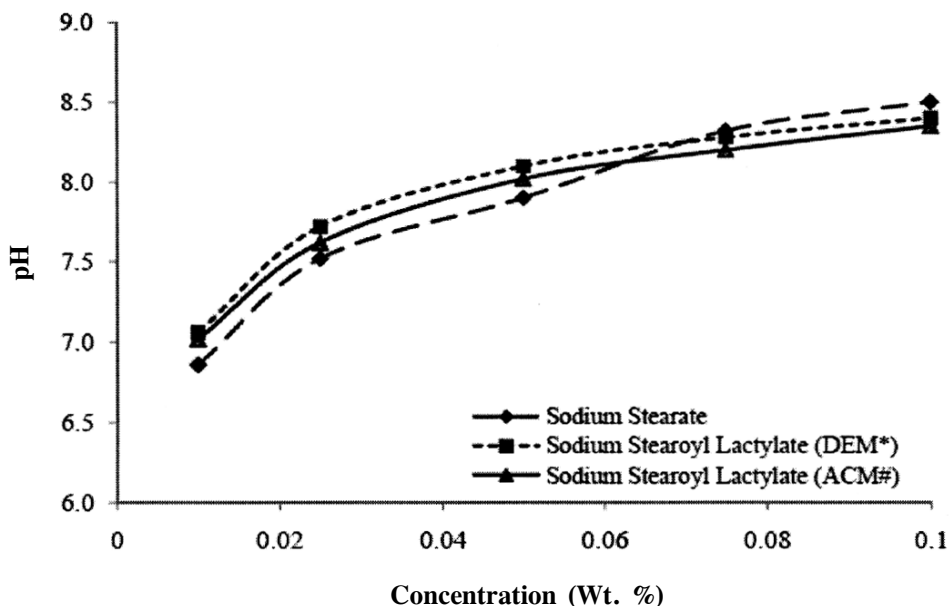


Fig. 3. Variation of pH with change in concentration of sodium stearyl lactylates and sodium stearate.

Emulsification power : An emulsion cannot be formed by two immiscible pure liquids. Emulsifying agent is usually needed to suspend one liquid into another. The Emulsifying power is judged by the time needed for separation of the 20 ml aqueous layer for the emulsion made under similar conditions. Higher the time required to separate the aqueous layer, better is the emulsifying power of surfactant. Fig. 5 shows the emulsifying power of stearyl lactylates and their sodium salts compared with the conventional surfactant sodium stearate at different concentrations. In general, the emulsifying power of surfactants increases with increase in concentration. The result in Fig. 5 indicates that higher surfactant concentrations give better emulsifying power. SSL showed better emulsification power than SS because of the presence of lactyl groups in the product which imparts the required HLB for it to act as better emulsifier. The emulsification power of SL prepared via ACM and DEM when compared showed that the DEM lactylate has better emulsifying power. This variation is expected due to high acidity of ACM product than in DEM lactylate. This speculation can be supported by the fact that when the product from DEM was completely neutralized it is having far better emulsification power. The separation

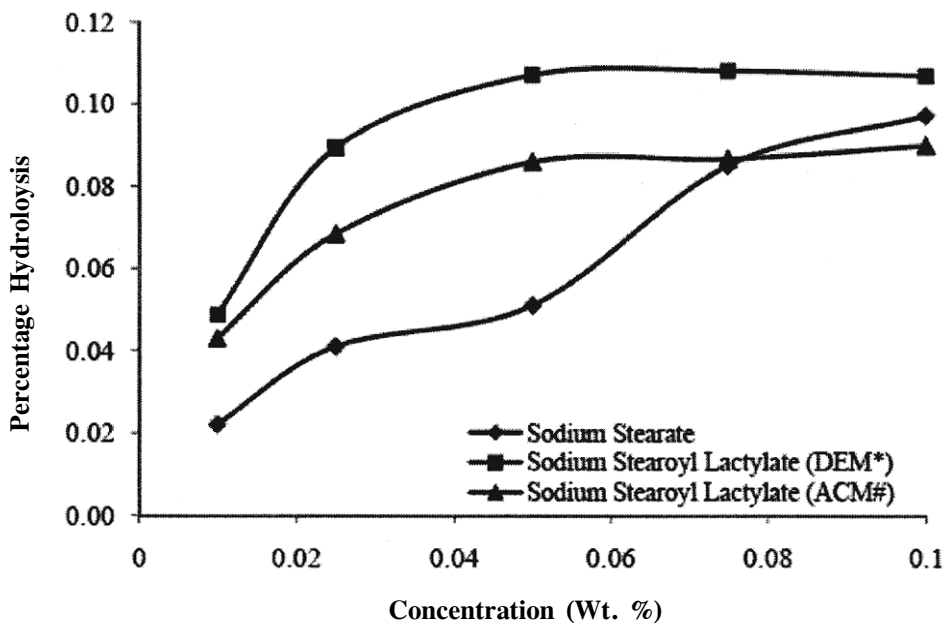


Fig. 4. Effect of change in concentration of aqueous solution on Percent Hydrolysis of sodium stearyl lactylates and sodium stearate.

