

## Removal of Surface Active Agents from a dilute solution by Adsorptive Bubble Separation Technique

Susmita Bose<sup>1\*</sup>, Arka SenChowdhury<sup>1</sup>, Anyesha Sarkar<sup>2</sup>, Soumyadip Das<sup>2</sup>, Goutam mukhopadhyay<sup>1</sup>

<sup>1</sup>BCDA College of Pharmacy & Technology, 78, Jessore Road (s), Hridapur, Kolkata-700127, India.

<sup>2</sup>Calcutta Institute of Pharmaceutical Technology & Allied Health Science, Banitala, Uluberia, Howrah-711316, India.

\* Corresponding Author: Susmita Bose, Email: [susmita.bose2@gmail.com](mailto:susmita.bose2@gmail.com)

### Abstract

Adsorptive bubble separation technique is a chemical process in which hydrophobic molecules are preferentially separated from a liquid solution using rising columns of foam. As in many chemical processes, there are competing considerations of recovery (i.e. the percentage of target surfactant that reports to the overhead foamate stream) and enrichment (i.e. the ratio of surfactant concentration in the foamate to the concentration in the feed). A crude method of moving upon the enrichment-recovery spectrum is to control the gas rate to the column. The enrichment and recovery depend on the hydrodynamic condition of the rising foam, which is a complex system dependent upon bubble size distribution, stress state at the gas-liquid interface, rate of bubble coalescence, gas rate. Here two surfactants have been taken viz. sodium lauryl sulphate (SLS) and Tetradecyltrimethylammoniumbromide (TTAB) and their enrichment and removal at various concentrations is studied. The results showed TTAB showed the highest enrichment (43.62) and recovery (87.25) at the lowest concentration 2nM and the corresponding values are (31.27) and (62.55) for SLS.

Key Words: Adsorptive Bubble separation Technique, sodium lauryl sulphate and Tetradecyltrimethylammoniumbromide.

### 1. Introduction

It is not usual in drug manufacturing unit that finished products sometimes fail to pass through the quality control steps of good manufacturing practices. In that situation, the faulty product is either discarded as waste or the active component is recovered from other inert excipients of drug formulations by suitable low cost method[1,2]. The different conventional methods used are solvent extraction, membrane separation, filtration, osmosis, distillation, precipitation, electrophoresis, chromatography, etc. I would like to explore the possibilities of 'Foam

Separation Method' are laden with many problem and inconveniences. This method also offers an important application in wastewater treatment and removal of toxic material in to prevent environmental pollution. This method is especially cost effective for separation of variable materials in large volume of very dilute solutions. This foam separation method has already made formidable presence and proved its worth in many separation activities e.g. separation of ore, heavy metal ions from dilute aqueous solutions, separation of component of natural products [3].

Adsorptive bubble separation technique, the generic name was proposed by Lemlich<sup>2</sup> (1966). This technique is based on differences in surface activity. Material, which may be molecular, colloidal, or macro particulate in size is selectively adsorbed or attached at the surface of bubbles rising through the liquid and is thereby concentrated or separated. A substance, which is not surface active itself, can often be made effectively surface active through union with or adherence to a surface- active collector[4]. The substance so removed is termed as colligend. This extends Adsorptive bubble separation method applicable to a quite wide range of substances including ions, molecules, precipitate, active carbon, minerals, proteins, and bacteria[5].

This method offers some advantages like absence of moving parts eliminating for seals, maximum maintenance, smaller floor space, larger transfer surface per unit volume of column resulting in high mass transfer rate, low construction cost. At low gas velocity (<0.5cm/sec) the bubble diameter is found to be strong function of the orifice diameter and a weak function of the gas velocity in the orifice [6]. At high gas velocity bubble diameter depends on gas flow rate. It is important to note the effect of the present of an electrolyte in solutions on the bubble size. Because of the surface tension and the electrostatic potential of the resultant ions at the gas-liquid interface smaller bubbles are formed in the presence of electrolytes in the water. Bubble size depends on electrolyte concentration and type of electrode[7].

