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Phase Equilibria of a Mixed Alkali Soap/ Carboxylic Acid/Water System

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ABSTRAK

Kajian awal telah dilakukan keatas fasa equilibria sistem tiga komponen air/ natrium kaprilat/asid oktanoik dan air/natrium kaprilat dan natrium dodesil sulfat (1:1)/asid oktanoik pada suhu 30°C. Pemisahan fasa dilakukan secara emparan berulang-kali. Dwibiasan telah diteliti dengan pengutub bersilang dan kekonsistenan, tekstur dan pola optik telah dikaji dengan menggunakan mikroskop berkutub.

Dari hasil penyelidikan yang didapati, satu gambarajah fasa telah dilukiskan yang mengandungi dua fasa larutan isotropik dan dua mesofasa. Kajian juga menunjukkan pengurangan berat asid oktanoik yang diperlukan bagi membentuk fasa hablur cecair lamela. Pengurangan nilai kepekatan kritikal misel juga berlaku terhadap sistem surfaktan campuran.

ABSTRACT

A preliminary investigation was carried out on the phase equilibria in the three component systems, water/sodium caprylate/octanoic acid, water/sodium caprylate and sodium dodecyl sulphate (1:1)/octanoic acid at 30°C. The phases were separated by repeated centrifugation. The birefringence was observed under cross-polarisers and their consistency, texture and optical pattern were examined under the polarizing microscope.

On the basis of the results obtained, a phase diagram was drawn that includes two phases of isotropic solution and two mesophases. Results also showed a decreased amount of octanoic acid utilized in obtaining the lamellar liquid crystal phase. The critical micelle concentration was also reduced for the mixed surfactant system.

Keywords: Mixed surfactant system

INTRODUCTION

The colloidal association structure has a long history and the most notable paper is one by Ekwall (1974), who meticulously obtained phase equilibria of many different kinds of surfactant systems. All of these studies were started by constructing a phase diagram and looking into the various phases formed. However these studies were only limited to a single surfactant system. Whenever surfactants are used on a commercial scale they are invariably mixtures. Commercial surfactants are mixtures as they are usually made from feedstocks which have mixed chain length (Login 1984). In addition it is found that in most practical applications well-chosen mixtures of surfactant can be made to perform better than the single surfactant (Clint 1975; Clint & Walker 1975).

Application of such theory to such systems is fairly recent (Clint 1990), which prompted this work to look into the phase equilibria of a mixed surfactant system. Emphasis is given to the formation of lamellar liquid crystalline phase. This is imperative in controlling product stabilities and properties.

The results of these studies are illustrated by means of triangle diagrams of the usual type. The lower left corner denotes 100% water (by weight), the lower right 100% surfactant and the upper 100% co-surfactant. Finally, the final phase diagram takes into account all the results and the location of the various phases.

METHODS AND MATERIALS

Materials

The chemicals, source and purity are given in Table 1. The sodium dodecyl sulphate was recrystallized using 95% ethanol. The others were used without further purification. Doubly distilled water was used.

TABLE 1
List of chemicals

Chemical	Source	Purity
Octanoic acid	Aldrich	99.5%
Sodium caprylate	Sigma	99.0%
Sodium dodecyl sulphate (SDS)	Merck	95.0%
Ethanol	Fluka	99.0%

Determination of Phase Equilibria

The phase equilibria were determined by titration to turbidity for the solution part of the system. The samples were then vortexed for mixing purposes. The samples were allowed to equilibrate in a water bath kept at 30°C. The phases were separated by means of centrifugation at high speed.

Surface Tension Measurement

A Fisher (model 215) surface tension analyser was used for measuring the interfacial tension. The samples of 50 ml with various concentrations of surfactant were prepared and run at a speed range of 0.1 in/min. The temperature was controlled at 30 ± 0.01°C.

Photomicroscopy

A Will (model V 365) polarizing microscope, attached to an Olympus camera (model OM-2) was used for photomicroscopy. Precleaned microscope slides and covers were selected, and then buffed with lint-free tissue immediately before use. A small sample was transferred from the sample tube on to the glass slide and sheared between the cover and was left for a few minutes for equilibration. The appearance of the sample was then observed between cross-polarisers. A representative region was then selected and photographed at a magnification of 100.

