FORMULATION OF BIPHASE CLEANING AGENTS AND THEIR CLEANING EFFECT ON OILY SOILED METAL SUBSTRATES

Omuku P.; Onwumelu H.A. and Egwuatu, C.I.
Department of Pure and Industrial Chemistry
Nnamdi Azikwie University, Awka, Nigeria
E-mail: patrickemm@yahoo.co.uk

ABSTRACT

Castor oil and olive oil (vegetable oil) used in the preparation of the soda soaps in this investigation were bought from Onitsha main market, Anambra state of Nigeria, while the soya bean oil was extracted from the soya bean seed. Ternary diagram was utilized in the determination of the various compositions of the biphase mixture (soap solution, kerosene and water) for the preparation of the biphase cleaning agents. The rating of the cleaning performance of the biphase cleaning agents formulated from the different vegetable oil soda soaps were examined via a three-member panel. Their judgement showed that castor oil had the best cleaning performance rating of 73% on the oily soiled metal surface. The trend observed in their cleaning performance capacity was castor oil>olive oil>soya bean oil. The solution of the soap alone could not effectively clean the oily soiled metal surfaces but the mixture of soap solution, kerosene and water performed the magic of not only effectively cleaning. The soiled metal substrates but did so with ease. The castor oil had the largest area of immiscibility of 220mm^2 while 148mm^2 and 156mm^2 were associated with olive oil and soya bean oil respectively. The best cleaning performance of the biphase mixture was observed with compositions, 40% soap solution, 40% kerosene and 20% water. This showed that the less the composition of water with a greater percentage of kerosene the more enhanced the cleaning capacity of the biphase mixture. For a more effective and easy way of cleaning oily soiled metal substrates, a biphase mixture of soap solution, kerosene and water in the ratio of 2:2:1 may do the wonder.

KEYWORDS: biphase, immiscibility, oil, ternary diagram, mixture

INTRODUCTION

Oily soil is one of the major obstacles encountered today by many industries especially the metal work and mechanical industries. This industrial challenge occurs as a result of the addition of grease to the machine parts in order to lubricate them and thereby reduce friction [1]. This problem necessitated scientists to look for effective and efficient way of removing the oily soil from the substrates. It was discovered that soap solution alone cannot effectively clean the oily soiled surface but the addition of water and kerosene to the soap solution perform the magic, hence the need for this research work is to properly determine the right proportions of kerosene, water and soap solution that can be mixed to obtain the right biphase cleaning agent for oily soiled metal surfaces [2]. For easy removal of oily soiled from metal substrates, a biphase cleaning agent containing a surfactants which are surface active agents interact with the surfaces of two phases of oil and water. A surfactant (soap) is made up of the hydrophilic part and hydrophobic (high hydrocarbon chain) part. The hydrophilic part makes the soiled compound sufficiently soluble in water. The presence of surfactant in detergents makes the latter to penetrate and wet soiled surfaces to displace and solubilize oily soiled and grease as well suspend certain oils in solution to prevent their redeposition[3].

The knowledge on the phase manifestation of the pseudo-ternary (water/kerosene/oil) or explicitly quaternary (water/sulfactant/ consultant/oil) mixtures has been systematized. At low surfactant concentration, there is a sequence of equilibria between phases, the lower (oil/water) micro-emulsion phase in equilibrium with the upper excess oil [4]. The following advantages can be obtained using biphase cleaning agents in comparism with normal soap solutions: Higher emulsion, stability, excellent product distribution on and in the substrate, pronounced breaking, very high internal softness, excellent surface smoothness, increased abrasion resistance and high washing permanence(s) the large variety of applications from enhanced oil recovery to nanoparticle synthesis as well as the steadily increasing number of research workers engaged in studies on biphase and micro-emulsions due to their unique properties, have made significant contributions to many branches of chemistry and technology and suggest that the potential of biphase and micro-emulsions as novel compartmentalized liquids will be even more significant in future (6) hence the need to embark on this work in a view to understanding better or improved biphase cleaning agent compositions [7-13].

MATERIALS AND METHODS

The vegetable oils (castor oil, olive oil) used in this investigation were bought from Onitsha main market, South East of Nigeria while the soya bean oil was extracted from its source.

