Dynamic interfacial tension of some sulphonate systems

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ABSTRACT

Nine pure sodium phenylalkane sulphonates, namely, 3-phenyltetradecane, 5-phenyltetradecane, 7-phenyltetradecane, 3-phenylhexadecane, 5-phenylhexadecane, 7-phenylhexadecane, 1-phenyldodecane, 1-phenyltetradecane and 1-phenylhexadecane sodium sulphonates, were prepared and their capabilities for lowering dynamic interfacial tension (D-IFT), were evaluated in n-octane/NaOH aqueous systems. The effects of surfactant structure and the concentration of added NaOH on the tension behaviour of these anionic surfactant systems, were studied. Tension behaviour of surfactant are considered the backbone for evaluating and designing practical formulations used for surfactant flooding systems.

Keywords: Sulphonate-alkane-NaOH system. Sulphonate structure and tension behaviour. Dynamic interfacial tension and Alkalinity.

INTRODUCTION

During the past decades, more and more attention has been drawn to the enhanced oil Recovery (EOR) projects and, in particular, surfactant flooding which is considered to be one of the most promising exploitation modes. A considerable amount of research work concerning the screening of formulations and mechanisms of surfactant flooding have been carried out by petroleum chemists [Shah, D.O. et al., (1972), Gale, W.W. and Sandvik, E. I. (1973), Wilchester, H. I. (1974)]. The Surfactants used in their early work were mainly petroleum sulphonates which consist of complex components of uncertain structures [Sandvik, E. L. et al., (1976), Knaggs, E. (1976), Smith, G. D. (1979)]. When such a kind of surfactant was used for flooding systems, several technical problems appeared. Interfacial tension, (IFT) measurements between these surfactant aqueous systems and crude oil, have not given explicable results. The great advantage of replacing crude oils by alkanes, in low tension studies, allows use of a whole scale of oil phase properties (form n-pentane to n-heptadecane) [Wade, W.H., and Schechter, R. S. (1977), Shah, D.O. and Walker, R. D. (1978), Wade, W.H. et al., (1978), Schechter, R.S. and Wade, W.H. (1980/1981)]. Moreover, this scale can also be used for comparison and evaluation of different surfactant systems and the introduction of the equivalent alkane carbon number (EACN) concept [Sandvik, E. L. et al., (1976), Knaggs, E. (1976), Smith, G. D. (1979)].

In short, using surfactants of definite structure and adopting the alkane scale are necessary for achieving explicit explanation for the interfacial behaviour studies of surfactant systems used for EOR [Wade, W.H., and Schechter R.S. (1977), Shah, D.O. and Walker, R.D. (1978), Wade, W.H. et al., (1978)]. Many other variables, such as surfactant molecular weight and concentration, cosurfactant type and concentration, electrolyte and alkali, have been investigated easily in current research works [Barakat, Y. et al., (1983), Rudin, J., and Wasan, D.T. (1992), Zhang, S.B. et al., (2004), Feng, J. et al., (2004), Rosen, M.J. et al., (2005)].

In this study, five pure terminal-and mid-position phenylalkane sulfonate sodium salts, were
prepared and the interfacial tension behaviour of these sulfonates against oil phase alkane carbon number (ACN). Also, the effect of added n-pentanol and n-octanol on the IFTs of these phenylalkane sulphonates, were studied.

**EXPERIMENTAL**

**Surfactants**

Nine sodium phenylalkane sulphonates of definite structure and high purity were prepared following the synthesis scheme which has been reported in literature [Doe, P.H. *et al.* (1977), El-Mergawy, S.A. (1989)].

1. Preparation of 3-phenyltetradecane, 5-phenyltetradecane, 7-phenylhexadecane, 5-phenyhexadecane and 7-phenylhexadecane, was conducted in the steps shown in figure [1(a)].

2. Preparation of 1-phenyldecane, 1-phenyltetradecane and 1-phenylhexadecane, was conducted in the steps shown in figure [1(b)].