RESULTS AND DISCUSSION

Studies disclosed concentration ranges with homogeneous isotropics in two parts of the system, one in the region with high water content and the other in the region with high caprylic acid content. These regions are called micellar, L_1 and inverse micellar, L_2 region respectively. The limits of these areas were determined by titrating only with the smallest amount of one component to the homogeneous solution until inhomogeneity occurred owing to the formation of another mesomorphous or liquid phase.

In the part of the system with a higher content of sodium caprylate and sodium dodecyl sulphate, liquid crystalline phases occurred. In the octanoic acid-free state, the mixed surfactant formed hexagonal liquid crystalline, E with water content ranging from 44 per cent to 55 per cent. The phase was identified by the rodlike projection pattern when observed under the polarizing microscope as in *Plate 1.* This phase maintained its structure up to 10 per cent of octanoic acid by weight.

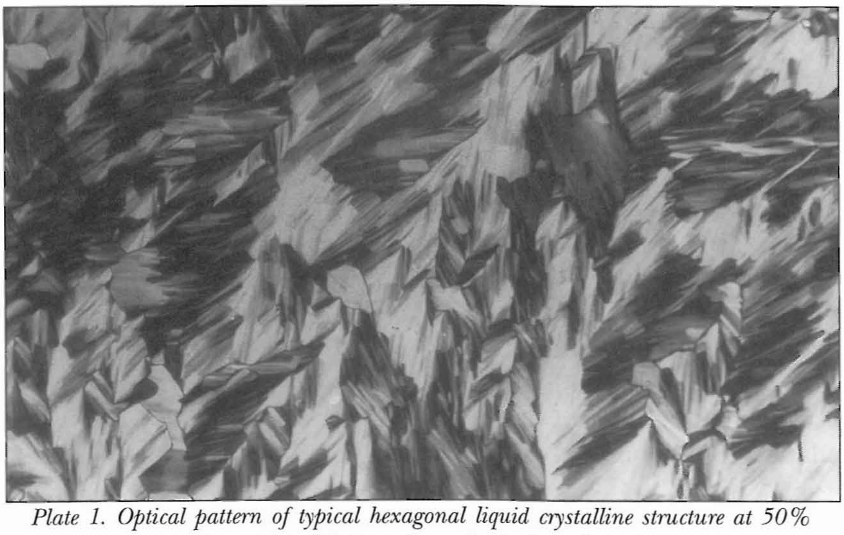


Plate 1. Optical pattern of typical hexagonal liquid crystalline structure at 50% by weight of both water and mixed surfactant

In the central part of the system another phase was observed and when looked at under the polarizing microscope exhibited a typical lamellar liquid crystalline, D pattern as in *Plate 2.* This region has a minimum water content of 16 per cent and a maximum of 85.5 per cent. When the results of these observations were entered in the phase diagram, *Fig. 1a* was obtained. The result is a typical three-component system employing water/surfactant/co-surfactant components. It is, however, interesting to note comparisons with the single surfactant system as in *Fig. 1b.* The result obtained for the single surfactant system is consistent with work done by Friberg *et. al.* (1966). It is obvious there exist differences in the respective regions especially the boundaries of each region.

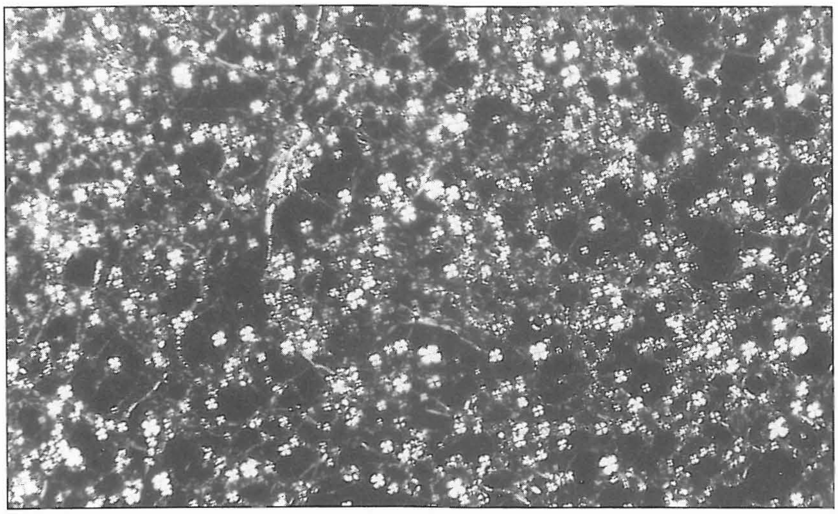


Plate 2. Optical pattern of typical lamellar liquid crystalline structure at a representation region of phase D

