JPIChE 49 (2) 2021: 11-17

Journal of Pakistan Institute of Chemical Engineers

journal homepage: www.piche.org.pk/journal

Impact of Water Content on Kinetics of $Ca(OH)_2$ and Alkyl Benzene Sulphonic Acid Neutralization Reaction.

K. Javed[1,2*], *M. Saleem*[1,3] *A. K. Durrani*[1]

Submitted: 26/03/2021, Accepted: 15/09/2021, Online: 07/10/2021

Abstract

The neutralization reaction of $Ca(OH)_2$ and alkyl benzene sulphonic acid (ABS) is catalyzed by the water which was added about 5 to 10% by weight in start of the reaction. The operational cost for separation of water is high and so the water should be at its minimum level in the reaction system to minimize the operational cost for separation of water. Kinetic study was completed at constant temperature 343 K and different initial water content (1.5, 4.4 and 8.7 weight percent) to determine the reaction kinetic parameters and impact of water content on the rate of reaction, conversion and reaction time for complete conversion. Integral method was used for data analysis of experimental data and to determine the rate equation from concentration time profiles. The neutralization reaction of $Ca(OH)_2$ and ABS is the second order autocatalytic reaction and estimated values of rate constant was 0.0081 liter/mol.min at 343 K and initial water content 1.5 weight percent. The highest rate of reaction was 0.024 mol/lit.min at 343 K and 1.5 weight percent of initial water and about 99.5 % conversion was achieved in 220 min. On increasing the initial water content, the rate of reaction also increased, and almost complete conversion was achieved in 160 min and 120 min when initial water content was 4.4 and 8.7 weight percent respectively. The water content in the end of the reaction was 5.02, 7.86 and 12 weight percent determined when the initial water content was 1.5, 4.4 and 8.7 weight percent respectively charged in the start of the reaction. More than 4.4 weight percent of initial water content isnot necessary becauseafter thatincrement inthe rate ofreaction wasnot significant.

Keywords: LABSA, Kinetic study, Calcium dodecyl benzene sulphonate, Anionic surfactant

1. Introduction:

Calcium salt of alkyl benzene sulphonic acid (CABS) is the derivative of alkyl benzene sulphonic acid which is water insoluble and extensively used in anhydrous or oil-based products. Unlike of sodium salt of alkyl benzene sulphonic acid, lubricity and water repellent properties of CABS are excellent. The calcium ion is electrostatically bonded with the two-linear alkyl benzene sulphonic acids. The linear chain of alkyl group consists of C9 to C14. The CABS is an important anionic surfactant and emulsifying agent used in agro-chemical formulations [1]. Therefore, its application in petrochemical products is outstanding.

Although literature on surfactants manufacturing is extensive [2-9] the published literature related to the manufacturing of CSABS is scarce. After all efforts only a few sources were found relevant [10] [11-17]. CABS is produced from the neutralization reaction of the $Ca(OH)_2$ and alkyl benzene sulphonic acid (ABS) [10-11]. The neutralization reaction of $Ca(OH)_2$ and alkyl benzene sulphonic acid is catalyzed by the water which was added about 5 to 10% by weight at start of the reaction [18].

In finished product the desired water content is less

[1]*Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan.*
[2]*GRADIENT Chemicals, 1 Km, Raiwind Bypass Road off Sunder Road, Raiwind, Lahore, Pakistan.*
[3]*Mir Chakir Khan Rind University of Technology, DG Khan, Pakistan*
Corresponding Author: khaqan_javed@yahoo.com

than or equal to 1 percent and excess amount of water is separated by azeotropic distillation [19]. The operational cost for separation of water is high and so the water should be at its minimum level in the reaction system to minimize the operational cost for separation of water. The optimum value of water was required to get the other operating parameters of the reaction. In this manner the reaction kinetics is seriously dependent on water content. So in this work the impact of water was studied on kinetics of neutralization reaction of $Ca(OH)_2$ and ABS in presence of iso-butanol to get the optimum value of initial water content for the reaction.

2. Material:

The lab grade $Ca(OH)_2$ was purchased from Merck. The commercial grade linear alkyl benzene sulphonic acid of 96 % active matter was purchased from the Tufail group of industries. The reagent grade organic solvent Iso-butanol was purchased from Merck.