![Synthesis scheme for the mid-position phenylalkane sodium sulphonates](image1)

![Synthesis scheme for the terminal-position phenylalkane sodium sulphonates](image2)
After being purified through desalting and deoiling steps [El-Mergawy, S.A. (1989)], the prepared surfactants were identified by MS, IR and HLB which indicated a purity not less than 95%.

**CMC and \( \gamma_{\text{cmc}} \) Determination**

Surface tension of the prepared sulphonates were measured as a function of surfactant concentration at 28°C for the mid-position phenylalkane sodium sulphonates and at 60°C for the terminal-position ones using Dagnon-Abribat Tensiometer, Prolabo [El-Koly, S.A. (1993)]. The critical micelle concentration (cmc) values were obtained by plotting the measured surface tension versus the logarithm of surfactant concentration (or concentration on a log scale). At the intersection of the straight line portions of the graph, the cmc can be located through the least-squares regression analysis [Draper, N.R and Smith, H. (1968)] as has been reported [Barakat, Y. et al., (1989), Rosen, M.J. Chapter 3. (1989)]. Figure (2) is an illustration for the location of cmc and \( \gamma_{\text{cmc}} \) values the obtained

![Graph](image-url)

**Fig. 2: An illustrative figure for the determination of CMC and \( \gamma_{\text{cmc}} \) values of a surfactant.**

| Surfactant structure | R1     | R2     | Surfactant designation | CMC  | Cmc  | Temp. |
|---------------------|--------|--------|------------------------|------|------|-------|
| C\(_2\)H\(_5\)     | C\(_5\)H\(_10\) | 3F C\(_5\)H\(_5\) | 190 | 34.1 | 28    |
| C\(_4\)H\(_9\)     | C\(_9\)H\(_19\) | 5F C\(_9\)H\(_5\) | 250 | 32.3 | 28    |
| C\(_6\)H\(_13\)    | C\(_7\)H\(_15\) | 7F C\(_7\)H\(_5\) | 340 | 30.6 | 28    |
| C\(_2\)H\(_5\)     | C\(_7\)H\(_15\) | 3F C\(_9\)H\(_5\) | 85  | 32.5 | 28    |
| C\(_4\)H\(_9\)     | C\(_11\)H\(_23\) | 5F C\(_5\)H\(_5\) | 175 | 30.1 | 28    |
| C\(_6\)H\(_13\)    | C\(_9\)H\(_19\) | 7F C\(_5\)H\(_5\) | 260 | 27.2 | 28    |
| n= 11,13,15         | 1Φ C\(_{12}\) | 5*     | 310 | 35.3 | 60    |
|                     | 1Φ C\(_{12}\) | 5*     | 150 | 36.7 | 60    |
|                     | 1Φ C\(_{12}\) | 5*     | 55  | 36.8 | 60    |

*These surfactants have Krafft points, 33, 47, and 58°C, [(El-Mergawy, S.A. (1989), Rosen, M.J. (1989)]
cmc and \( \gamma_{\text{cmc}} \) values are given in Table (1).

**Dynamic Interfacial Tension (D-IFT)**

D-IFT between sulphanate aqueous systems and n-Octane, was measured at 28°C using the spinning interfacial tensiometer developed by Cayias, Schechter and Wade [Cayias, J.L. et al., (1975)] the spinning tube was filled first with the aqueous surfactant solution then a droplet of an oil phase (n-octane) was introduced through a special syringe. Temperature control was achieved using the built-in cell heater and insulating muff provided on Model 300 Spinning Drop tensiometer, manufactured by the University of Texas at Austin, USA. For the work reported herein, the D-IFT values of 1-phenylalkane sulphonates, were measured at 60°C to avoid precipitation of surfactants.

