

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Synthesis, Characterization and Aqueous Properties of a polymerisable nonionic surfactant Exposure.

Salah. M. El-Kousy<sup>a</sup>, Yahiya. A. Youssef<sup>b</sup>, Waseam. A. Hassan<sup>c</sup>, Mohammed A. Tawila<sup>c</sup>, and Moneer M. Basuni<sup>a,d,c\*</sup>.

<sup>a</sup> Faculty of Science, Department of Chemistry, Moneufia University, EGYPT.

<sup>b</sup> Textile Research Division, National Research Centre, Dokki, Giza, 12311, Egypt

<sup>d</sup> EBCA R&D Polymer Center ,Egyptian British co. for Chemical and Auxiliaries, EGYPT.

<sup>c</sup> Zewail City, University of Science and Technology, 6th, October City, 12588 Giza, EGYPT.

### ABSTRACT

A study A polymerisable surfactant (AS-25 MA) has been prepared via direct esterification reaction between a nonionic surfactant (Emuldac A S -25) and meth acrylic acid then used via emulsion polymerization reactions to prepare hydrophobic alkali-swellable modified emulsions (HASE) to choose the best emulsion having the optimum thickening effect via the variation of polymerizable surfactant (AS-25 MA) ratio, ethyl acrylate (EA) to meth acrylic acid (MAA) ratio and N-methylol acrylamide (NMA) ratio in monomer mixture. The physical properties of this chosen emulsion were evaluated and its application as a thickening agent in the conventional printing pastes of textiles and paint formulations was investigated.

**Keywords:** polymerisable surfactant, alkali-swellable emulsion, printing, paints, thickening agent.

*\*Corresponding author*

## INTRODUCTION

Water-soluble hydrophobically associating polymers are of interest for many industrial applications such as cosmetics, latex paints, pharmaceuticals, foods, water treatment, controlled release of bioactive materials, drilling fluids, and oil recovery, where they are used to increase viscosity in the aqueous phase. Hydrophobically associating polymers impart unusual rheological properties to aqueous fluids. Enhanced viscosification, shear thickening or dilatant rheology, and viscosity which is less sensitive to ionic strength of the fluid have been found. In addition, improved mechanical and thermal stability [1-3]. Surfactant plays an important role in emulsion polymerization. Polymerizable surfactants can solve the deficiencies of traditional surfactants and enhance the application functions of emulsion in addition to improve the stability of the lattices, as opposed to electrolytes, as well as freeze or thaw the water sensitivity of the film formed with this aim, extensive studies have been performed on hydrophobic acrylic derivatives to obtain a whole comparison of their behavior with conventional water-soluble polymers [4]. The print pastes also require a thickening agent to control the flow and penetration of the paste. Acrylic copolymers have been synthesized by emulsion, inverse emulsion, solution and suspension techniques. Among these, the emulsion route is preferred due to easy control and high molecular weight of the polymer obtained in the readily useable latex. This process also eliminates the use and recovery of expensive/polluting organic solvents. Powdered thickening agents are also known to be very effective, but they are difficult to handle due to dust and lumping problems [5]. The synthesized polymeric associative thickeners include acrylic-based polymers derived from acrylic acid or acrylate esters among others [6]. The incorporation of a small amount (less than 1% mol%) of hydrophobic groups into the polymer backbone of a water-soluble polymer (added during the process) dramatically alters the rheological properties of the resulting material. [7-10]. Associative acrylic thickeners operate to thicken aqueous systems to which they are added by the associations, such as adsorption on dispersed phase surface and aggregation in solution akin to micellization, between the hydrophobic groups on the thickener molecules and moieties on the other component in the system, similar to the associations of conventional surfactants. Because associative thickeners comprise at least two hydrophobic groups, a network of associations is established by hydrophobic interaction. This network increases the viscosity of the aqueous composition. When compared with nonassociative thickeners, associative thickeners produce a more favorable (i.e., more Newtonian) rheology profile. Associative thickeners have the ability to hold the latex in a well-dispersed state versus the flocculated state typical of systems thickened with nonassociative thickeners, associative thickener systems generally had improved optical properties over comparable nonassociative systems in addition to associative thickeners can yield good pigment dispersion or flocculation, depending on the correct matching of dispersants and pigment type [11-13]. Latex paints contain several types of particles including polymer binder, primary pigment, extenders, and colorants. When the paints contain associative thickeners, control of particle dispersion can be very complicated due to the interaction of the particles with dispersants, surfactants, and the associative thickener itself. The most common thickeners commonly found in paints is known as hydrophobically-modified alkali-swallowable emulsion (HASE) [14-17]. It is also used as viscosity modifier in paper coating to improve the appearance and printability of paper [18-19]. HASE thickeners are based on a polyelectrolyte backbone, usually methacrylic acid (MAA) and ethylacrylate (EA) copolymer, with pendant hydrophobes (i.e., hydrophobes that are attached to the backbone with polyethylene oxide chains). In this work a wide range of HASE was synthesized with systematic changes in the MAA, EA and C18PM monomers ratios [10]. The paper presents studying the application of the maximum thickening effect of the prepared HASE thickener in water-borne coating and textile printing. The gloss and thickening effect of the paint composition as well as the colour strength and fastness properties of the printed textile fabrics were also investigated.