Preparations

Soap: 200g each of the oil was run into a beaker, using the appropriate saponification value for the determination of the appropriate quantity of NaOH to be used, small amount of NaOH solution (7%) concentration was added and stirred to form emulsion. The mixture was then heated in open flame. The remaining more concentrated (50%) solution of NaOH was added simultaneously in small amount to the emulsified oil. The heating and stirring continued until saponification was almost completed. Salting out was done using saturated brine which separates soap and aqueous layer containing the glycerine and dirts. The aqueous layer was drawn out by decantation. In order to ensure complete absence of oil from the soap, more water and lye were added to the soap which was boiled with steam to aid the saponification. The brine-washing soap had a grainy appearance. The 'neat soap' was obtained by gradually adding water while boiling until the mass lost its grainy texture and became smooth and gelatinous, which led to two physical forms of soap. The desired neat soap at the top and the nigre at the bottom.

Biphase Cleaning Agent

The preparation of the biphase cleaning agent from a mixture of kerosene, soap solution and water was achieved using a ternary diagram. Different proportions of the mixture was arrived at by choosing a point [6.7] on the ternary diagram to get the value of each soap solution, draw a line perpendicular to the soap solution axis. This was also applied to the kerosene and water axis. When the temperature (room temperature, 30^0C) and the pressure (1 atm) were kept constant, the volume of kerosene (Vk), soap solution (Vs) and water (Vw) variables are related to each other by Vk + Vs + Vw = 100%. In this method, the volume of the component mixture at the constant temperature and pressure are expressed by means of an equilateral triangle. Weigh out the appropriate volumes as obtained from the ternary diagram into a beaker and shake vigorously to obtain emulsion or biphase in which biphase is our target.

Metal Substrates

The 3 by 4 metal panels were prepared and washed using a commercial detergent (omo) with warm water they dried at room temperature (30^0C) for several hours to obtain homogenous surface.

Soil

The soil was prepared by a mixture of 50g of paint thinner, 10g of mineral oil (engine oil), 4g of vegetable oil, 10g of clay and 4.5g of graphite powder [3]. The mixture was agitated for 30min and was left for 3 days before use [3].

Soil Metal Panels

4cm^3 of the prepared soil each was used to soil a metal panel by pouring it on the metal and spreading with the help of a party brush so as to improve uniformity.

Cleaning Test for the Removal of Oily Soil on Metal Plates

Sponge is prewetted with 10cm^3 of the biphase cleaning agent. The cleaning was done in such a way that the scrubbing action is perpendicular to the direction of soiling. The prewetted sponge was used to clean the soiled metal plate for 10 cycles. The cleaning performance was evaluated by comparing the cleanliness of the washed/scrubbed panel to that made on cleaned unsoiled test panel and other soiled panels with different degrees of paint thinner. The same cleaning test was repeated over the remaining soiled metal panels with other biphase cleaning agents from other soap at the same concentration. A panel of three member was set-up to judge the cleaning performance of these biphase cleaning agents.

RESULTS AND DISCUSSION

Table 1: Effect of Castor Oil Soda Soap on Miscibility of Kerosene and water

S/No	Soap solution cm^3	Kerosene cm^3	Water cm^3	Phase distribution
1	5	85	10	Emulsion
2	10	85	5	Emulsion
3	10	75	15	Emulsion
4	20	70	10	Biphase
5	25	60	15	Biphase
6	10	60	30	Biphase
7	30	60	10	Biphase
8	70	20	10	Biphase
9	30	55	15	Biphase
10	20	55	25	Biphase
11	15	50	35	Biphase
12	50	40	10	Biphase
13	40	40	20	Biphase
14	20	40	40	Biphase
15	10	35	55	Biphase
16	30	35	35	Biphase
17	40	35	25	Biphase
18	10	25	65	Biphase
19	20	15	65	Biphase
20	5	10	85	Emulsion

