Studies on The Interfacial Tension and Surface Tension of Oil /Water Emulsion

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ABSTRACT This paper deals with the effect of the various factors on the interfacial tension and surface tension of oil/water emulsions. The factors includes surfactant concentration, temperature, electrolyte, aging and co-surfactant. Interfacial tension has been emphasized a tool to test the efficiency of surfactant in forming oil/water emulsions as well as in maintaining their stability. Some workers in this field believe that interfacial tension is the only significant factor in the interface stability, since oil/water system is a system of two immiscible liquids and in which surfactant and co-surfactant must be added for lowering interfacial tension to form stable system.

Introduction:-

The effect of the following factors on the interfacial tension and surface tension of oil/water emulsions is been studied and analyzed in this article, the factors which were being studied are as under:-

a) Surfactant concentration b) Temperature c) Electrolytes d) Aging e) Co-surfactant

Surfactant concentration:

It has been observed that as the concentration of surfactants increases . The interfacial tension and source tension of kerosene oil/water emulsion shows decline, first rapidly then slowly. This lowering of interfacial and surface tension is due to desorption. This adsorption shows tendency to reach a more or less constant value. Such a result is in harmony with the view that the adsorbed material from mono layer on the surface. As the concentration of the surfactant is gradually increased the amount adsorbed increases until a complete monolayer is formed. The efficiency of the surfactants was found to have the following order,RL-1,RL-2,RL-3.1.2% RL-3 reduces the interfacial tension of kerosene oil/water interface from 48dynes/cm to 3.51dynes/cm. The results are in good agreement with earlier work.

Effect of Temperature:

Temperature shows an adverse effect on interfacial tension and surface tension. The decrease in linear with rise in temperature. This also proves the work of earlier workers.

Effect of Aging:

The result shows with the increase of aging time from 0 hrs to 2 hrs. the interfacial tension and surface tension of oil/water emulsions have a linear decrease in their values. But with further aging the values of interfacial tension and surface tension gets stabilized.

Effect of Electrolytes:

The effect of various electrolytes viz. NaCl, $CaCl_2$, and $AlCl_3$ on the interfacial tension and surface tension was studied. The concentration of surfactants was kept constant while the concentration of electrolytes varied in the range of 100, 200, 400, 800 and 1000 ppm. It is observed from the studies that in the case of electrolytes viz. NaCl, $CaCl_2$ and $AlCl_3$ the fall in interfacial tension and surface tension with all the three electrolytes is maximum when $AlCl_3$ is used. It is also concluded that the valency of cation also play an important role in lowering the interfacial and surface tension. The lowering of interfacial tension and surface tension is higher at the lower concentration i.e. 100, 200, & 400 ppm. But with the further increase of electrolyte concentration i.e. 800 and 1000 ppm the fall in values of interfacial tension and surface tension becomes linear and does not depend upon the surfactant used.

Effect of Co surfactant:

The study of the effect of co-surfactant on the interfacial tension of kerosene oil/water + 1% surfactant interface shows that lowering of interfacial tension is more at 0.1 % and 0.2% concentration of n-hexanol(co-surfactant) in case of RL-1 and RL-2 after that the decrease becomes linear while in the case of RL-3 change become linear after 0.4% of n-hexanol respectively. The same phenomenon is observed in the case of surface tension of oil/water emulsion, with the addition of co-surfactant becomes more effective in the lowering of interfacial tension of oil/water interface with addition of 100ppm of NaCl.

Interfacial tension has been emphasized a tool to test the efficiency of surfactant in forming oil/water emulsions as well as in maintaining their stability. Some workers in this field believe that interfacial tension is the only significant factor in the interface stability, since oil/water system is a system of two immiscible liquids and in which surfactant and co-surfactant must be added for lowering interfacial tension to form stable system. According to Gibb's law the monomers of added surfactant/co-surfactant absorbed at the interface and tend to orient themselves in a particular manner. Lowering of the interfacial tension at liquid/liquid interface is characteristic property of surfactant. This property becomes sometimes complicated by the following phenomena.

Interfacial tension does not attain equilibrium over a long period of time (phenomena of slow aging)

Interfacial tension vs concentration curve passes through a minimum at a certain concentration fairly close to the C.M.C.