**RESULTS AND DISCUSSION**

**The Prepared Sulphonates**

Two sets of phenyltetradecane and phenylhexadecanes sodium sulphonate isomers, were prepared following the synthesis route shown in Figure (1(a)). Each set consists of three isomers in which the benzene ring is attached to carbon atoms number 3,5 and 7. Thus, the prepared sulphates are designated 3\( \Phi \)C\(_{14}\)S, 5\( \Phi \)C\(_{14}\)S, 7\( \Phi \)C\(_{14}\)S in the first set and 3\( \Phi \)C\(_{16}\)S, 5\( \Phi \)C\(_{16}\)S, 7\( \Phi \)C\(_{16}\)S in the second set. In Figure 1(b), 1-phenyldodecane, 1-phenyltetradecane and 1-phenylhexadecane were also prepared and designated 1\( \Phi \)C\(_{12}\)S, 1\( \Phi \)C\(_{14}\)S and 1\( \Phi \)C\(_{16}\)S, respectively.
surface activities of three isomers could be demonstrated by adopting an imaginary surface molecular arrangement model [Zhang. S.B, et al., (2004)]. Shown in figure (3).

It is well known that molecules with the same electric charge repel each other. Having the same hydrophilic group (SO₃⁻), a certain distance is assumed between the surfactant molecules. This distance is equal for the three tetradecylbenzene sulphonate isomers. 3ΦC₁₄S isomer has a long linear lipophilic group (R₂ = C₇H₁₅, Table 1) and is more spatial around molecules that would allow the single bond of carbon chain turn around freely, so that this longer chain winds itself exposing CH₂ group on the outermost layer and to have the shorter R₁ chain covered (Figure 4a), so the surface energy of 3ΦC₁₄S is the highest. The difference in length between R₁ and R₂ of 5ΦC₁₄S is smaller.

The longer R₂ chain is not easy to wind itself and the shorter R₁ chain remained uncovered by R₂, so comparatively more CH₃ groups are on the outermost layer (Figure 4b) and the surface energy of 5ΦC₁₄S is lower than 3ΦC₁₄S. The two chains, R₁ and R₂ of 7ΦC₁₄S are both short and similar in length. The possibility of winding themselves or covering each other is rare. The two terminal CH₃ groups of each molecule are exposed on the outermost layer (Figure 4c), so the surface energy of 7ΦC₁₄S is the lowest. It can be inferred that the surface activity of 3ΦC₁₆S > 5ΦC₁₆S > 7ΦC₁₆S. Based on these result, one can reach a conclusion that molecular structure of surfactant would dictate the molecular arrangement state and the fraction of coverage of the CH₃ group decide the capability of lowering the surface tension.

Terminal-position phenylalkane sodium sulphonates, 1ΦC₁₂S, 1ΦC₁₄S and 1ΦC₁₆S have kraft points 38, 47 and 59°C, respectively [El-Mergawy. S.A. (1989)]. For the maximum effectiveness in surface tension reduction, surfactants are normally used above their kraft point [El-Mergawy. S.A. (1989), Rosen, M.J. Chapter 5, (1989)]. That is why cmc and gcmc values of these surfactants, are measured at 60°C. Table (1) lists the obtained values. Increasing the length of the

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**Fig. 4:** An Imaginary molecular arrangement illustrating that:
(a) No CH₃ groups are exposed (b) CH₃ groups of the longer chains are exposed, and (c) CH₃ groups of two chains are exposed on the outermost layer.
linear alkyl group from C_{12} to C_{16} resulted in a considerable decrease in cmc values, whereas an insignificant change in $\gamma_{\text{cmc}}$ values, was detected.

**Dynamic Interfacial Tension in Alkane/Aqueous System**

In figure 3, similar tendency is shown by three curves. At the beginning, the interfacial tension decreases as time goes on, then reaches the minimum; that is, the equilibrium is reached. At the beginning, the adsorption rate, at n-octane/ water interface, is faster than the desorption rate, resulting in the decrease of interfacial tension [Rosen, M.J. Chapter 2. (1989)]. As both rates become equal, the interfacial tension would not vary any more and equilibrium is established.