The reaction was conducted in 1000 mL glass round bottom four necked reaction flask. The reaction flask was equipped with the adjustable RPM motor driven agitator with 45° turbine blades. The reaction system was fixed on the electric heater and connected with temperature controller and other accessories. The total reflux condenser was installed at one neck of the reaction flask and connected with the water circulation.

3. Method:

The reaction completion was determined by concentration of ABS which was determined by the acid number of the reaction system. $Ca(OH)_2$ is insoluble in reaction system but remains in suspension and similarly insoluble in titrant solvent. The titration of $Ca(OH)_2$ taking time and difficult to determine the sharp endpoint. ABS is soluble in solvent and accurately titrate with alcoholic KOH with comparative quick sharp end point. The total acid number was determined by the standard test method ASTM D664. Reagent grade KOH (potassium hydroxide) was used as titrant and prepared 0.1 N standard solution in iso-propanol. CABS is an anionic surfactant and the active matter of CABS was determined by the standard test method ASTM D 3049 89 for synthetic anionic ingredient by cationic titration. The water content in CABS was determined by volumetric Karl Fischer titration methods ASTM E 203 01. The Karl Fischer reagents are purchased from Merck.

The kinetic parameters were calculated by the analysis of experimental data. The Integral method [20] was used for data analysis or to determine the kinetic parameters of $Ca(OH)_2$ reaction with ABS for the synthesis of CABS in different organic solvents. The chemical reaction for the $Ca(OH)_2$ and linear alkyl benzene sulphonic acid (ABS) is given in E1 and the generic form of this reaction is given in E 1.1.

$$2\ C_6H_5C_nH_{2n+1} + Ca\ (OH)_2 \rightarrow Ca(C_6H_5C_nH_{2n})_2 + 2\ H_2O \quad (E1)$$

$$2\ ABS + Ca\ (OH)_2 \rightarrow CABS + 2\ H_2O \quad (E1.1)$$

Where n = linear alkyl chain of C_{10} to C_{13}. The reaction was proceeded at constant temperature and samples were taken after interval of 20 minutes to determine the concentration of ABS. At start, the viscosity of the reaction mixture was low but proportional to the conversion and at the end of the reaction a high viscous fluid was observed. Methodology for kinetic study of reaction of $Ca(OH)_2$ and ABS at different temperature is given in figure 1. The experimental data was analyzed to determine the kinetic parameters of $Ca(OH)_2$ and ABS for synthesis of CABS in iso-Butanol and study the impact of water content on rate of reaction, conversion and reaction time. The rate equation and order of reaction was determined by integral method and corelated by the experimental data [21].

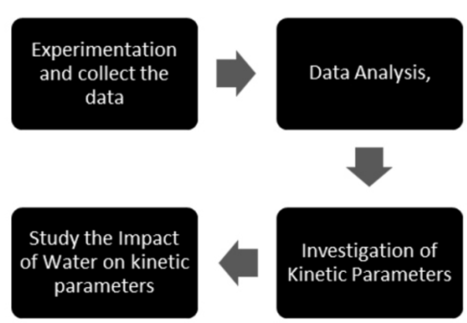

Figure 1: Methodology for kinetic study of reaction of $Ca(OH)_2$ and ABS at 343 K in presence of iso-butanol.

The concentration time profile indicated that the trend was more likely to autocatalytic irreversible reaction as shown in figure 2. The experimental data of ABS concentration was plotted verses time and it was observed that at start of the reaction the change in concentration was slower than the middle of the reaction. As reaction proceeded the change in concentration was steeper but again at the end of the reaction the change in concentration became slow and approaches to zero. Theoretically this behavior was very close to autocatalytic reaction mechanism. The concentration profiles were steeper in the middle of the reaction as the initial water concentration was high.

The experimental values of ABS were used to estimate the time conversion profile of ABS as shown in figure -3. Initially the experimental data of ABS concentration was used to test supposed rate equation to get the closest correlation to satisfy the experimental data.