It is the concentration of Bencroft(1,2) and later Z.Samec(3) that the adsorbed substance from the film having two surfaces between the two immiscible liquids one decidedly towards water and other towards oil when two liquids come into contact at a common surface, a mutual pull is exerted with a resulting reduction in surface tension and this pull tends to cause one liquid to spread over the other. The stronger the force of adhesion between the molecules of two liquids, the smaller the interfacial tension and greater the degree of spreading. If the force of adhesion is as great as or greater than the force of cohesion of the spreading liquid, the liquid will spread until it forms a continuous molecular film.

An experimental method was devised by Bencroft and Tucker to show that surface tension of emulsifying film is higher on the side of emulsified liquid. A pre-requisite for the formation and subsequent stability of emulsion in the lowering of interfacial tension. A substance capable of being adsorbed at the surface thereby decreasing the interfacial tension will act as a emulsifier or an efficient surfactant, Bencroft and Tucker(4) who applied the theory of Gibbs, which assumes that the film has two surface tensions. When it is in contact with different phases these two surface tensions are not necessarily equal and the film will tend to curl towards the side having the higher surface tension.

In all emulsions the dispersed liquid is in the side of the film having the higher surface tension. The low surface tension between the two liquids as usually measured is the difference between surface tension on the two sides of the films. The interfacial tension measured against a variety of hydrocarbons tends to change with times. The direction of change is most often towards higher interfacial tension the magnitude of these changes being depends on the surfactant concentration and alcohols used as co-solvents. The study of oil/water interface by using anionic, cationic, and non-ionic (ManoxolOT, Cetyl Pyridiumbromide and sodsulpho succinate) have been carried out. The study of various electrolytes viz NaCl, $CaCl_2$, $AlCl_3$ have been observed and concluded that electrolytes having the larger the size of cation is more effective in lowering the interfacial tension(5). Verdesevrkii et al (6) have given a rapid method for the determination of interfacial tension and COSE(7) (welting angle at oil/water interface) of aqueous surfactant solutions for the evaluation of their effectiveness in enhanced oil recovery by flooding.

LiSchramm(8) studied interfacial tension of the system particularly where the tension may be of very low magnitudes and concluded that the determination of interfacial tension may be useful for diverse reasons ranging from interactions at a molecular level to determining the influence of synthetic and natural surfactant on capillary number on EOR. In view of this the interfacial tension of oil/water interfaces were investigated by using the present surfactants not employed hitherto, which are of great industrial and technical importance (8,6) attempts to have been made to correlate their interfacial tension and surface tension lowering efficiency under the influence of various factors such as concentration temperature, aging, electrolytes etc of oil/water interfaces.

Experimental:
Materials used:-
Water:- Doubly distilled water having a conductivity. 1×10^{-6} ohm^{-1}cm^{-1} was employed through the course of investigation carried.

Oil:- Sufficiently large quantity of kerosene oil having 0.7948 g/mL sp gr doubly distilled and stored to ensure uniformity throughout the course of investigation.

Surfactants:- surfactants viz- RL-1, RL-2 and RL-3 used were prepared.

Electrolytes:- NaCl, $CaCl_2$, $AlCl_3$ were all of anal R grade BDH product.

Alcohol:- Hexanol used was of BDH AR grade.

Methods of Interfacial tension and surface tension measurements:-
Recent literature study reveals that much work has been done on crude oil-gas system as compared to the work available regarding measurement of very low interfacial tension between aqueous solutions and crude oil. DePhilleppe et al(10) after Mccaffery(11) have been able to use drop shape analysis to determine the interfacial tension between aqueous solution and ditumen at elevated temperature and pressures. Captive drop method has also been successful to determine interfacial tension. However Hrkins(42) earlier catalogued several methods for the determination of surface interfacial tension of liquids, but drop weight method has been considered by him the most accurate and appropriate. Hence through out the present investigation drop weight method has been used for the measurement of interfacial tension.