## EXPERIMENTAL

### Material

**Methacrylic Meth acrylic acid and Ethyl acrylate** were obtained from Arkema Co., France

**Emuldac AS 25- SC**, a mixture of cetyl \ stearyl ethoxylate, a product of SASOL company (Italy), flakes, M.W (1532g), cloud point = 76-80, HLB (16.6), conc. (100%).

**NaOH** : 0.2 N NaOH solution prepared for titration.

**Lutropur MSA** Methane sulfonic acid,  $\text{CH}_3\text{SO}_3\text{H}$ , a product of BASF company (Germany), M.W. 96.1,  $d=1.35\text{g/ml}$ , conc. 70% in water.

**N-methylol acrylamide**, White crystals, product of Sigma-Aldrich Company, USA.

**Galaxy les70** Sodium lauryl ether sulfate, (conc. (68%)) was obtained from Galaxy Co., India.

**A commercial pigment** (Navy blue KRL-E, supplied by Kemiteks, Turkey).

**Textile reactive dyestuff** (CI Reactive Black 5, 150%), supplied by Saraf Dyechem industry, India .

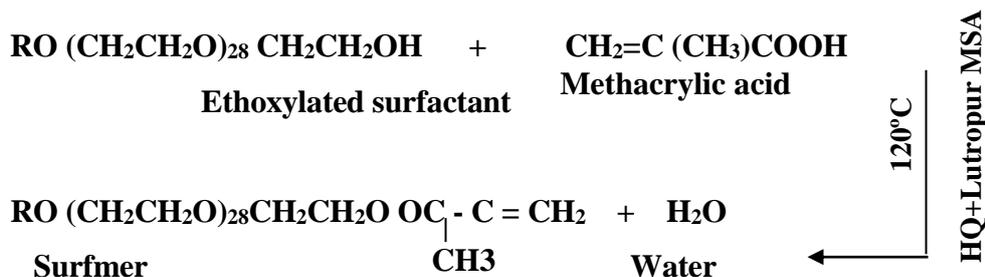
**Hydroquinone: (HQ)**, a product of TNN company (China), off-white powdery crystals, M.W=110, M.p.=172°C, active matter 99-100%.

**Three commercial synthetic thickeners**, namely EBCA THICK 30 (HASE thickener 30% conc., EBCA Co., Egypt), ACRYSOL RM-7 (HASE thickener conc. 30%, Dow Co., USA), and Ebca print 38 (nonassociative synthetic thickener 25% conc., EBCA Co., Egypt) were used throughout this work.

**EBCA PRINT 227** (textile binder conc. 40% , EBCA Co., Egypt) was also applied. All other chemicals used are of laboratory reagent grade.

#### Preparation of polymerisable surfactant AS-25 MA

In 250ml 3- neck flask equipped with stirrer, condenser, thermometer and air inlet, 100 gm (0.0653 mole) of surfactant Emuldac AS-25 was charged into the flask, the temperature was raised to 120°C by using heating plate and the stirring rate was adjusted at 100 rpm after surfactant melting., then a mixture of 19.6 gm (0.23 mole) methacrylic acid (MAA) 3.5 mole MAA per mole surfactant , 0.2 gm hydroquinone (HQ 0.0018mole) to prevent polymerization of meth acrylic acid by high temperature of esterification and 2 grams Lutropur MSA (70%≈0.015 mole) as catalyst is added then the temperature was raised to 120°C and hold for 4 hrs., at all time a continuous stream of air is purged through flask to prevent polymerization of monomer via oxidation of hydroquinone to quinone. After the 4 hrs the liberation of water was stopped and the reaction product was discharged, filtered and cooled. Synthesis of surfmer is represented by the following general scheme.



Where: R is a mixture of  $\text{C}_{16}\text{H}_{33}$  and  $\text{C}_{18}\text{H}_{37}$  chain.