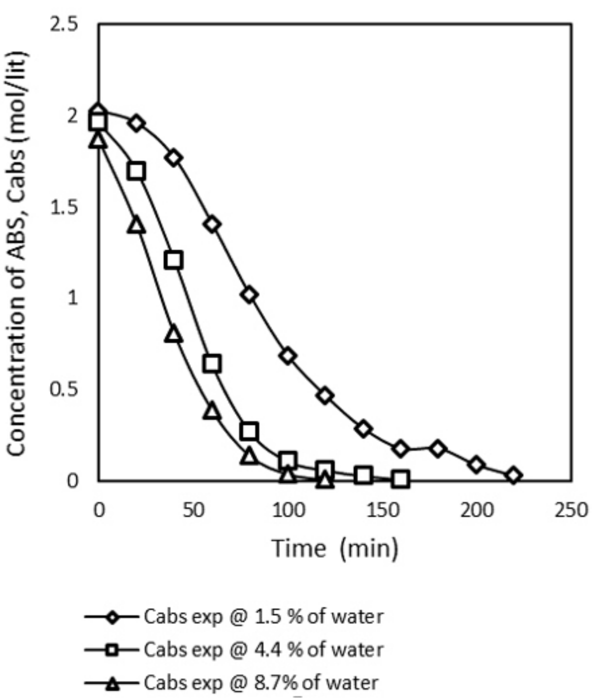

Figure 2: Concentration profiles of ABS at 343 K and different initial water concentration.

The data was tested on first order and second order unimolecular irreversible reaction by using equation E-2, and E-3 respectively.

$$-\ln\left(\frac{C_{abs}}{C_{abso}}\right) = k * t \qquad \text{(E-2)}$$

$$\frac{1}{C_{abs}} - \frac{1}{C_{abso}} = k * t \qquad \text{(E-3)}$$

The least square method was used to develop the mathematical correlation and estimated that the R-squared value for equation E-2 and E- 3 were 0.89 and 0.41 which were not close enough to satisfy the supposed rate equation for the synthesis of CABS by neutralization reaction of $Ca(OH)_2$ and ABS at 343 K.

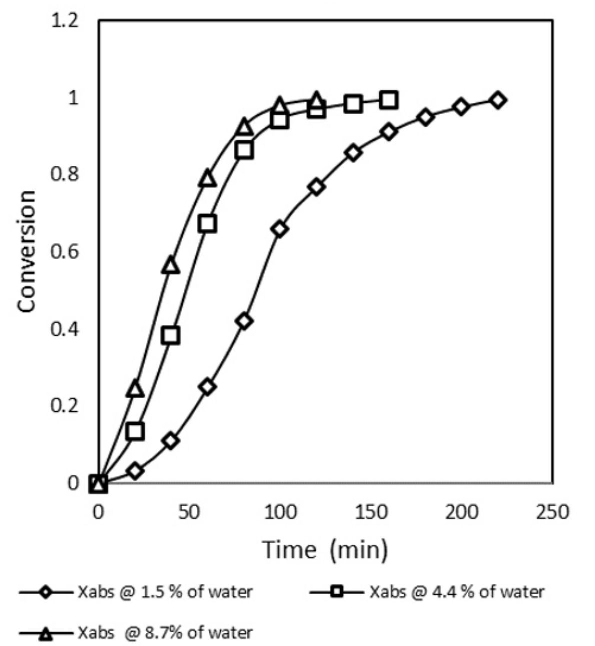

Figure 3: Conversion of ABS with time at 343 K and different initial water concentration.

After testing the unimolecular irreversible first order and second order kinetic the second order irreversible autocatalytic reaction kinetics was supposed. Here the water is the by product and autocatalyzed the reaction as conversion increased. The reactions were conducted at 343 K and 1.5, 4.4 and 8.7 weight percent of initial water content and supposed irreversible autocatalytic reaction with second order mechanism and the supposed rate equation is given in equation E-4 and its modified form in terms of ABS was given in E-5 and integral form is given in E-6.

$$-r_{abs} = -\frac{dC_{abs}}{dt} = k * C_{abs} * C_w \qquad \text{(E-4)}$$

$$-\frac{dC_{abs}}{dt} = k * C_{abs} * (C_{abso} + C_{Wo} - C_{abs}) \qquad \text{(E-5)}$$

$$ln\left[\frac{C_{abso}\,(C_o - C_{abs})}{C_{abso}\,(C_o - C_{abs})}\right] = (C_{abso} + C_{Wo}) * k * t \qquad \text{(E-6)}$$

The kinetic test of equation E-6 from the experimental data was plotted and least square method for linear regression was used to test the supposed rate equation at initial water content of 1.5, 4.4 and 8.7 weight percent as shown in figure-4, 5 and 6 respectively.