The densities of both phases was determined by means of pykometer at the temperature used in experiments , r the radius of dropping tip which was measured by a travelling microscope. The interfacial tension r^{a-w} is then calculated from the following equation:

$$r^{a-w} = \frac{v(d - d^1)g}{2rF(\frac{r}{v^{\frac{1}{3}}})}$$

Where 'v' is the volume of the single drop 'r' the radius of droping tip, g is the gravity , d & d¹ densities of aqueous and oil phase respectively F(r/v$^{1/3}$) is a correction factor.

Surface tension:- $r^{air-w} = \frac{vag}{2r(rv^{\frac{1}{3}})}$

Interfacial tension and surface tension Measurements:-
Effect of concentration of surfactants:-
2% (wt/vol) aqueous solution of different single surfactants viz RL-1, Rl-2, RL-3 were prepared. The different concentration viz 0.1, 0.2 , 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% of above sets have been obtained by diluting their stock solutions and interfacial tension against kerosene oil one by one at constant temperature of 25 1^{0}C . The results are shown in table 1 and plots between concentration of surfactants and IFT are represented in figure-1. The surface tension of above sets have also been measured in the same manner and the results presented in the table II and figure-2 respectively.

Effect of temperature:-

The interfacial tension and surface tension of all the above sets of surfactants at a constant concentration of 1% wt/vol a different temperature viz 20⁰, 30⁰, 40⁰, 50⁰, 60⁰, and 70⁰ have been measured respectively. The result provided in table III IV and figure 3-4.

Effects of Aging:-

The interfacial/surface tension of all the above sets of the surfactant at a constant concentration 1% wt/vol and temperature i.e. 25±1⁰C have been measured in the time range of 0,1,2,4,6,8 and 10 hours respectively. The result presented in table V-VI and figure 5-6.

Effect of Electrolytes:-

The effect of electrolytes regarding their nature and concentration and interfacial tension and surface tension at different concentration viz- 100, 200, 400, 800 and 1000 ppm of NaCl, CaCl$_2$ and AlCl$_3$ respectively. The results are summarized in table VII a-c and VIII a-c figure 7-12.

Effect of co surfactant in Hexanol:-

In order to study the effect of n-hexanol as co-surfactant on the interfacial/surface tension, of interface, the concentration of surfactant were kept constant i.e. 1% wt/vol and concentration of n-hexanol was varied in the range of 0.1, 0.2, 0.4, 0.6, 0.8 and 1% wt/vol have been studied. The result presented in table IX-X and figure 13-14 respectively.

The effect of co-surfactant on the interfacial tension of kerosene/water + 1% surfactant 100ppm NaCl have been studied by adding different concentration of co surfactant viz 0.1, 0.2, 0.4, 0.6, 0.8, and 1% vol respectively. The results is provided in table XI and figure 15.

Table-I
Effect of Emulsifier concentration on the IFT
Oil: Kerosene;   Temperature: 25⁰C

S. No	Concentration %	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0.1	39.53	35.04	33.08
2.	0.2	28.72	27.06	25.56
3.	0.4	22.55	20.03	18.25
4.	0.6	16.06	14.52	12.51
5.	0.8	13.21	11.75	9.35
6.	1.0	10.05	8.03	5.83
7.	1.2	8.09	6.02	3.51

Table-II
Effect of Emulsifier concentration on the Surface Tension
Oil: Kerosene;   Temperature: 25 ⁰C

S. No	Concentration %	Surface Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0.1	49.25	45.06	42.19
2.	0.2	37.90	36.52	34.40
3.	0.4	29.21	27.90	24.95
4.	0.6	22.56	20.31	18.30
5.	0.8	15.39	13.25	11.21

| 6. | 1.0 | 12.40 | 9.56 | 7.65 |
| 7. | 1.2 | 10.20 | 8.45 | 6.19 |

Table-III
Effect of Emulsifier concentration on the IFT
Oil: Kerosene;   Surfactant conc. : 1% wt/vol

S. No	Temperature ⁰C	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	20	10.25	7.95	5.73
2.	30	9.62	7.57	5.26
3.	40	9.15	7.08	4.82
4.	50	8.50	6.44	4.25
5.	60	8.02	5.92	3.90
6.	70	7.63	5.43	3.61

Table-IV
Effect of Emulsifier concentration on the IFT
Oil: Kerosene;   Surfactant conc. : 1% wt/vol