### **1.1.Principle**

In Adsorptive Bubble Separation Method, as described before, depends upon the differences in physico-chemical properties of particles. Under equilibrium conditions of dilute solutions adsorption of surface-active species from bulk solution at a gas liquid interface can be quantitatively described as Gibbs' equation as [8-10]-

$$\frac{\tau}{C} = -\frac{1}{RT} * \frac{d\gamma}{dC} \quad (1)$$

$\tau$  is the surface excess of the adsorbed solute (i.e. concentration at the surface g.mole/cm<sup>2</sup>),  $C$  is the bulk equilibrium concentration, and can be considered a distribution factor,  $\gamma$  is the surface tension, 'R' is the gas constant, and T is the absolute temperature. The value of  $\frac{d\gamma}{dC}$  may be readily determined from the slope of  $\gamma - C$  plot. Better separation would always occur below the Critical Micelle Concentration.

## **2.Aims and Objectives**

2.1 To study the enrichment and removal of Surface Active Agents and some Organic Compounds from a dilute solution by Adsorptive Bubble Separation Technique.

2.2 To study the effect of following variables on the enrichment ratio, separation ratio and percentage of recovery of the separation process:

- Concentration of drug
- Concentration of collector
- pH of the feed solution
- Gas flow rate
- Column diameter
- Presence of electrolyte

Here, I would like to introduce some surface-active agents like-Tetradecyltrimethylammoniumbromide (TTAB), which is a cationic surfactant and Sodiumlaurylsulphate (SLS), which is an anionic surfactant. I studied some characteristic properties of them i.e. performance criteria, %Removal, Critical Micelle Concentration, Relation with Surface Tension, Surface Excess Concentration, etc.

In next part my work is as follows:

1. Study of enrichments and removal of TTAB, SLS at various concentrations.
2. Study of enrichments and removal of some anionic and cationic surface-active agents.
3. Study of enrichments of some organic compounds, drugs like Antibiotics (both cationic and anionic) by ABSM.
4. Comparison of %removal and enrichments at different condition.
5. I chose drugs like Gentamycin Sulphate, Neomycin Sulphate as a cationic surface active drugs, and Penicillin-G as an anionic surface active drug. I will study their percentage recovery with or without those above surface-active substances.

## **3.Materials and Methods**

### **Physicochemical Properties of Surfactants**

#### **Cetremide:**

- |                        |                                     |
|------------------------|-------------------------------------|
| 1. Molecular formula : | C <sub>17</sub> H <sub>38</sub> BrN |
| 2. Molecular weight :  | 364.5                               |
| 3. IUPAC name :        | Tetradecyltrimethylammoniumbromide  |
| 4. Appearance :        | White or creamy powder              |

5. Solubility : At room temperature, the following solubility data have been reported
- a) Freely soluble in water
  - b) Sparingly soluble in ethanol 95%
  - c) Soluble in chloroform

**Table1. Column specification:**

Column internal diameter (cm)	Cross sectional area (cm <sup>2</sup> )	Superficial velocity (cm/sec)	Volume flow rate (cm <sup>3</sup> /min)
4.2	13.86	0.030	25.60

### 3.1. Experimental Procedure

The surfactant, Sodiumlaurylsulphate (SLS) and Tetradecyltrimethylammoniumbromide (TTAB/Cetremide) from stable foam and surfactant were adsorbed on the foam-bubble interface. As the foam ascends the column, the liquid present in the inter bubble space decreases due to drainage of liquid downward, while surfactant concentrate in the interface of the gas bubble and liquid. And then its concentration was measured by trimetric assay method or UV spectrophotometer or HPLC method [11].

**For assay of TTAB:** Produce 100ml. Transfer 25ml to a separator, add 25ml of chloroform, 10ml of 0.1M sodium hydroxide and 10ml of freshly prepared 5%w/v potassium iodide. Shake well and discard the chloroform layer. Shake with three quantities chloroform with 10ml and add 40ml of dilute HCl. Titrate with 0.05M potassium iodate until the deep brown color is almost discarded. Each ml of 0.05M potassium iodate is equivalent to 0.03364gm of Cetrimide (C<sub>17</sub>H<sub>38</sub>BrN) [12].