#### Preparation of acrylic thickener

In 250 ml three neck flask equipped with magnetic stirrer, condenser,  $\text{N}_2$  inlet thermometer and heater, a mixture of 29.9 gm (1.66 mole ) distilled water and 0.1 gm of Galaxy les70 was charged and the temperature was adjusted to polymerization temperature (85°C). Then the pre-emulsion was prepared by mixing 30 gm monomer [mixture of 18.6 gm ethyl acrylate (Et.A), the pre-emulsion is stirred well by magnetic stirrer at 500 rpm, 9 gm meth acrylic acid(MAA) and 2.4 gm of polymerisable surfactant (AS-25 MA)], 0.9 gm of Galaxy les70 and 29.1 gm (1.61mole ) distilled water into the flask, the pre-emulsion is stirred well by magnetic stirrer at 500rpm for 1hr. The initiator solution is prepared by dissolving 0.2gm of sodium persulfate (0.0008mole) in 9.8gm distilled water(0.54 mole). Then the temperature of flask contents is raised to 85°C and the stirring rate was adjusted at 200 rpm. The pre-emulsion and initiator solution were added continuously over 4hrs, the temperature remain constant at 85±2. After the addition was finished the reaction temperature was hold for 2 hrs to ensure high percentage of monomer conversion, then the flask charge was cooled, filtered and the precipitate was weighted and the viscosity of 1% solid is measured.

## Measurements and analysis

### Degree of esterification of polymerizable surfactant

Degree of esterification can be determined by titration of the three solutions A, B, and C with 0.2 N NaOH solution where A is the solution of 1 gram of the esterification reactants before the esterification process in 50 gram water at 30°C, B is the same as A but with substitution of the acid catalyst with water, and C is the solution of 1 gram of the produced ester in 50 gram water at 30°C.

degree of esterification =

$$\frac{100 * (V_A - V_C)}{F * V_B}$$

where :  $V_A, V_B,$  and  $V_C$  are the NaOH volumes consumed by the solutions A, B, and C respectively, and  $F =$

$$\frac{\text{the theoretical amount of MAA should undergo esterification to get 100\%}}{\text{the total amount of MAA used}}$$

### Solid content

This test is used to evaluate the solid material in the polymer emulsion (nearly equal polymer content). A sample of  $1.2 \pm 0.1$  gm was weighted into a flat-bottomed glass dish. The sample was gently tilted and spread for 3hrs. in ventilated oven maintained at  $105 \pm 2^\circ\text{C}$ . The film was cooled and weighted; the non-volatile matter was calculated as follow:

Solid content % =

$$\frac{(C-A) * 100}{B}$$

Where, A: weight of empty dish in gram, B: grams of sample used, C: weight of dish and content after heating in grams.

All sample are adjusted at solid content 20% by thinning with water and thus 1% solid = 5% polymer emulsion

### Thickner Viscosity

The polymer solution viscosity is measured according to ASTM-D2196-99 using RVD VE Brookfield viscometer with spindle 4 and speed 3 at  $24^\circ\text{C}$ . The polymer solution was measured in distilled water at different concentration of polymer solid (solid content range 20-30) after adjusting the pH at 7.5-8 with aqueous ammonium hydroxide solution (25%). All sample are adjusted at solid content 20% by thinning with water and thus 1% solid = 5% polymer emulsion.

### Gloss of painted surface

Sheen glossmeter was used for determining gloss of painted surface. It consists of:

- A light source which is projected at an angle of  $60^\circ$  on the surface under test.
- A photocell unit viewing the area at an angle of  $60^\circ$  to the tested surface connected to an indicator with a gloss scale multiplier for accurate comparison of mat and low gloss finishes.
- A transformer with adjustable output control.

Measurement of gloss was performed by standardizing the equipment with a stander plate, which amount to 100% gloss followed by placing the sample and recording the gloss reading.

**Colour measurements**

The colour measurements were determined on a Hunter Lab UltraScan PRO spectrophotometer with a D65 illuminant and 10° standard observer. Color strength (K/S) and CIE L\* a\* b\* C\* h° values of the printed samples were measured at the respective wavelength of maximum absorption for each dye. The relative colour strength (K/S) of printed fabrics was measured by the light reflectance technique using the Kubelka–Munk equation .

$$K/S = \frac{(1 - R)^2}{2R}$$

Where R is the reflectance of the printed fabric at λ<sub>max</sub>, K is the absorption coefficient and S is the scattering coefficient.

**Fastness testing**

The printed samples were tested, after washing-off using 2 g/l nonionic detergent at the boil for 30 min, according to ISO standard methods [1]. The specific tests were: ISO 105-X12 (1987), colour fastness to rubbing; and ISO 105-C02 (1989), colour fastness to washing in which 5 g/l soap solution was used at a temperature of 50°C for 45 min (liquor ratio 50:1). Washing and rubbing fastness of dye can be divided into two broad categories: (Alt.) the alteration or shade change of the sample on washing, (SC) the staining on adjacent cotton fabrics and (SW) the staining on adjacent wool fabrics after carrying out washing and rubbing test methods.