S. No	Temperature ⁰C	Surface Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	20	12.50	10.16	7.75
2.	30	11.75	9.64	7.30
3.	40	11.20	9.15	6.85
4.	50	10.60	8.50	6.40
5.	60	10.12	7.95	5.95
6.	70	9.70	7.45	5.50

Table-V
Effect of Aging on the IFT
Oil: Kerosene;   Surfactant conc. : 1% wt/vol
Temperature : 25 ±1⁰C

S. No	Time Hrs.	Surface Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0	10.05	8.03	5.83
2.	1	9.21	7.40	5.20
3.	2	8.73	7.00	4.70
4.	4	8.50	6.80	4.50
5.	6	8.46	6.60	4.40
6.	8	8.45	6.58	4.40
7.	10	8.30	6.50	4.30

Table-VI
Effect of Aging on the Surface Tension
Oil: Kerosene;   Surfactant conc. : 1% wt/vol
Temperature : 25 ±1⁰C

S. No	Concentration %	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0	12.40	9.96	7.65
2.	1	11.85	9.20	7.05
3.	2	10.80	8.75	6.15
4.	4	10.35	8.25	5.00

5.	6	10.10	8.05	4.90
6.	8	9.00	7.95	4.85
7.	10	9.00	7.95	4.85

Table-VII (a)
Effect of Electrolytes on the Interfacial Tension
Oil: Kerosene;   Surfactant conc. (RL-1) 1% wt/vol
Temperature: 25 1⁰C

S. No	Concentra- tion %	Interfacial Tension, dynes/cm		
		NaCl	$CaCl_2$	$AlCl_3$
1.	100	9.20	8.50	6.20
2.	200	7.30	6.20	4.00
3.	400	5.20	4.10	2.90
4.	800	4.80	3.90	2.20
5.	1000	4.50	3.70	2.00

Table-VII (b)
Effect of Electrolytes on the Interfacial Tension
Oil: Kerosene;   Surfactant conc. (RL-2) 1% wt/vol
Temperature: 25 1⁰C

S. No	Electrolyte Conc. ppm	Interfacial Tension, dynes/cm		
		NaCl	$CaCl_2$	$AlCl_3$
1.	100	7.90	7.51	6.00
2.	200	6.50	6.10	3.91
3.	400	5.20	4.10	2.80
4.	800	3.51	3.05	2.00
5.	1000	3.00	2.70	1.90

Table-VII (c)
Effect of Electrolytes on the Interfacial Tension
Oil: Kerosene; Surfactant conc. (RL-2) 1% wt/vol
Temperature: 25 1⁰C

S. No	Electrolyte Conc. ppm	Interfacial Tension, dynes/cm		
		NaCl	$CaCl_2$	$AlCl_3$
1.	100	5.0	4.7	4.2
2.	200	4.1	3.8	3.5
3.	400	2.3	2.0	1.6
4.	800	1.9	1.7	1.3
5.	1000	1.5	1.3	1.0

Table-VIII (a)
Effect of Electrolytes on the Interfacial Tension
Oil: Kerosene; Surfactant conc. 1% wt/vol
Temperature: 25 1⁰C

S. No	Time Hrs.	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	100	11.35	10.60	8.90
2.	200	9.40	8.70	6.75
3.	400	7.60	6.45	5.40
4.	800	5.85	5.50	4.85
5.	1000	5.50	4.90	4.15

Table-VIII (b)
Effect of Electrolytes on the Surface Tension
Oil: Kerosene;   Surfactant conc. 1% wt/vol
Temperature: 25 1⁰C

S. No	Time Hrs.	Surface Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	100	8.96	8.45	7.95
2.	200	6.80	6.30	5.60
3.	400	5.60	5.30	4.90
4.	800	5.10	4.80	4.35
5.	1000	4.80	4.25	3.75

Table-VIII (c)
Effect of Electrolytes on the Surface Tension
Oil: Kerosene;   Surfactant conc. 1% wt/vol
Temperature: 25 1⁰C

| S. No	Time Hrs.	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	100	6.55	6.25	5.90
2.	200	4.65	4.30	4.00
3.	400	3.65	3.55	3.30
4.	800	3.30	3.15	3.00
5.	1000	3.25	3.05	2.85