Graphs of weight fraction of water versus weight fraction of surfactant were plotted to facilitate comparison between the two systems. *Fig 2* shows the region for the micellar solution, L_1 of the system. The minimum water intake of 0.53 weight fraction is increased to 0.55 for the mixed surfactant system. The critical micelle concentration, cmc of the mixed surfactants of 0.022 mol/1 is found to be lower than the cmc of the single component (*Fig 3*). This is due to the presence of sodium dodecyl sulphate molecules forming a mixed micelle with the sodium caprylate molecules, thus increasing the stability of the micelles and reducing the cmc value. A calculation for theoretical value base on equation

$$\frac{1}{CMC} = \frac{\alpha}{CMC_1} + \frac{(1-\alpha)}{CMC_2} \qquad [1]$$

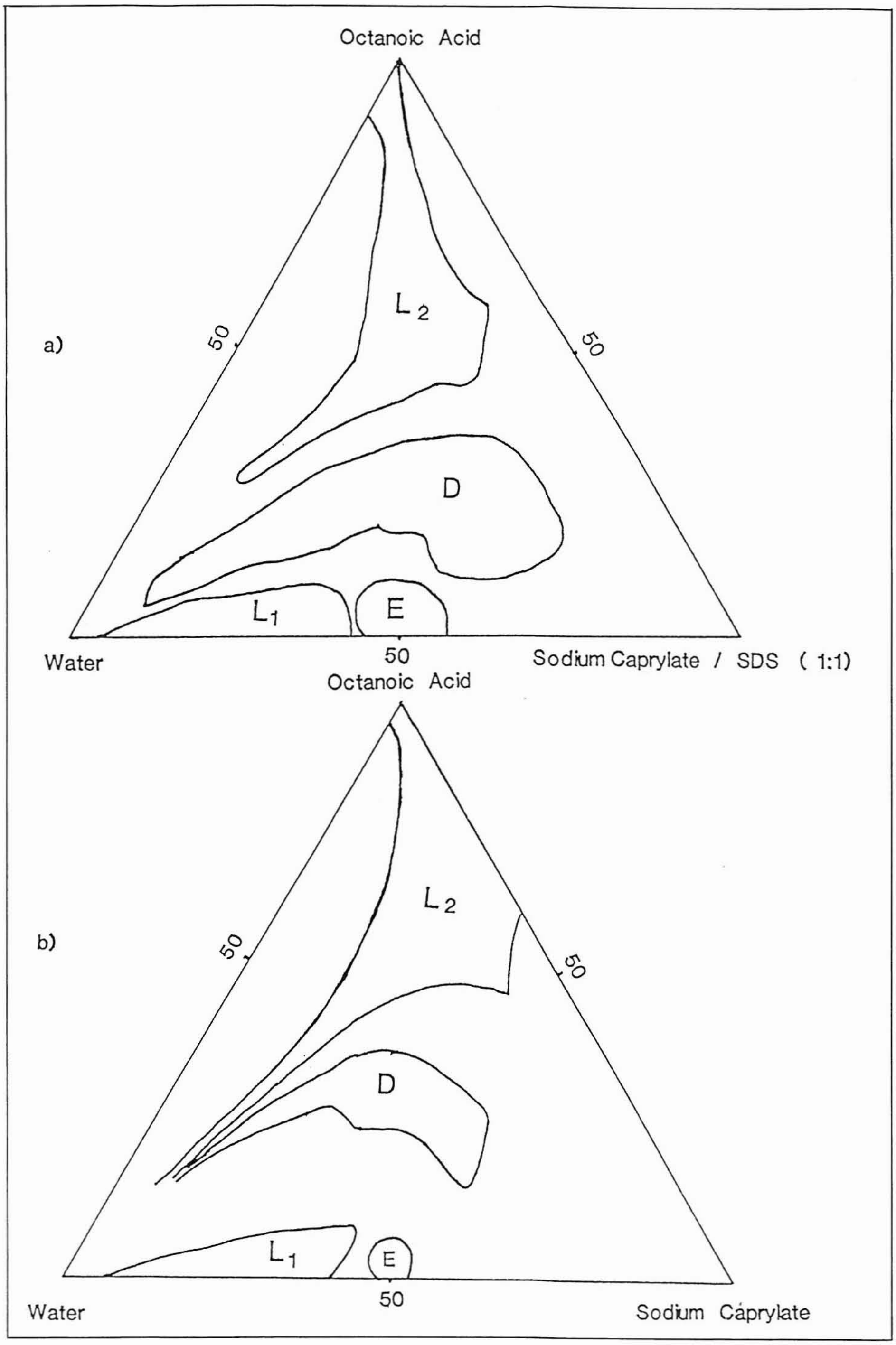


Fig. 1. Phase equilibria at 30°C of: a) water/sodium caprylate/SDS (1:1)/octanoic acid and b) water/sodium caprylate/octanoic acid

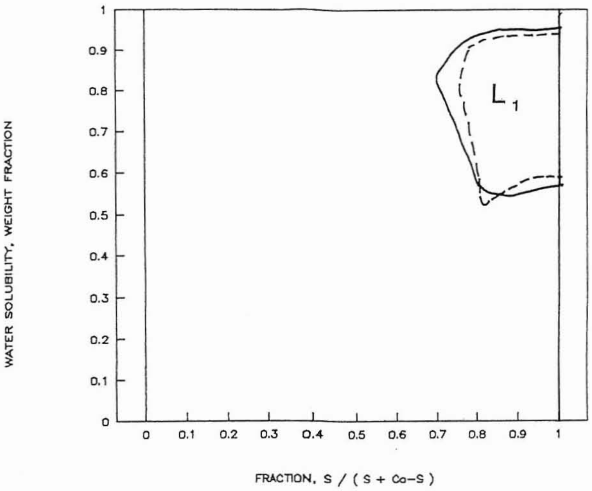


Fig. 2. The solubility of water (weight fraction) in sodium caprylate: sodium dodecyl sulphate (S)/octanoic acid (Co-S) (———) and sodium caprylate (S)/octanoic acid (Co-S) (- - - -) mixture (weight fraction) for the micellar, L_1 phase

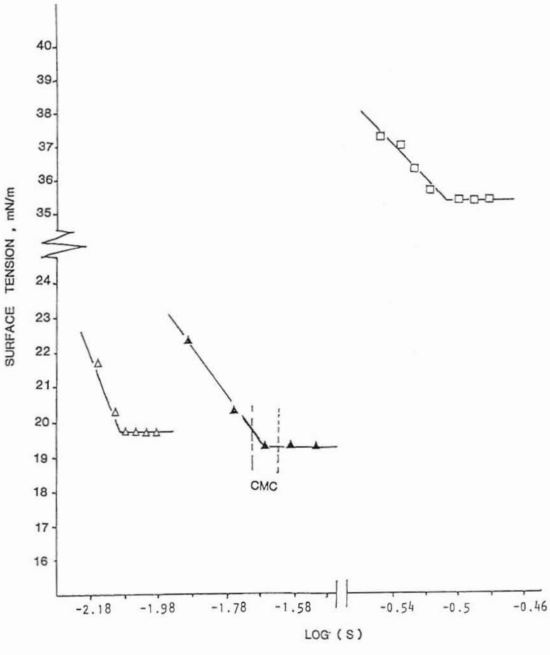
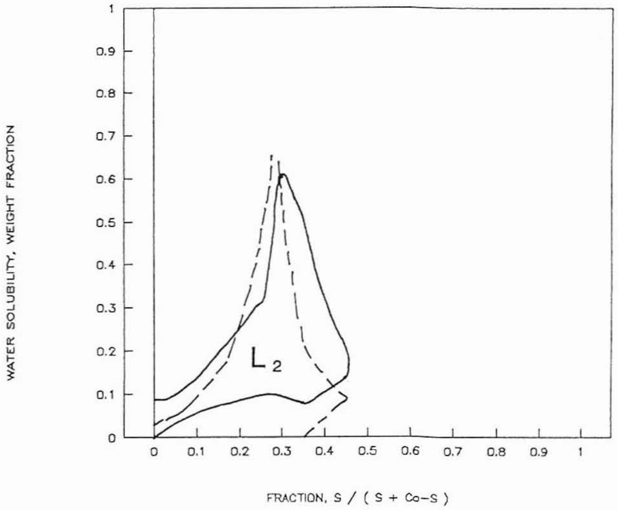