**For assay of SLS:** Produce 1000ml with water. To 20ml add 15ml chloroform, 10ml dilute sulfuric acid and 1ml dimethyl yellow oracet blue B solution. Shake well. Titrate with 0.004M Benzethonium Chloride until the chloroform layer becomes green. Each ml of 0.004MBenzothonium Chloride is equivalent to 0.001154gm of sodium alkyl sulphate (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S) [13-15].

### 3.2. Performance Criteria

The following performance parameters were determined for each experiment:

**Enrichment ratio (Er):**

It is the ratio of drug concentration in the foamate ( $C_f$ ) and the drug concentration in the initial feed solution ( $C_i$ ).

**Separation ratio (Sr):**

It is the ratio of drug concentration in the foamate ( $C_f$ ) and the drug concentration in the residual solution ( $C_r$ ).

**Percentage of recovery (Rp):**

It is the percentage of the ratio of amount of the mass of drug in the foamate and the mass of drug in the foamate and the mass of drug in the initial feed solution [16-20].

**4. Results and Discussions**

From the fig 3, it is clearly indicated that the recovery and enrichment of the surfactant TTAB was found decreases as the concentration increases. The corresponding data are shown in table 4 and 5. At the minimum concentration i.e. 2nM the value of enrichment and recovery were found 43.62 and 87.23 respectfully. The concentrations were varied from 2nM, 2.25nM, 2.5nM and 2.75nM. Similar pattern was found in all the concentrations.

**Table2. Surface Tension vs. Concentration of TTAB & Determination of CMC of TTAB 34 °C**

Concentration ( mM)	Surface Tension (dyne/cm)	Surface Excess Concentration
3.25	41.02	Slope from graph= 7.70 $\tau = 3.0484 \cdot 10^{-10}$ (g.mole/cm <sup>2</sup> )
3.12	41.02	
3.00	41.02	
2.87	42.00	
2.75	43.01	
2.50	45.33	
2.25	47.33	
2.00	49.33	

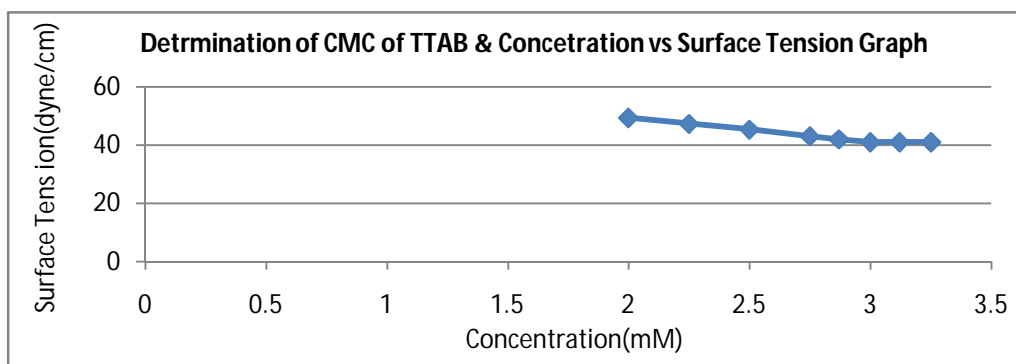


Fig.1 Concentration vs. Surface tension.

From the curve (concentration vs. surface tension) we can easily found:-

- a) Surface Excess Concentration, b) CMC of the substance, c) It can be used as a standard curve

**Table3. Surface Tension vs. Concentration of SLS & Determination of CMC of SLS at 35°C**

Concentration mM	Surface Tension	Surface Excess Concentration
8.25	24.25	Slope from graph= -8.33 $\tau = 3.28 \times 10^{-10}$ gmole/cm <sup>2</sup>
8.12	24.25	
8.06	24.25	
8.03	24.25	
8.00	24.25	
7.96	24.51	
7.935	25.00	
7.87	25.51	
7.75	27.38	
7.67	28.52	
7.50	30.46	
7.37	31.24	