Table-IX
Effect of Co-surfactant on the Interfacial Tension
Oil: Kerosene;   Surfactant conc. 1% wt/vol
Temperature: 25 1⁰C   Co-surfactant : n-Hexanol

S. No	Co-sur- factant Conc. %vol/ vol	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0.1	9.1	7.2	5.0
2.	0.2	8.0	5.8	4.1
3.	0.4	6.5	3.6	3.0
4.	0.6	4.1	3.2	2.5
5.	0.8	3.5	2.8	2.0
6.	1.0	3.0	2.5	1.9

Table-X
Effect of Co-surfactant on the Interfacial Tension
Oil: Kerosene;   Surfactant conc. 1% wt/vol
Temperature: 25 1⁰C;   Co-surfactant : n-Hexanol

S. No	Co- surfactant Conc. % vol/vol	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0.1	11.15	9.20	6.85
2.	0.2	10.05	7.90	6.15

S. No	Co-surfactant Conc. % vol/vol	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
3.	0.4	8.50	5.65	4.65
4.	0.6	6.15	5.20	3.80
5.	0.8	5.70	4.80	3.30
6.	1.0	5.10	4.40	2.75

Table-XI

Effect of Hexanol on the Interfacial Tension of Kerosene+ Surfactant + NaCl/Water Interface
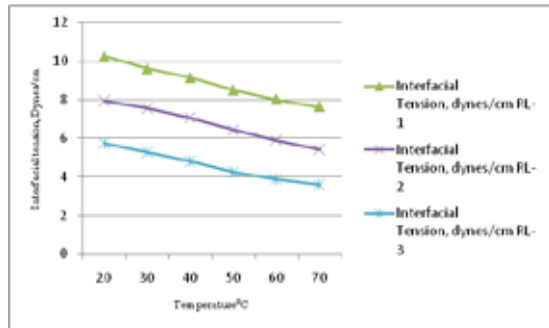Oil: Kerosene; Surfactant conc. 1% wt/vol
Temperature: 25 1^{0}C; NaCl : 100 ppm

S. No	n-Hexanol1% vol/vol	Interfacial Tension, dynes/cm		
		RL-1	RL-2	RL-3
1.	0.1	3.50	1.71	1.45
2.	0.2	2.15	1.30	0.91
3.	0.4	1.53	0.75	0.42
4.	0.6	1.02	0.52	0.23
5.	0.8	0.70	0.33	0.16
6.	1.0	0.50	0.25	0.10
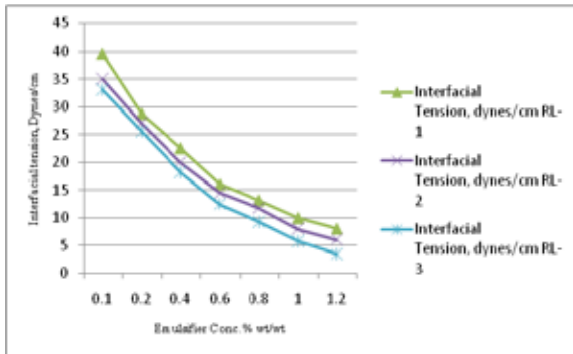
Graph-1:- Effect of Emulsifier Concentration on the Interfacial Tension
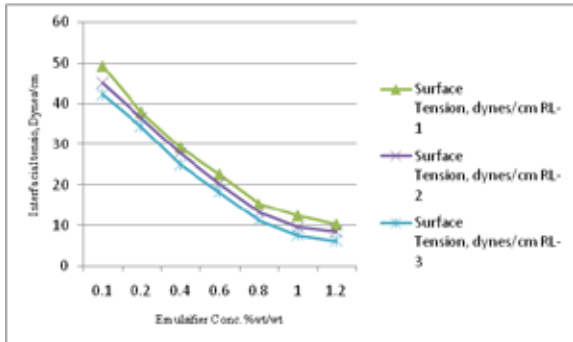
Graph-2:- Effect of Emulsifier Concentration on the surface tension.