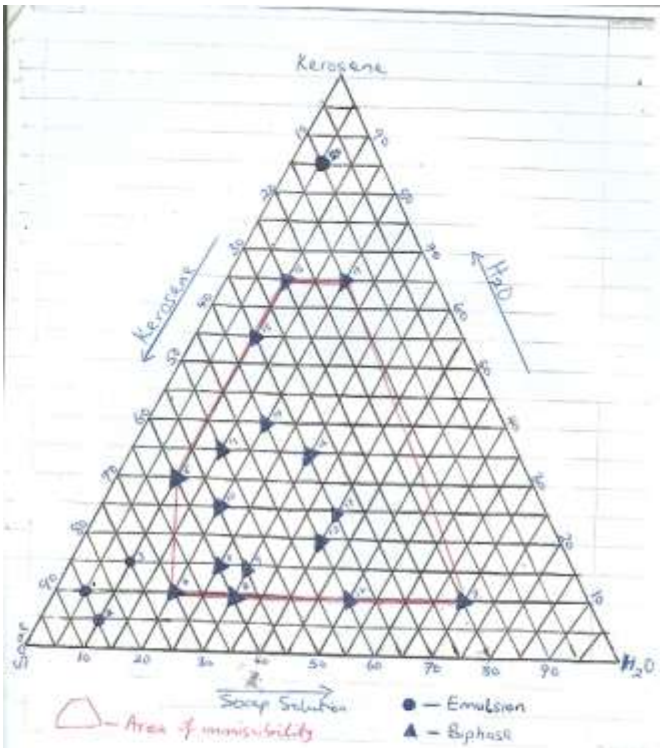

Fig. 1: Ternary diagram showing the effect of castor oil soda soap on miscibility of kerosene and water

Table 2: Effect of Olive Oil Soda- Soap on Miscibility of Kerosene and water

S/No	Soap solution cm^3	Kerosene cm^3	Water cm^3	Phase distribution
1	5	90	5	Emulsion
2	5	80	15	Emulsion
3	15	80	5	Emulsion
4	10	70	20	Emulsion
5	20	70	10	Emulsion
6	15	60	25	Emulsion
7	25	60	15	Emulsion
8	30	55	15	Biphase
9	20	55	25	Biphase
10	10	55	35	Biphase
11	10	40	50	Biphase
12	50	40	10	Biphase
13	20	35	45	Biphase
14	35	35	30	Biphase
15	45	10	45	Biphase
16	30	30	40	Biphase
17	10	20	70	Biphase
18	60	20	20	Biphase
19	25	10	65	Biphase
20	70	10	20	Biphase

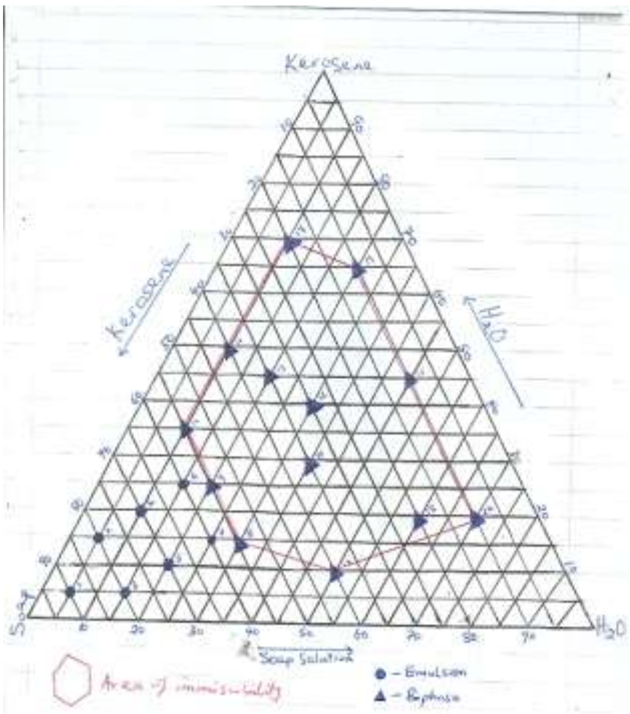

Fig. 2: Ternary diagram showing the effect of Oliver oil soda soap on miscibility of kerosene and water

Table 3: Effect of Soya Bean Oil Soda-soap on Miscibility of Kerosene and water

S/No	Soap solution cm^3	Kerosene cm^3	Water cm^3	Phase distribution
1	30	60	10	Biphase
2	20	60	20	Biphase
3	10	60	30	Biphase
4	10	70	20	Emulsion
5	30	45	25	Biphase
6	50	40	10	Biphase
7	40	40	20	Biphase
8	20	40	40	Biphase
9	40	35	25	Biphase
10	20	35	45	Biphase
11	10	30	60	Biphase
12	10	20	70	Emulsion
13	25	20	55	Biphase
14	20	10	70	Biphase
15	50	10	40	Biphase
16	20	70	10	Emulsion
17	50	25	25	Biphase
18	10	80	10	Emulsion
19	5	75	20	Emulsion
20	15	65	20	Emulsion