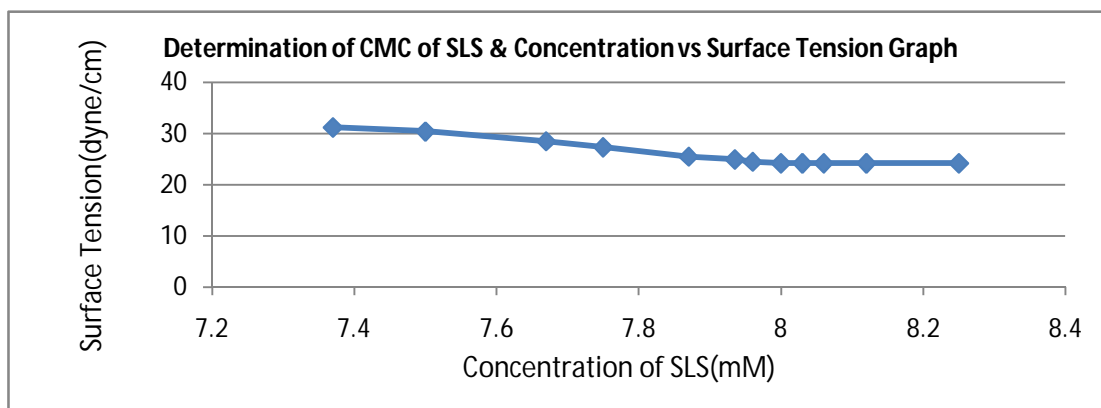


Fig2. Concentration vs. Surface tension

From the curve (Concentration vs. Surface Tension) we can easily found:- a) Surface Excess Concentration, b) CMC of the substance, c) It can be used as a Standard Curve.

**Experimental Results and Graph:-**

**Table4. Removal of Tetradecyltrimethylammoniumbromide (TTAB) with Time, (At 35degC, with superficial gas velocity 0.03 cm/s at pH-7)**

Conc. of TTAB	$\theta$ min	Vf	Vr	Feed mg	R mg	F mg	Cr mM	Cf mM	Er mM	Sr mM	% Rp
2mM	30	2	98	67.28	20.18	52.14	0.61	77.50	38.75	126.63	77.50
	60	2	98	67.28	20.18	53.15	0.61	79.62	39.81	130.09	79.01
	90	2	98	67.28	20.18	54.53	0.61	81.64	40.82	132.43	81.05
	120	2	98	67.28	20.18	55.60	0.71	82.64	41.32	115.75	82.65
	150	2	98	67.28	20.18	56.51	0.71	83.99	41.99	117.63	84.00
	180	2	98	67.28	20.18	58.01	0.78	86.22	43.11	109.84	86.23
	210	2	98	67.28	20.18	58.70	0.81	87.24	43.62	106.92	87.23
	240	2	98	67.28	20.18	59.85	0.91	88.95	44.47	97.43	90.00
2.25mM	30	3	97	75.69	23.29	53.82	0.71	53.33	23.70	74.69	71.11
	60	3	97	75.69	23.29	55.50	0.71	53.99	24.41	75.62	73.33
	90	3	98	75.69	23.76	57.18	0.72	56.66	25.18	78.51	75.55
	120	3	97	75.69	23.53	60.00	0.71	59.45	26.42	83.26	79.28
	150	3	97	75.69	23.42	60.55	0.71	60.00	26.66	83.56	80.00
	180	3	97	75.69	23.29	64.33	0.71	63.74	28.33	89.28	85.00
	210	3	97	75.69	23.49	66.03	0.720	65.43	29.08	90.88	87.25

(Time= $\theta$ , Foam volume=Vf, Residual volume=Vr, Foam amount=F, Residual amount=R, Residual concentration=Cr, Foamate concentration=Cf, Enrichment ratio=Er, Separation ratio=Sr, percentage recovery=%Rp).