The R-squared value was 0.965 for the reaction of $Ca(OH)_2$ and ABS at 343 K and 1.5 initial weight percent of water as shown in figure 4. The supposed rate equation of second order irreversible autocatalytic reaction mechanism satisfied the experimental data and the rate constant was

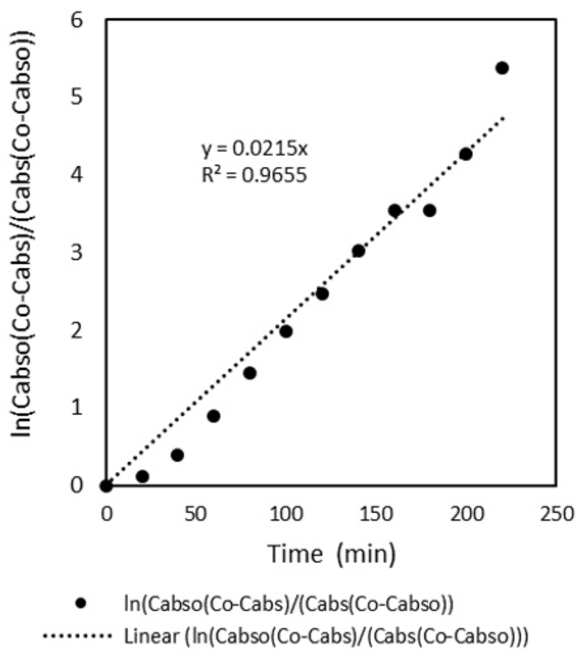

Figure 4: Test for the second order autocatalytic rate equation for the synthesis of calcium alkyl benzene sulphonate at 343 K and initial water at 1.5 weight percent.

In the same manner the experimental data for the reaction at 343 K and 4.4 weight percent of initial water was tested and the corelated curve was plotted as shown in figure 5. The R-squared value in figure 5 was 0.969 which was very close and satisfied the experimental data. The experimental data of reaction at 343 K and 8.7 initial weight percent of water was tested from equation E-6 and plotted as shown in figure 6 where the R-squared value was 0.948 which shows that the supposed rate equation satisfied the experimental data.

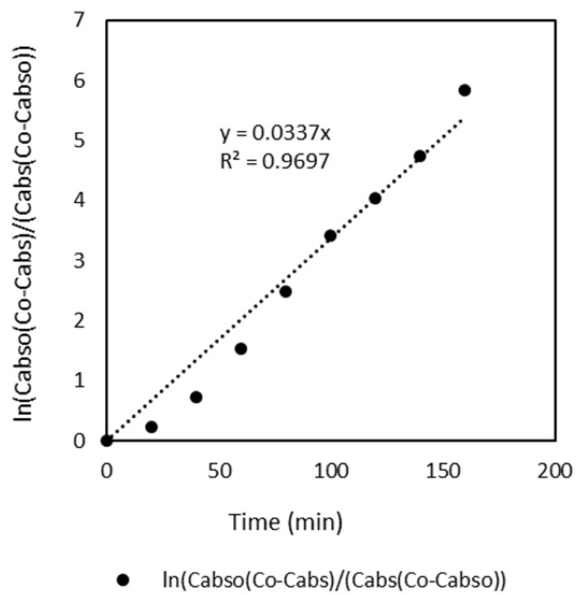

Figure 5: Test for the second order autocatalytic rate equation for the synthesis of calcium alkyl benzene sulphonate at 343 K and initial water at 4.4 weight percent.

The estimated rate equation for the reaction of $Ca(OH)_2$ with the ABS at 343 K in the presence of iso-butanol is given in E-7.

$$-\frac{dC_{abs}}{dt} = 0.0081 * C_{abs} * (C_{abso} + C_{Wo} - C_{abs}) \qquad \text{(E-7)}$$

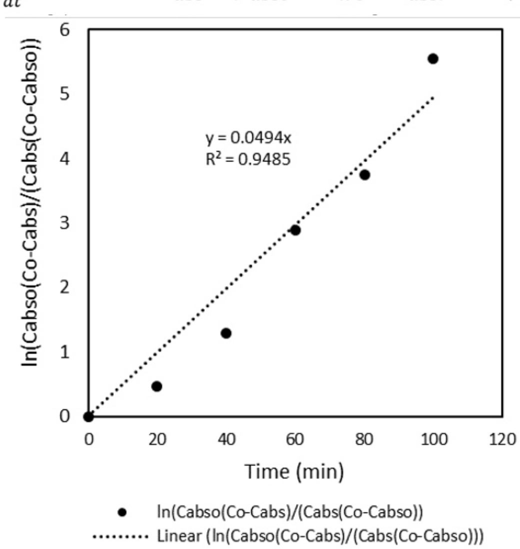

Figure 6: Test for the second order autocatalytic rate equation for the synthesis of calcium alkyl benzene sulphonate at 343 K and initial water at 8.76 weight percent.