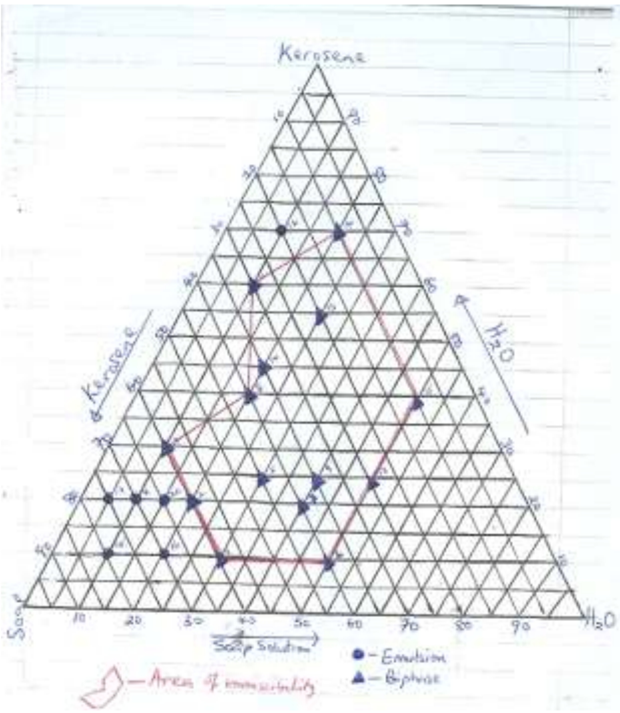

Fig. 3: Ternary diagram showing the effect of soya bean oil soda soap on miscibility of kerosene and water

Area of Immiscibility

The phases obtained when immiscible kerosene and water mixes with soap were emulsion and biphase mixtures. Area of immiscibility is the region where biphase mixture occurs. The area of immisicibility is measured by counting square method (7). Counting square method involves counting the number of square that fell within the region of biphase mixture in the ternary diagram. The area of each square of the graph sheet (graph paper) used in this work was $4mm^2$. In each of the formulations, the area of immisicibility was given as $N4mm^2$ (where N= no of squares within the region of biphase mixture). In the ternary diagrams (Figure 1, 2 and 3), the region where the biphase mixture was formed is the portion circled in each of the ternary diagram. Other areas formed are the emulsion phases. The calculation of the area of immiscibility was done for the different soda soap following the order in which they were emulsified (Table 4).

Table 4: Area of Immiscibility of the different vegetable oil soda soap solution

Soap	Area of immiscibility (mm^2)	Saponinfication No.	Hydrophobic chain length	Degree of unsaturation
) Castor oil	220	180	C_{18}	One
) Olive oil	148	196	C_{18}	One
) Soya bean oil	156	192	C_{18}	Two

It was discovered that castor oil soda soap had the largest area of immiscibility with a value of $220mm^2$ and consequently occurred with the least region of emulsification. Olive oil soda soap occurred with the smallest area of immiscibility with the value put as $148mm^2$ but had the greatest area of emulsification. The observable trend in the area of immiscibility of the vegetable oil soda soap was castor oil>soya bean oil> olive oil.

The performance of the biphase cleaning agents formed from the various compositions of the vegetable oil soda soap, kerosene and water was examined by judge of three-member panel. Their judgement were recorded in form of total rating score of 100% (table 5).

Table 5: Cleaning performance of a biphase cleaning agent with varying composition of 25% soap, 25% kerosene and 50% H_2O

S/n	Vegetable oil	% performance 3-member panel			Total	% average performance	Saponification No.	Carbon hydrophobic chain length	Degree of unsaturated
		1st	2nd	3rd					
1	Castor oil	70	60	60	190	63	180	C_{18}	One
2	Olive oil	60	60	60	180	60	196	C_{16}	One
3	Soya bean oil	60	60	50	170	57	192	C_{18}	Two

Table 6: Cleaning performance of 30% soap, 30% kerosene and 40% water composition

S/n	Vegetable oil	% performance			Total	% average performance	Saponification No.	Carbon hydrophobia chain length	Degree of unsaturated
		1st	2nd	3rd					
1	Castor oil	60	70	70	200	66	180	C_{18}	One
2	Olive oil	70	60	60	190	63	196	C_{16}	One
3	Soya bean oil	60	60	60	180	60	192	C_{18}	Two

Table 7: Cleaning performance of 40% soap, 40% kerosene and 20% water composition

S/n	Vegetable oil	% performance			Total	% average performance	Saponification No.	Carbon hydrophobe chain length	Degree of unsaturated
		1st	2nd	3rd					
1	Castor oil	70	80	70	220	73	180	C_{18}	One
2	Olive oil	80	70	60	210	70	196	C_{18}	One
3	Soya bean oil	70	60	60	190	63	192	C_{18}	Two

The composition of 25% soap solution, 25% kerosene and 50% water gave percentage mean performance of 63% for the castor oil soda soap while 60% and 57% average performance rating score were associated with the olive oil soda soap and soya bean soda soap respectively (Table 5). The castor oil had the largest area of immisicibility, least saponification number but with greatest cleaning performance rating capacity-the trend in the average performance rate correlates neither with the saponification number nor the area of immiscibility but may be said to vary with the degree of unsaturation to certain extent. It can be said that the greater the degree of unsaturation the less the mean performance of the vegetable oil soda soap.