From the fig 4, it is clearly indicated that the recovery and enrichment of the surfactant SLS was found decreases as the concentration increases. The corresponding data are shown in table 6 and table 7. At the minimum concentration i.e. 7nM the value of enrichment and recovery were found 31.7 and 62.55 respectfully. The concentrations were varied from 7nM, 7.25nM, 7.5nM and 7.75nM. Similar pattern was found in all the concentrations. The lowest value was found at the highest concentration i.e. 7.75nM. The enrichment was found 23.61 and the recovery was 47.3. This is due to the fact that at the lowest concretion the surfactant was at the high adherence capacity with others. So adsorption was found maximum. But at the concretion increases the molecular structure and the bonds of the surfactant become more and less adherence to separate.



**Table5. Removal of Tetradecyltrimethylammoniumbromide (TTAB) with Time, (At 35degC, with superficial gas velocity 0.03 cm/s at pH-7)**

Conc. of TTAB	$\theta$ min	Vf	Vr	Feed mg	R mg	F mg	Cr mM	Cf mM	Er mM	Sr mM	% Rp
2.5mM	0			84.10							
	30	2	98	84.10	23.54	50.46	.071	75.00	30.00	105.04	60.00
	60	2	98	84.10	23.54	53.82	0.71	80.00	32.00	112.04	64.00
	90	2	98	84.10	23.23	55.50	0.76	82.49	32.99	107.83	65.99
	120	2	98	84.10	26.91	57.18	0.81	85.00	34.00	104.14	68.00
	150	2	98	84.10	26.91	60.55	0.81	85.00	34.00	104.14	71.99
	180	2	98	84.10	27.10	62.35	0.83	87.00	34.80	104.69	75.89
	210	2	98	84.10	28.00	67.11	0.84	99.74	39.89	117.48	79.80
	240	2	98	84.10	29.30	70.57	0.93	104.89	41.95	112.66	84.02
2.75 mM	0			92.51							
	30	2	98	92.51	23.54	47.36	0.71	70.39	25.59	98.59	51.20
	60	2	98	92.51	23.54	53.82	0.71	80.00	29.09	112.09	58.18
	90	2	98	92.51	20.18	58.87	0.63	87.49	31.81	138.43	63.63
	120	2	98	92.51	23.54	60.55	0.71	89.90	32.69	125.91	65.45
	150	2	98	92.51	29.12	63.91	0.88	94.99	34.54	107.94	69.08
	180	2	98	92.51	30.00	67.99	0.91	101.05	36.74	110.67	73.50
	210	2	98	92.51	30.27	71.99	0.91	107.00	38.90	116.55	77.82
		240	2	98	92.51	30.27	75.85	0.91	112.75	41.00	122.82

(Time= $\theta$ , Foam volume=Vf, Residual volume=Vr, Foam amount=F, Residual amount=R, Residual concentration=Cr, Foamate concentration=Cf, Enrichment ratio=Er, Separation ratio=Sr, percentage recovery=%Rp)

**Table6. Removal of Sodium Lauryl Sulphate(SLS) with Time (At 34degC, with Superficial gas velocity at pH-7)**

Conc. of TTAB	$\theta$ min	Vf	Vr	Feed mg	R mg	F mg	Cr mM	Cf mM	Er mM	Sr mM	% Rp
7.75 mM	0			223.49							
	30	2	98	223.49	25.51	89.39	0.90	154.98	19.99	172.20	40.00
	60	2	98	223.49	25.82	92.14	0.91	159.75	20.61	175.54	41.23
	90	2	98	223.49	26.01	94.98	0.92	164.67	21.24	178.98	42.50
	120	2	98	223.49	27.00	99.02	0.95	171.68	22.15	180.71	44.31
	150	2	98	223.49	27.91	101.28	0.98	175.60	22.65	179.18	45.32
	180	2	98	223.49	28.10	103.96	0.99	180.24	23.25	182.06	46.52
	210	2	98	223.49	28.20	105.55	0.99	183.00	23.61	184.84	47.23
	240	2	98	223.49	29.00	110.64	1.02	191.83	24.75	188.06	49.51
7.50 mM	0			216.28							
	30	2	98	216.28	25.71	91.91	0.90	159.35	21.24	177.05	42.40
	60	2	98	216.28	25.99	95.18	0.91	165.02	22.00	181.34	44.01
	90	2	98	216.28	26.23	97.86	0.92	169.67	22.62	184.42	45.31
	120	2	98	216.28	27.00	100.59	0.95	174.40	23.25	183.57	46.51
	150	2	98	216.28	28.12	102.71	0.99	178.08	23.74	179.87	47.49
	180	2	98	216.28	28.85	107.08	1.02	185.65	24.75	182.00	49.51
	210	2	98	216.28	29.13	108.16	1.03	187.53	25.00	182.06	50.01
	240	2	98	216.28	29.92	112.46	1.05	194.98	25.93	185.69	52.00