The estimated differential rate equation was compared with the experimental time concentration data and plotted in figure 7.

4. Discussion:

The rate of reaction was the important parameter which was really affected by the initial concentration of water. As the initial concentration of water increases the rate of reaction increased rapidly. The rate of reaction was plotted versus concentration ratio of C_{ABS}/C_{ABSO} and given in figure 8. The peak value of rate of reaction was 0.0195 mol/lit.min when the initial water content was 1.5 weight percent and the peak value of rate of reaction was increased to 0.0285 mol/lit.min when the initial water content was 4.4 weight percent as shown in figure 7. The highest value of peak rate of reaction was observed 0.0335 mol/lit.min where the initial water content was 8.7 weight percent as shown in figure 7. The rate-concentration curves are also indicating the trend of autocatalytic reactions.

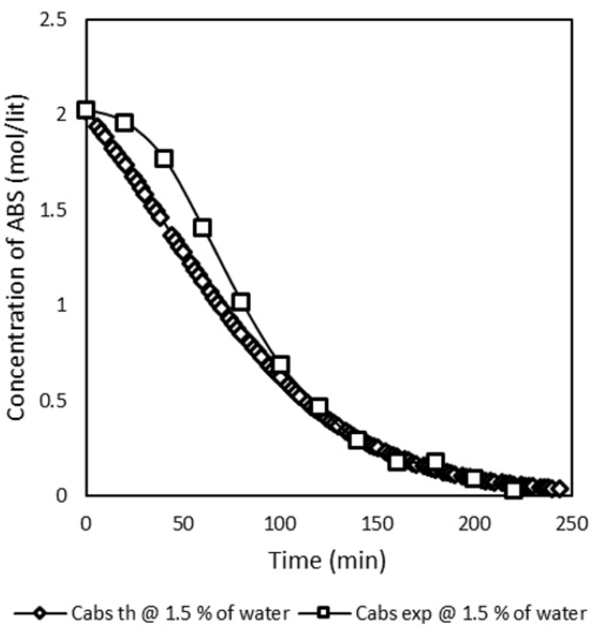

Figure 7: Comparison of experimental and theoretical concentration of ABS at 343 K and initial water at 1.5 weight percent.

The higher amount of initial water content increases the rate of reaction but unfortunately the excess amount of water in the reaction system increases the separation cost in purification step. The difference between peak rate of reaction at initial water content of 1.5 weight percent to the initial water content of 4.4 weight percent was about two times of the difference between peak rate of reaction at initial water content of 4.4 weight percent to the initial water content of 8.7 weight percent. On increasing initial water content, the total water content in the finished product also increases. It was observed that the excess amount of water is not necessary beyond the initial 4.4 weight percent by which the total water content in the finished product was 7.5 weight percent achieved.

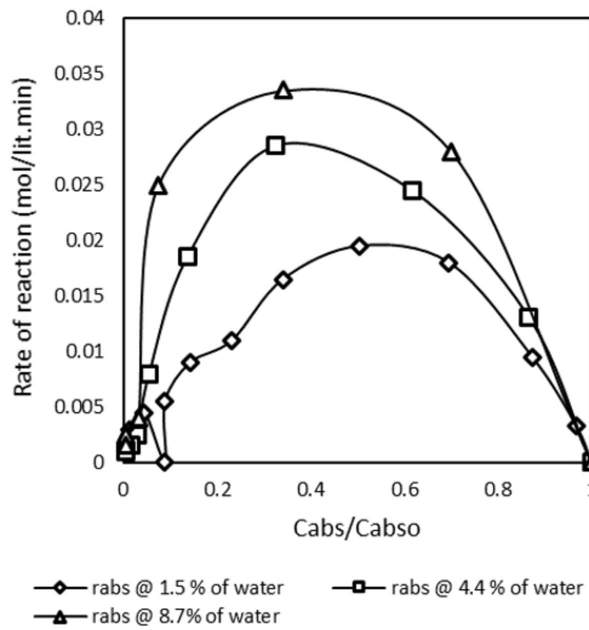

Figure 8: Peak value of rate of reaction of ABS and water content in the end of the reaction with respect to the initial water content.