Fig. 3. The surface tension versus logarithm of concentration; □, sodium caprylate; △, sodium dodecyl sulphate, SDS and ▲, sodium caprylate: SDS (1:1) systems.

where α is the mole fraction of surfactant 1, gives a ratio of 0.021 mol/1, which indicates an ideal behaviour for this mixture. *Fig. 2* also shows that the mixed system uses a lower amount of surfactant of 0.70 weight fraction as compared to 0.75 for the single surfactant.

For the inverse micellar phase, L_2 (*Fig. 4*), studies show that the higher water solubility region is shifted to the right-hand side between 0.3 to 0.45 weight fraction of surfactant axis for the mixed surfactant. The lower water solubility region is shifted upward to about 10 per cent. The continuous water solubility occurring between 0.27 to 0.3 weight fraction of single surfactant system dissappears and the mixed surfactant dissolves in up to 60 per cent water. The solubility of water in octanoic acid is also increased from 3.5 to 9.5 per cent and this indicates a higher amount of water molecules can be solubilized in the inverse micelle formed by the surfactant.



Fig, 4. The solubility of water (weight fraction) in sodium caprylate: SDS (S)/octanoic acid (Co-S) (——) and sodium caprylate (S)/octanoic acid (Co-S) (- - - -) mixture (weight fraction) for the inverse micellar, L_2 phase.

Fig 5 shows a typical lamellar liquid crystalline, D located in the middle part of the diagram. The figure shows a shift of 10 to 30 per cent weight of surfactant in the mixed surfactant system, reducing the amount of octanoic acid needed to form the lamellar liquid crystalline structure. The minimum water intake is reduced to about 17 per cent and the maximum is increased to 85 per cent. The whole phase is larger and this indicates a better stability for the system. In order to illustrate the arrangement of the surfactant molecules in this two system, a representative region, A (*Fig. 5*) consisting of 30, 45 and 25 per cent water, surfactant and cosurfactant respectively is selected and observed under the polarizing microscope. The mixture of the single surfactant shows a typical lamellar liquid crystal with oily streak structure as in *Plate 3*. The mixture containing the mixed surfactant exhibits another typical lamellar liquid crystal with maltese cross structure as in *Plate 3*. The results gave evidence of the possible molecular arrangement of the surfactant molecules in the lamellar liquid crystal. Addition of sodium dodecyl sulphate obviously created a temporary disorder in the molecular arrangement and changed the optical pattern of the whole organization, while still maintaining the overall lamellar liquid crystalline structure.