Graph-3:-Effect of Temperature on the Interfacial Tension.
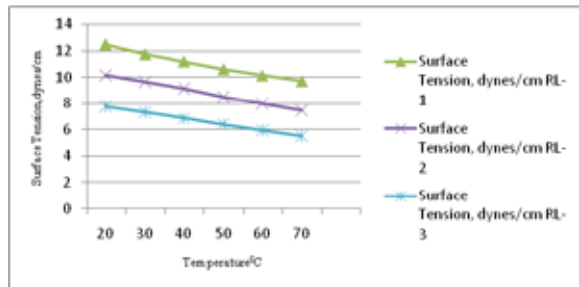
Graph-4:- Effect of Temperature on the surface tension.
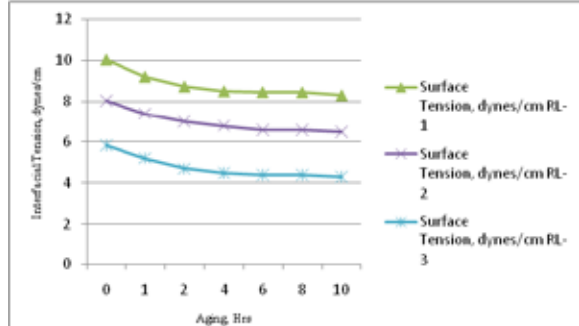
Graph-5:-Effect of Aging on the Interfacial tension.
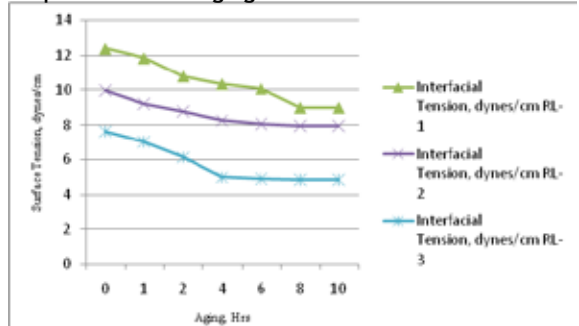
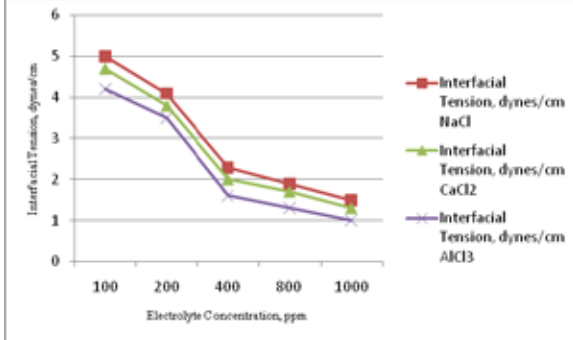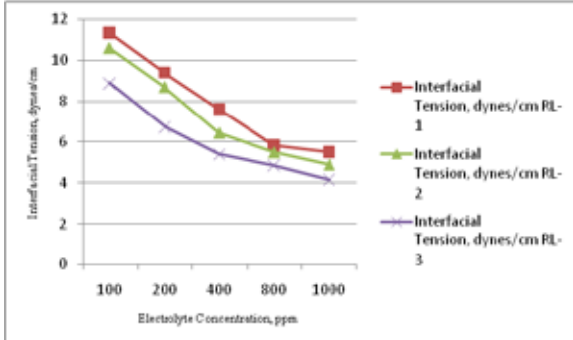Graph-6:-Effect of Aging on the surface tension.
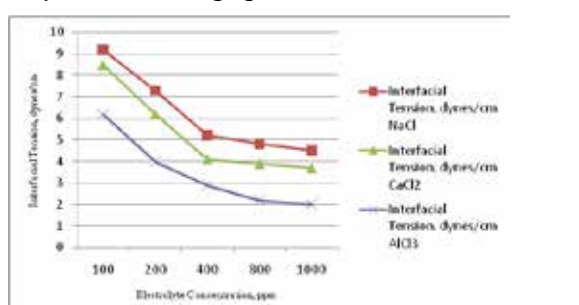
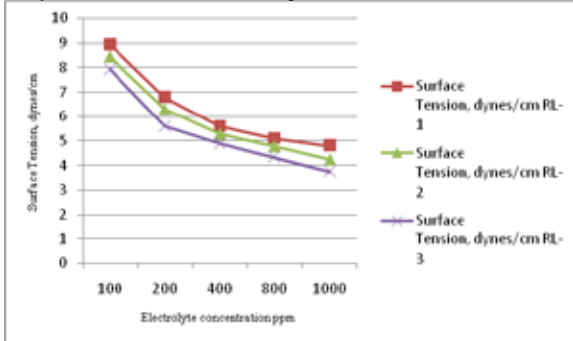Graph-7:- Effect of Electrolytes concentration on the Interfacial tension.
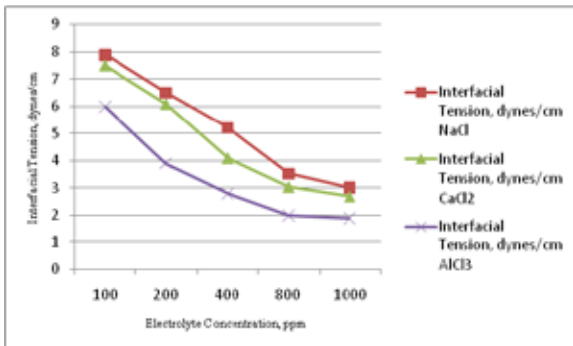
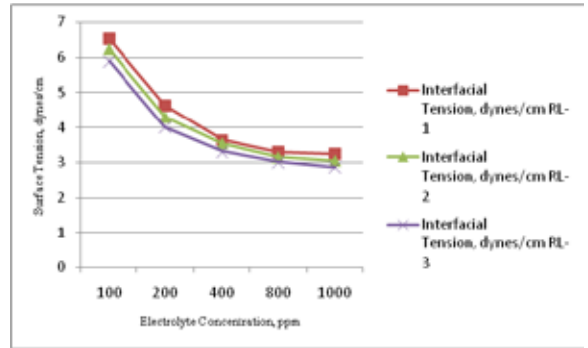**Graph-8:- Effect of Electrolytes on the Interfacial tension.**