The kinetic parameters are helpful to determine optimum reaction time which relates to the operational cost (electricity, thermal etc.) and productivity of CABS. In addition, kinetic parameters are important for estimating and optimizing the separational cost. Reaction time was determined 3.6, 2.6 and 2 hr at initial water content 1.5, 4.4 and 8.7 weight percent respectively. By decreasing reaction time, the electricity cost and thermal cost also reduces. The water content is important because in post separation process water is removed and that should be at its minimum level. The separation process and their impact are not scope of this work but seriously depending on water content in the product.

Symbol	Description	Unit
C_{abs}	Concentration of ABS	[mol/L]
C_{abso}	Initial concentration of ABS	[mol/L]
k	Rate Constant	lit/mol.min.
t	Time/reaction ime	min
C_W	Water concentration	[mol/L]
C_{Wo}	Initial concentration of water	[mol/L]
$-R_{abs}$	Rate of reaction on basis of ABS	[mol/dm^3.min^{-1}]
C_o	Total concentration of the reaction system	[mol/L]

References:

1. H. J. S. Mirgal, *J Disper Sci Technol,* vol. 18, no. 1, pp. 11-36, 2007.
2. D. Yuying, "Improve the method for preparing lauryl sodium sulfate". China Patent CN106977428A, 21 August 2018.
3. W. Breitzke, "Aqueous preparations of sodium lauryl sulfate and myristyl sulfate having a low cloud point useful in making toothpastes". United States Patent US4876035A, 24 October 1989.
4. G. E. Harrison, "Process for the production of fatty alcohols". Patent WO1994010112A1, 29 October 1992.
5. Y. Zhiwu, "Fatty alcohol sulfonation method". China Patent CN106380428A, 11 November 2017.
6. G. V. Nguyen, "Method for preparation of and compositions of low foam, non-gelling, surfactants". Patent EP2421813A1, 29 Feburary 2012.
7. H. R. Guilloty, "Process for making ethoxylated fatty alcohols with narrow polyethoxy chain distribution". Patent US4223163A, 16 September 1980.
8. K.-H. Schmid, "Fatty alcohol mixtures and ethoxylates thereof showing improved low-temperature behavior". Patent US5276204A, 04 January 1994.
9. R. GHOSH, "Alkylphenol ethoxylates and a process for preparing the same". Patent WO2015079451A1, 04 June 2015.
10. Greisinger.United States of America Patent 2402325, 1946.
11. L.-a. Marion, "Basic Alkaline earth metal sulphonates and method of making same". US Patent US 2779784A, 29 January 1957.
12. S. Shore, "Prepration of Alkaline Earth Alkyl Benzene Sulphonates". United States of America Patent 3719596, 6 3 1973.
13. Emanuel, "Improved process for making alkaline-earth metal salts of alkaryl.". EP Patent EP0135920A1, 1984.
14. E. Stamatakis, "Process for making alkaline earth metal salts of alkaryl sulphonic acid". Patent 4615841A, 7 october 1986.
15. Wellbrock, "Process for the prepration of Alkaline Earth Metal Salts of Allkyl Benzene Sulphonic Acid". United States of America Patent 4279837, 1981.

16. Q. Zhengliang, "Method of prodn. of solid solefonate 102 and produced farm chemical emulgent". China Patent 1132198A, 1996.

17. N. Xinrong, "Method for preparing Calcium Alkyl Benzene Sulphonate Methanol solution". China Patent CN103922974A, 2016.

18. E. Stamatakis, "process For Making Alkaline-earth Metal Salts Of Alkaryl Sulfonc Acds". United States of America Patent 4,615,841 , 1986.

19. W. Wellbrock, "process for the Preparation of Alkaline Earth Metal Salts of Alkyl Benzenesulfoncacds". United States of America Patent 4,279.837 , Jul. 21, 1981

20. O. Levenspiel, "Interpretation of Batch Reactor Data," in *Chemical Reaction Engineering*, W. Anderson, Ed., United States of America , John Wiley & Sons, 1999, pp. 38-75.

21. H.S. FOGLER, "Collection and Analysis of Data," in *Elements of Chemical Reaction Engineering*, third ed., New Delhi, Prentice-Hall of India, 2004, pp. 223-243.

22. J. Lawrence, "Surfactants Chromatography," in *Encyclopedia of Separation Science*, Elsevier Science Ltd., 2000, pp. 4318-4327.