(Time= $\theta$ , Foam volume=Vf, Residual volume=Vr, Foam amount=F, Residual amount=R, Residual concentration=Cr, Foamate concentration=Cf, Enrichment ratio=Er, Separation ratio=Sr, percentage recovery=%Rp)

**Table7. Removal of Sodium Lauryl Sulphate(SLS) with Time (At 34degC, with Superficial gas velocity at pH-7)**

Conc. of TTAB	$\theta$ min	Vf	Vr	Feed mg	R mg	F mg	Cr mM	Cf mM	Er mM	Sr mM	% Rp
7.25 mM	0			209.07							
	30	2	98	209.07	29.23	105.60	1.03	183.09	25.25	177.75	50.51
	60	2	98	209.07	29.91	109.82	1.05	190.40	26.26	180.95	52.53
	90	2	98	209.07	30.12	114.97	1.06	199.33	27.49	188.04	55.01
	120	2	98	209.07	30.81	120.23	1.09	208.45	28.75	191.23	57.51
	150	2	98	209.07	31.01	125.50	1.09	217.59	30.01	199.62	60.03
	180	2	98	209.07	31.81	130.68	1.12	220.00	30.34	196.42	62.51
	210	2	98	209.07	32.00	139.03	1.13	224.05	30.90	198.27	65.02
7.00 mM	0			201.86							
	30	2	98	201.86	28.91	106.03	1.02	183.83	26.26	180.22	52.53
	60	2	98	201.86	29.01	111.04	1.02	192.52	27.50	188.74	55.01
	90	2	98	201.86	29.58	116.08	1.04	201.26	28.75	193.51	57.51
	120	2	98	201.86	29.91	119.27	1.05	206.79	29.54	196.94	59.90
	150	2	98	201.86	30.01	123.19	1.06	213.58	30.51	201.49	61.03
	180	2	98	201.86	31.01	126.26	1.09	218.91	31.27	200.83	62.55
	210	2	98	201.86	31.85	131.24	1.12	227.54	32.50	203.16	65.02

(Time= $\theta$ , Foam volume=Vf, Residual volume=Vr, Foam amount=F, Residual amount=R, Residual concentration=Cr, Foamate concentration=Cf, Enrichment ratio=Er, Separation ratio=Sr, percentage recovery=%Rp)