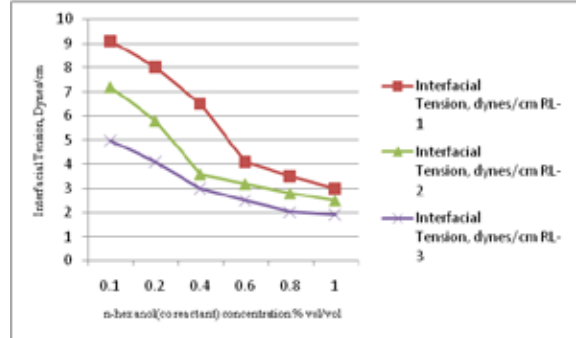**Graph-9:- Effect of Electrolytes on the Interfacial tension.**

Graph-10:- Effect of Electrolytes on the Surface tension.
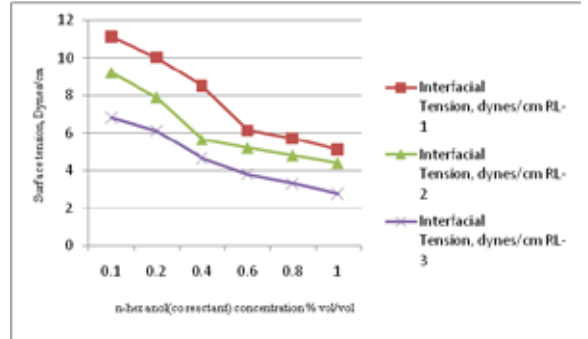

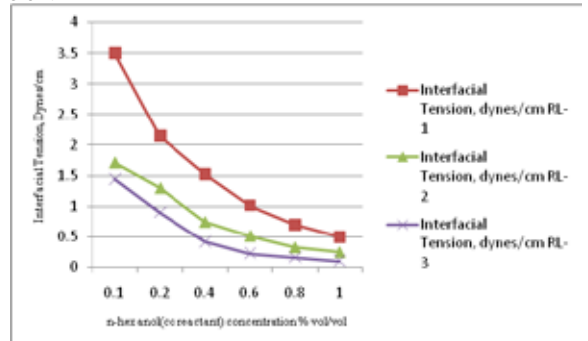**Graph-11:- Effect of Electrolytes on the Surface tension.**

Graph-12:- Effect of Electrolytes on the Surface tension.