The minimum interfacial tension of 3 $\phi$ C_{14} S, 5 $\phi$ C_{14} S and 7 $\phi$ C_{14} S isomers differ in magnitude. The interfacial tension can be lowered to 1.5x10^{-1} mN/m by 3 F C_{16} S, to 8.5x10^{-3} mN/m by 5 $\phi$C_{16} S and to 2.8x10^{-3} mN/m by 7$\phi$C_{16} S, respectively (Figure 3). The minimum interfacial tension of 3 $\phi$ C_{16} S, 5 $\phi$ C_{16} S and 7 $\phi$ C_{16} S isomers is reduced to 9.5x10^{-2} mN/m by 3 F C_{16} S, to 4.5x10^{-3} by 5 $\phi$ C_{16} S, and to 1.5x10^{-3} by 7 F C_{16} S, respectively (Figure 3). This is in accordance with $g_{\text{cmc}}$ values given in Table 1.

This reduction in interfacial tension values of three isomers of tetradecyl- and hexadecyl-benzene sodium sulphonates, can also be explained on molecular structure. As the benzene ring shifts toward the middle of the alkyl chain, the fraction of coverage of CH$_3$ groups of the surfactant molecules would increase, resulting in the increase of the capability for lowering interfacial tension. It is obvious from figure (6) and (7) that in the investigated sets of tetradecyl- and hexadecyl-benzene sodium sulphonates, the position of phenyl group along the linear alkyl chain is very important.

Dynamic interfacial tension, D-IFT, values decrease when phenyl group approaches the terminal carbon atoms of alkyl chain. D-IFT values of 3 $\phi$ C_{14} S, 5 $\phi$ C_{14} S and 7 $\phi$ C_{14} S can be lowered to 15x10^{-2}, 85x10^{-3} and 28x10^{-4} mN/m, respectively. Similarly, D-IFT values of 3 $\phi$ C_{16} S, 5 $\phi$C_{16} S and 7 $\phi$ C_{16} S can be lowered to 95x10^{-3}, 45x10^{-4} and 15x10^{-4} mN/m, respectively. From this sequence, one can deduce that 1-phenyltetradecane and 1-phenylhexadecane sodium sulphonate isomers will have higher D-IFT values than that obtained by 3 $\phi$ C_{14} S or 3 $\phi$ C_{16} S, respectively.

![Fig. 5: Dynamic Interfacial tension behaviour of three phenylhexadecane sodium sulphonate isomers](image-url)
**Effect of Alkalinity on D-IFT**

Figures (6) and (7) show that only the dynamic interfacial tension of 3 F C\textsubscript{14} S and 3 F C\textsubscript{16} S decrease as alkalinity increases without the appearance of v-shaped curve. However, 3 Φ C\textsubscript{14} S and 3 F C\textsubscript{16} S precipitate when alkalinity is greater than 24 and 22 g/L, respectively. But each of 50C\textsubscript{14} S and 7FC\textsubscript{14} S gave (D-IFT)\textsubscript{min} values at their respective optimum alkaliniti of 24 g/L and 12 g/L NaOH, respectively. Similarly, each of 5ΦC\textsubscript{16} S and 7ΦC\textsubscript{16} S gave their (D-IFT)\textsubscript{min} values through v-shaped curves at optimum alkalinity of 22 and 8 g/L NaOH. The difference in alkalinity tolerance is attributed to molecular structure, i.e., terminal-
position phenylalkane sodium sulphonates have the least alkalinity tolerance, whereas, mid-position phenylalkane sodium sulphonates show the highest alkalinity tolerance to NaOH. Some investigators postulated an imaginary surfactant molecular arrangement model illustrating the effects of electrolyte on the interfacial tension of 3-phenyl-, 5-phenyl-, and 7-phenylalkane isomers [Zhao, G.X. (1991)]. The addition of electrolyte to solutions of ionic surfactants in aqueous solution causes an increase in the aggregation number presumably because of compression of the electrical double layer surrounding the ionic heads [Rosen, M.J. Chapter 3. (1989)]. For the investigated anionic phenylalkane sodium sulphonate isomers; Na\(^+\) would compress the double layer and shorten the molecular distance on interface [Zhao, G.X. (1991)]. As NaOH concentration increases, the molecular distance is shortened readily and the number of molecules on the unit area would also increase gradually, then the winding of long chain would tend to be “stretched” gradually, leading to the decrease of interfacial tension.