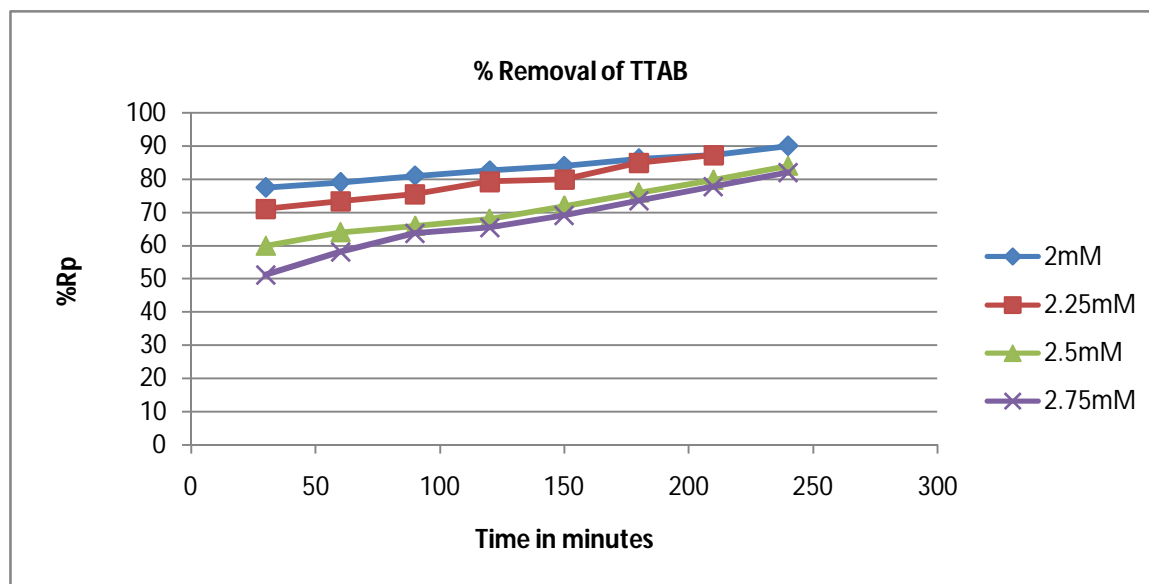


Fig.3 %Rp vs. Time

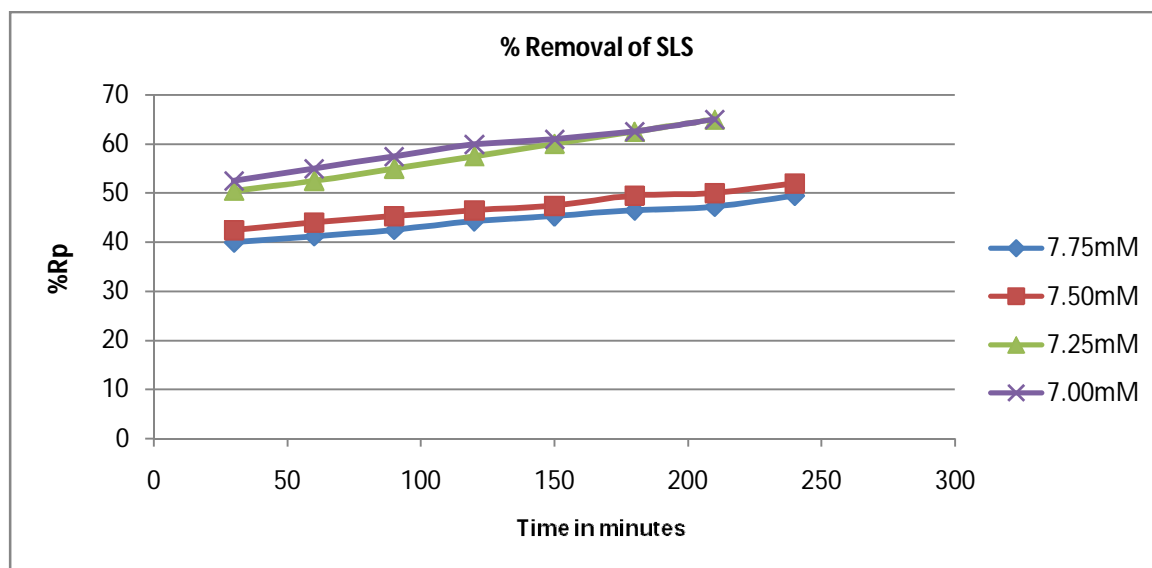


Fig.4 %Rp vs. Time

The above profile is useful in predicting optimum concentration of TTAB and SLS in feed and maximum time required to remove substantial amount of TTAB and SLS respectively from the feed solution. The above profile also helps to determine mass transfer coefficients.

## 5. Conclusion:

Adsorptive bubble separation technique is the oldest but very economic which can be used to separate surfactant from their dilute solution. Here TTAB and SLS showed the good results during their separation and recovery from dilute medium. This technique can also be useful to separate other organic or drug materials from their mixture.

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