Graph-13:- Effect of Co-surfactant on the interfacial tension.

Graph-14:- Effect of Co-surfactant on the surface tension.

Graph-15:- Effect of Co-surfactant conc. On the Interface of oil/water + Surfactant   +NaCl

Results and Discussion:-
Emulsifier Concentration:-
Graph 1-2 and data present in 1-11 table shows that as concentration of surfactants increases, the interfacial tension of kerosene oil/water interface and surface tension of

oil/water interface and surface tension of oil/water system decreases respectively. Lower of Interfacial tension and surface tension shows first rapid fall but as the concentration of emulsifier increases the change in interfacial and surface tension becomes less and less, there being tendency towards a constant value for the interfacial and surface tension. The lowering of interfacial / surface tension is due to adsorption. This adsorption shows tendency to reach a more or less constant value such a result in harmony with the view that the adsorbed material forms a monolayer on the surface. As the concentration of the agent is gradually increased the amount adsorbed increases until a complete monolayer is formed.

The efficiency of the emulsifier added to the system to increase the oil recovery by surfactant flooding is indicated by the ability to reduce the interfacial tension of the system. So, here is concluded that RL-1 has the lower efficiency and RL-3 the greatest the order being RL-1>RL-2> RL-3.

1.2% RL-3 reduces the interfacial tension of kerosene oil/ water interface from 48 dynes/cms to 3.51 dynes/cm, while the same percentage of surfactant surface tension comes down to 5.50 dynes/cm, the results are in good agreement with the earlier work(12,13)

Effect of temperature:-
Table III-IV and graph 3-4 shows that interfacial tension and surface tension decreases with increasing temperature in the same manner. In the above observation data shows a linear decrease with the rise in temperature. This also proves the work of earlier workers(14)

Effect of Aging:-
Result present in table V-VI and graph 5-6 depict that with increase of aging time from 0 hrs the interfacial tension and surface tension of system shows linear interfacial/ surface tension values starts stabilizing and gets stabilized after the 6 hrs of the aging time.

Effect of Electrolyte:-
Table-VII(a-c) VIII(a-c) and graph (7-12) represent the effect

of NaCl, $CaCl_2$ and $AlCl_3$ on the kerosene/water interface and air/water interface. The concentration of the surfactant was kept constant while the concentration of electrolyte varied in range of 100, 200, 800, 1000 ppm. Study of the data leads in the following conclusions:

In the case of electrolytes viz NaCl, $CaCl_2$ and $AlCl_3$ the fall in interfacial tension and surface tension with all the three surfactant is maximum when $AlCl_3$ is used . It is concluded from the data provided in tables that the valency of cation plays an important role in effecting the interfacial /surface tension.

It can also be seen from the above table that the low concentration of electrolyte i.e. 100, 200, and 400 ppm fall in interfacial and surface tension is more in comparison to higher concentration of electrolyte. Lowering of interfacial surface tension in case of all the three surfactant with addition of electrolyte is the same.

Effect of co-surfactants:-
The effect of co-surfactant(n-hexanol) on the interfacial tension of kerosene oil/water + 1% surfactant interface have been measured by adding different concentration of n-hexanol viz 0.1, 0.2, 0.4, 0.6, 0.8, and 1 % vol/vol. the results provided in table IX and graph 13 shows the lowering of interfacial tension is more at 0.1 and 0.2 % concentration of n-hexanol in case of RL-1 and RL-2 after that decreases becomes linear while in case of RL-3 change becomes linear after 0.4% of n-hexanol respectively.

In case of air/water +1% surfactant interface tension, the decrease with the increase of n-hexanol concentration is more upto 0.2% in case of RL-1 and RL-2 while in case of RL-3 it is upto 0.3 % of n-hexanol. After that the decrease becomes linear an all the three cases.

The results presented in table XI and graph-15 shows that the co-surfactant becomes more effective in the lowering the interfacial tension of kerosene/water + 1% surfactant interface with the addition of 100 ppm of NaCl.

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