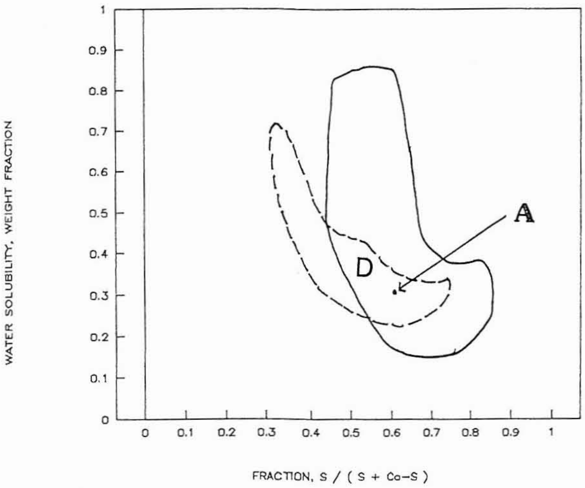
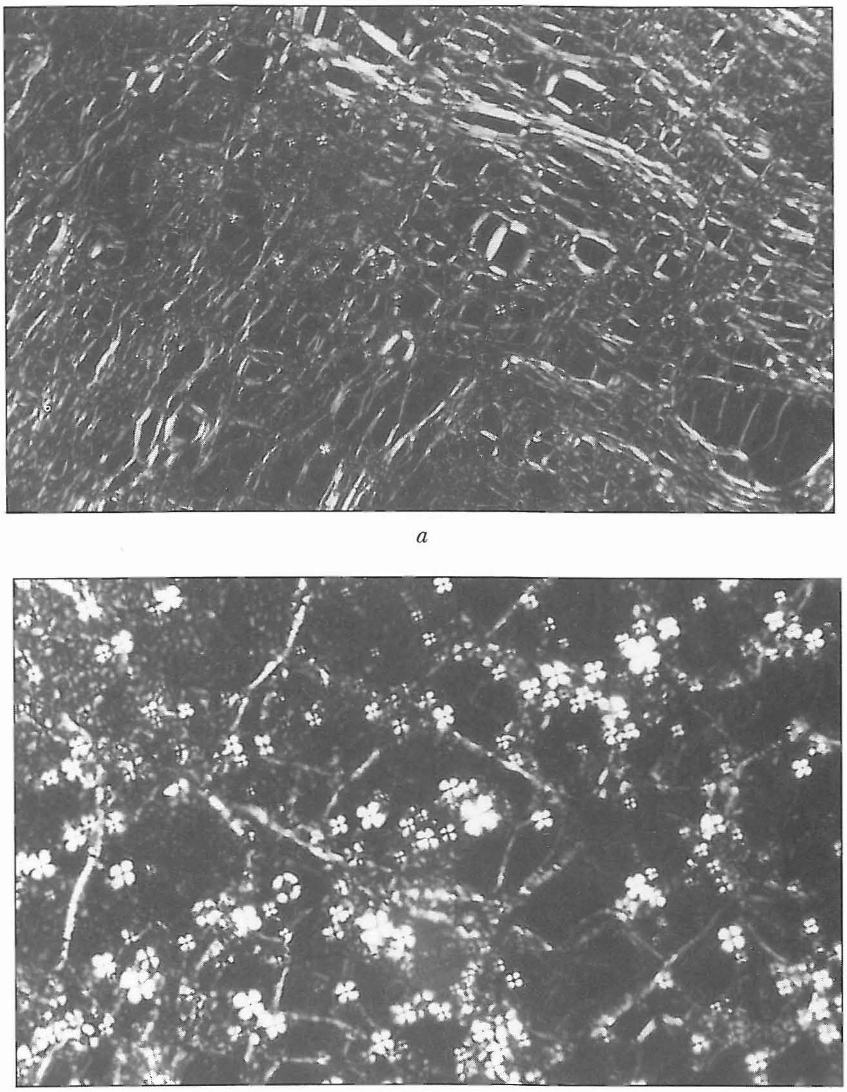


Fig. 5. The water weight fraction versus weight fraction of sodium caprylate; SDS (S)/octanoic acid (Co-S) (——) and sodium caprylate (S)/octanoic acid (Co-S) (- - - - -) mixture for the lamellar liquid crystalline, D mesophase

Comparison of the hexagonal liquid crystalline region is however omitted as the main interest was in the lamellar state. Therefore such an investigation and comparison would have insignificant relevance for further examination and is considered unwarranted.

The above results demonstrate that there is a difference in a mixed surfactant system. This is largely due to the formation of a mixed micelle containing amphiphilic molecules of different hydrocarbon chain length which in this case (C-8 and C12) an increase of about 0.504 nm in length. The stability of the system is also increased as shown by the increase in the lamellar liquid crystalline region. Further investigation will be reported on the stability of this system by use of light scattering and low-angle X-ray diffraction in a forthcoming article. Nevertheless, it is important to realize that the phase equilibria studies presented give a quantitative distinction between single and mixed surfactant systems.



a

b

Plate 3. Optical pattern of 30, 45 and 25 percent water, surfactant and cosurfactant shows: a) oily streaks for single surfactant b) maltese crosses for mixed surfactant

ACKNOWLEDGEMENTS

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