In figure (8), increasing NaOH concentration causes a steady decrease in D-IFT of 1-phenylalkane sodium sulphonates. However, precipitation of these surfactants was observed at 24, 22, and 16g/l NaOH for 1\(\Phi\)C\(_{12}\) S, 1\(\Phi\)C\(_{14}\) S and 1\(\Phi\)C\(_{16}\) S, respectively. Although D-IFT measurements were carried out at 60°C, i.e., above the Krafft point of these surfactants [El-Mergawy. S.A. (1989)], addition of a co-surfactant is necessary in these formulations in order to prevent precipitation and to achieve lower interfacial tensions [Zhang. S.B. et al., (2004)].

**Conclusions**

1. In an alkane/ aqueous system of mid-position phenyl-tetradecane and phenylhexadecane sodium sulphonate isomers, IFT decreases as the phenyl group shifts toward the middle of the alkyl chain.
2. The minimum IFT of the investigated isomers differs in magnitude and their capabilities for lowering IFT follow the sequence: 7-phenyl-isomers > 5-phenyl-isomers > 3-phenyl-isomers. This sequence is in accordance with g\(_{\text{enc}}\) values of these isomers.
3. Dynamic interfacial tension minimum (D-IFT)\(_{\text{min}}\) values of 5-phenyl-and 7-phenylalkane isomers, are achieved through v-shaped curves at their respective optimum alkalinity. D-IFT of 3-phenylalkane isomers decreases as alkalinity increases without the appearance of v-shaped curve.

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**Fig. 8: Dynamic Interfacial Tension of three 1-phenylalkane sodium sulphonates against n-Octane as a function of alkalinity**
4. Ultralow (D-IFT)\textsubscript{min} values are obtained by 7FC\textsubscript{16} S and 5FC\textsubscript{16} S isomers if compared with 7FC\textsubscript{14} S and 5FC\textsubscript{14} S. These (D-IFT)\textsubscript{min} values are achieved at lower NaOH concentrations.

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REFERENCES

1. Barakat, Y., Gendy, T.S., Mohamad, A.I. and Youssef, A.M., “CMC of Some Ethoxylated Alkylphenol-Formaldehyde Nonionics” British Polymer J. 21(5): 383 (1989).

2. Barakat, Y.; Fortney, L.N.; Schechter, R.S., Wade, W.H., Yiv, S.H., and Graciaa, A. “Criteria for Structuring Surfactants to Maximize Solubilization of Oil and Water. II-Alkyl Benzene Sodium Sulphonates”. J. Coll. Interface Sci., 92(2): 561 (1983).

3. Cayyas, J.L, Schechter R.S. and Wade W.H. “The Measurement of low Interfacial tension via the spinning Drop Technique.” ACS Symposium Series, No. 8: Adsorption at Interface, Paper. 17: 234 (1975).

4. Doe, PH, EL Emary. M. Schechter, R.S. Wade, W.H. “Surfactant for Producing Low Interfacial Tensions. I : Linear alkyl benzene sulphonates.” J. Amer. Oil Chemists. Soc. 54(12): 570-577, (1977).

5. Draper N.R. and Smith, H. “Applied Regression Analysis, John Wiley and Sons Inc. New York (1968).

6. El-Kholy, S.A. “A Study on Some Applications for Some Surface-Active Agents, Ph.D. Thesis, Faculty of Women, Ain Shams University, Cairo, Egypt, (1993).

7. El-Mergawy S.A. “Laboratory Evaluation of Some Alkylbenzene Sulphonates for Enhanced Oil Recovery” Ph. D. Thesis, Faculty of Science, Ain Shams University, Cairo, Egypt, (1989).