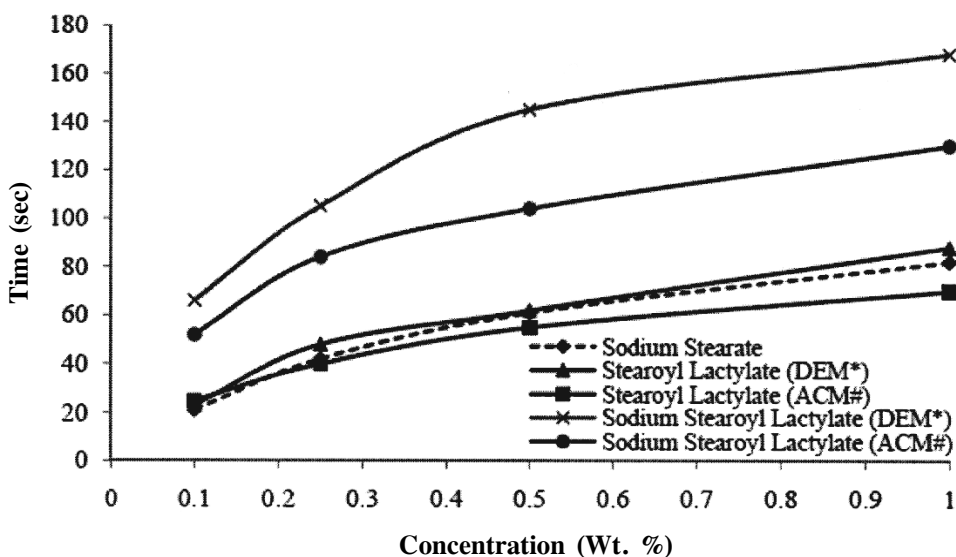


Fig. 5. Emulsification power of stearyl lactylates, their sodium salts and sodium stearate.

time for the aqueous phase increases from 52 to 168 seconds for SSL while, from 21 to 88 seconds for SL and SS for 0.1 to 1.0% respectively.

Surface tension : Initially the surfactants added to the aqueous solution forms the monolayer at the surface and the additional surfactants gets into the bulky phase of the solution. At a specific concentration known as the critical micellar concentration (CMC), the surfactant molecules aggregate into micelles. This CMC value is of practical importance since it is the minimal concentration of surfactant required to solubilize hydrophobic molecules in water. Fig. 6 shows the consolidate report of surface tension of stearyl lactylates and their sodium salts. The surface tension of SS decreases significantly from 38.1 mNm^{-1} to 32.5 mNm^{-1} for the concentration of 0.1 to 1.0% respectively. SL is found to be more effective than SS in reducing the surface tension to 28.3 mNm^{-1} at 1.0% concentration. Whereas SSL has shown improved performance in surface tension reduction as compared to SL and SS since it has attained CMC at lower concentration. The surface tension becomes constant