The trend observed in the cleaning performance of the biphase composition of 30% soap solution, 30% kerosene and 40% water was castor oil > olive oil> soya bean oil with values 66%, 63% and 60% respectively. It was observed that as the compositions of soap solution and kerosene increased from 25% to 30% with a corresponding decreased in the value of water from 50% to 40%, the average cleaning performance increases (from 63% castor oil, 60% olive oil and 57% soya bean oil to 66% castor oil, 63% olive and 60% soya bean oil).

The most enhanced cleaning performance was observed in the composition of 40% soap solution, 40% kerosene and 20% water for the biphase mixture. Castor oil with area of immiscibility 220mm^2 and C_{18} saturated hydrophobic carbon chain length had the best effective cleaning capacity of 73% average performance rate. The observable trend in the cleaning performance was castor oil> olive oil> soya bean oil. This trend in the performance rating was observed for the various compositions of the biphase mixture. It was also noticeable that the C_{18} mono saturated hydrophobic chain length had the best cleaning performance rating.

CONCLUSIONS

The biphase composition of 40% soap solution, 40% kerosene and 20% water gave the best cleaning performance rating of 73% for castor oil, soda soap, 70% for olive oil soda soap while soya bean oil soda soap had 63% performance rating. The area of immiscibility of castor oil soda soap was $220mm^{2,}$ while $156mm^2$ and $148mm^2$ were associated with soya bean oil and olive oil respectively.

Generally, it was observed that the biphase mixture of soap solution, kerosene and water had a more enhanced and more effective for cleaning oiled soiled metal substrate when compared to the cleaning effects of ordinary soap solution alone.

References

1. Bidjiet, K. P. and MOulik, P. S. (2001). Uses and Application of Microemulsions. *Current Science,* Vol. 80, No. 8 pp. 990-1000.

2. Kumar, P. and Mittal, K. L. (1999). Handbook of Microemulsion. *Science and Technology, Marcel Dekkar Inc. New York* pp. 755-771.

3. Larsson, K. and Osborne, D. W., Peshek, C. V. and Chipman, R. J. (1991). Microemulsion and Emulsions in foods. *Am. Chem. Soc. Washington D.C.* pp. 44-50

4. Gan, L. M. and Chew C. H. (1996). Polymene materials Encyclopedia *CRC Press, Boca Raton.* P. 4321.

5. Larsson, K. (1994). Lipids: Molecular Organization, Physical Functions and Technical Applications. *Oily Press, Dundee Scotland*. p.9.

6. Baran, J. R. Pope, G.A. and Wade, W. H. (1998). Mixed Sufactant Systems for Microemulsion formation with chlorinated hydrocarbons. *Am. Cad. Environ. Engg. Washington DC.*

7. Tondre, C. (2000). Surfactant –Based Separations, Science and Technology. *ACS Symp. Ser. 740, AM. Chem. Soc.,* Washington DC. Pp. 279-280.

8. Sharma, K.K. and Sharma, K.L. (1999). A Textbook of Physical Chemistry. *Vikas Publishing House PVT Ltd, New Delhi,* 4th Revised Edition, pp. 320- 331.

9. Ibemesi, J. A. (1994). Physical Chemistry for Tertiary Institution. *Snaap Press Enugu.* pp. 82-84.

10. Peter, B. (1978). Detergent and Laundry Products. *Household Pest Control* 2nd edition pp. 10-22.

11. Ruldolf, W. (2007). Water Precipitation Softening system for detergent, bleaching and hand dishwashing agents. *Paul and Paul Philadephia* PA. US pp. 3-8.
12. Silberg, S. (2000). The Molecule Nature of Matter and change. *Information Division Unilever Ltd, London* 2nd edition, pp. 441-445.

13. Richard, P. S. et al (2001). Solution of I-butyl-3-methyl imidazolium hexafluorophosphate in aqueous ethanol, a green solution for dissolving hydrophobic ionic liquids. *J. Chem. Commun. pp. 2070-2071.*