8. Feng, J.; Rodriguez, C.; Izawa, T.; Kunieda, H. and Sakai, T. “Effect of Novel Alkanolamides on the Phase Behaviour and Surface Properties of Aqueous Surfactant Solution” J. Disper. Sci. Tech., 25(2): 163-172 (2004).

9. Gale, w.w. and Sandvik, E.I. “Tertiary surfactant Flooding : petroleum sulfonate composition – efficiency studies”. Paper SPE 3804, presented at Improved Oil Recovery symposium of SPE, Tulsa, April, 1972, SPE J., 191(August 1973).

10. Kanaggs, E. “Petroleum sulfonale utilization in enhanced oil recovery systems” Paper SPE 6006 Presented at the 51st Annual Fall Technical Conference of SPE, New Orleans, (October 1976).

11. Rosen, M.J. “Surfactants and Interfacial Phenomena-Adsorption of Surface-Active Agents at Interfaces- The Electrical Double Layer, 2nd Ed., Chapter 2, John Wiley and Sons, New York, 64-84 (1989).

12. Rosen, M.J., “Surfactants and Interfacial Phenomena micelle Formation by Surfactants”, 2nd Ed. Chapter 3, John Wiley & Sons, New York, 108-114 (1989).

13. Rosen, M.J., “Surfactants and Interfacial Phenomena-Reduction of Surface and Interfacial Tension by Surfactants 2nd Ed. Chapter 5, John Wiley & Sons, New York, 212-228 (1989).

14. Rosen. M.J, Wang. H, Shen. P, and Zhu. Y. “Ultralow Interfacial Tension for Enhanced Oil Recovery at very low Surfactant concentrations”. Langmuir, 21: 3349-2356. (2005)

15. Rudin J., and Wasan D.T. “Mechanisms for lowering of interfacial tension in alkali/ acidic oil systems: Effect of added surfactant. Industrial and Engineering Chemistry Research, 31(8): 1899-1906 (1992).

16. Sandvik, E.L., Gale, W.W. and Denekas, M.O., “Characterization of petroleum sulfonates” paper SPE 6120 Presented at the 51st Annual Fall Technical Conference of SPE, New Orleans, (October1976).
17. Schechter, R. S. and Wade, W.H. “Annual Report Research on Tertiary Oil Recovery,” Energy Research Administration Grant. The University of Texas at Austin, (1980/1981).

18. Shah, D.O. and Walker, R.D. “Research on chemical oil Recovery System”, Fifth and Sixth Semi-Annular Report, Engineering and Industrial Experimental station, College of Engineering, University of Florida, Gainesville, USA, (1978).

19. Shah, D.O., Tamgeedi, A., Falco, J.W. and Walker, R.D. “Interfacial instability and spontaneous formation of microemulsion” Alche. J., 18(6): 1116 (1972).

20. Smith, G.D. “Commercial Surfactants: An Overview”, in solution chemistry of surfactants, K.I. Mittal Ed., plenum press, New York, 1: 195-216, (1979).

21. Wade, W.H., Morgan, J., Jacobson, J., Salager, J.L. and Schechter, R.S. “Interfacial Tension and Phase Behaviour of Surfactant Systems” SPE J. 242-252 (August 1978).

22. Wade, W.H. and Schechter, R.S. “Capturing that Hidden Oil Discovery”, March 4 (1977).

23. Wilchester, H.I. “Laboratory studies on oil recovery with aqueous dispersions of oil-soluble sulfonates”. Paper SPE 4742 presented at the Improved Oil Recovery Symposium of SPE, Tulsa (April, 1974).

24. Zhang S.B., Xu Y., Qiao W.H. and Li S.H. “Interfacial tensions upon the addition of alcohols to phenylalkanes sulphonate monoisomer systems”. Fuel 83: 2059-2063 (2004).

25. Zhao, G. X, “Physical Chemistry of Surfactants.” Peking university Press. pp. 426-453 (1991).