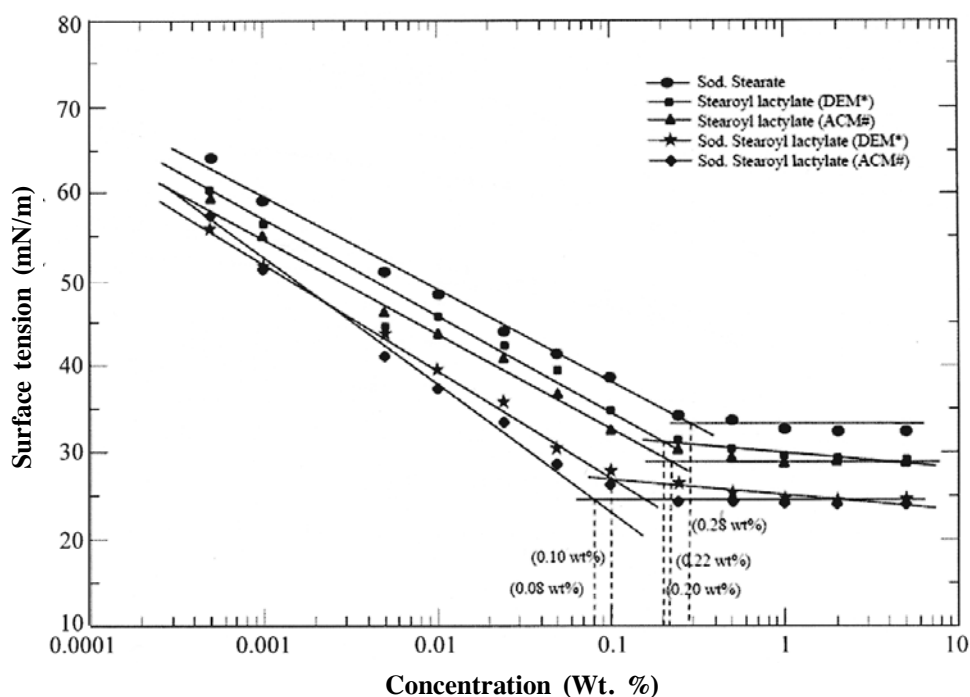


Fig. 6. Equilibrium surface tension curves of stearyl lactylates, their sodium salts and sodium stearate.

to 24.6 mNm^{-1} due to beginning of micelles formation in the vicinity of reaching the CMC at 0.08–0.10% of SSL concentration. This difference in surface activity of SL and SSL can be attributed to the presence of different counter ion species in the two surfactants and to the difference in their relative solubility in aqueous solution. The difference in miscellar aggregation behavior of SL and SSL in aqueous systems could also be considered a factor responsible for the difference in their surface activity. The presence of varying amounts of surface active impurity in SL and SSL may be another reason for the difference in their surface activity.

Wetting performance : Among the performance properties we have studied wetting behaviors of products synthesized using the Canvas Disc method. The time required to sink the canvas disc in surfactant solution is measured as wetting time. Minimum is the time required for sinking the disc, higher is the wetting power of surfactant. In general, as the surfactants concentration increases, the wetting time decreases i.e. wetting power of the surfactants increases with increasing concentration. Fig. 7 shows the concentration dependence of wettability for stearyl lactylates and their sodium salts. Wetting time for 0.1% of SSL are 71–89 seconds while for 1.0% 133–162 seconds are required. Stearyl lactylates and their sodium salts entail less time to wet the surface of canvas disc in comparison with SS. This effect can be ascribed to the

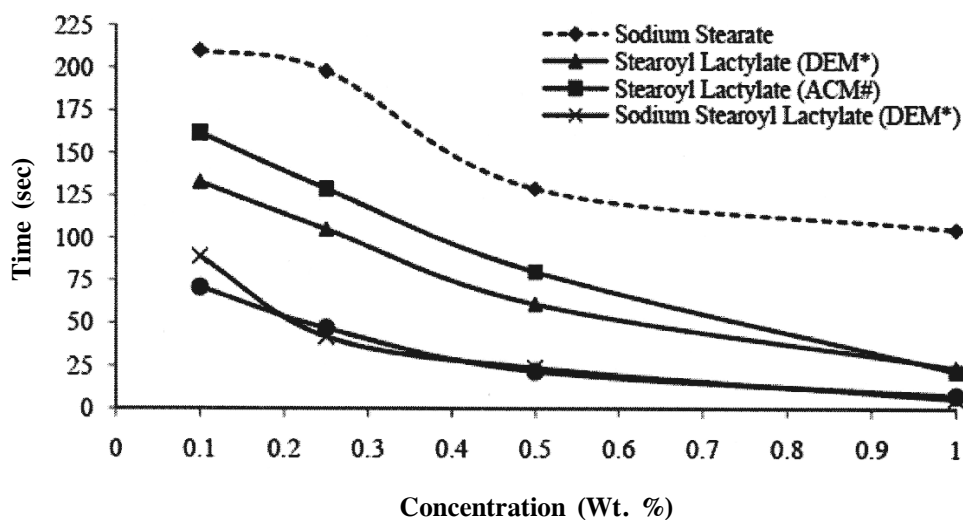


Fig. 7. Wettability of stearyl lactylate, its sodium salts and conventional surfactant at different concentrations.

presence of lactyl groups in them. Moreover, when acidity of SL was neutralized with alkali it conveyed hydrophilicity to the resulting product. Therefore, the wetting efficacy of SSL is much better even at low concentration.

CONCLUSIONS

Stearoyl lactylates can be successfully synthesized by both base-catalyzed direct esterification method (DEM) and esterification using acid chloride as intermediate (ACM). The products obtained from both the methods have comparable characteristic values. With DEM the reaction was rapid even at moderate vacuum while ACM being multi-step process is very time consuming. The performance of sodium stearoyl lactylates depends not only on the average degree of polymerization but also on the extent of neutralization. Hence, the SSL obtained by DEM showed good emulsification power and low extent of hydrolysis even at relatively high concentration of aqueous solution.

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