**Result and discussion**

**Degree of esterification of (AS-25 MA)**

$$F = \frac{\text{M.Wt of MAA * used Wt of sursactant}}{\text{M.Wt. of surfactant * used Wt. of MAA}} = \frac{86 * 100}{1532 * 19.6} = 0.2864$$

$$V_A = 10.2 , V_B = 9.7 , V_C = 7.5 .$$

$$\text{Degree of estrification} = \frac{100 * (V_A - V_C)}{F * V_B} = \frac{100 * (10.2 - 7.5)}{0.2864 * 9.7} = 97.19\%$$

**Optimum surfmer (AS-25 MA) concentration**

The data listed in table (1) and figure (1) indicate that the surfmer (AS-25 MA) percents more effective on thickening effect, the viscosity is too low at 6% (AS-25 MA) and increasing gradually until 12% (AS-25 MA) and then start to decrease again with increasing (AS-25 MA)The thickening effect in absence of (AS-25 MA) is due to electrostatic mutual repulsion between (-ve) charges raised on -COOH groups of methacrylic acid after neutralization, causing intelgement in molecule and increasing in viscosity, and due to hydrogen bond formation , but the thickening effect in presence of (AS-25 MA) is due to electrostatic repulsion, hydrogen bond formation, and hydrophobic association.The optimum concentration of (AS-25 MA) that give higher viscosity is 12%.

**Table 1: Effect of (AS-25 MA%) concentration on thickening effect**

Polymer code	MAA	EA	(AS-25 MA)	viscosity (cps)
T1	32	62	6	18700

T2	30	62	8	23000
T3	28	62	10	25400
T4	26	62	12	32000
T5	24	62	14	28600
T6	22	62	16	23300

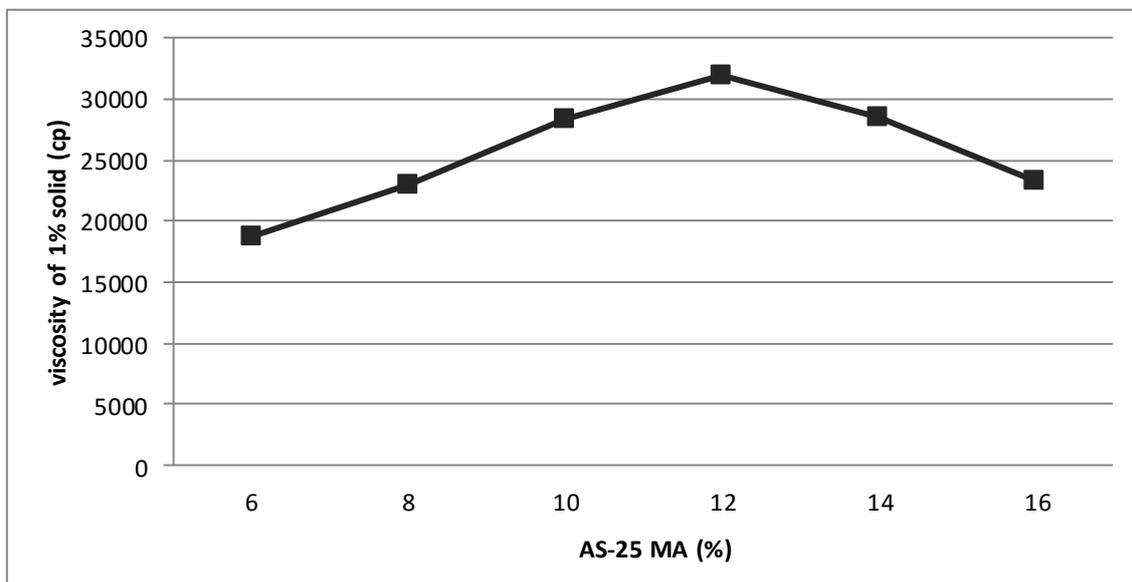


Figure 1: Effect of (AS-25 MA) concentration on the thickening effect of the product

**Optimum ethyl acrylate (EA) and methacrylic acid (MAA) ratios**

The data listed in table (2) and figure (2) indicate that , the weight ratio between ethyl acrylate and methacrylic acid is more effective on thickening effect ,where the thickening effect change from 32000 cp ( Et:MAA=62:26) to 45000 cp.( EA:MAA=56:32) at constant ratio 12% of (AS-25 MA) of total monomer..The optimum EA:MAA ratio that give higher viscosity is 56:32. the increasing dosage of monomer, lead to the increasing viscosity of the polymer obtained, due to the increased molecular weight of the polymer leading to the increasing viscosity of the polymer obtained [22,23].At higher monomer concentration the polymerization solution becomes very viscous, so the stirring becomes too difficult and the distribution of reactants may be insufficient and hence the conversion of monomer to polymer decreases [22-25].

**Table 2: Effect of EA to MAA ratio on the thickening effect**

Polymer code	conc. of MAA (%)	conc. of EA(%)	conc. of (AS-25 MA) (%)	viscosity of 1% solid (cps)
T7	24	64	12	26000
T4	26	62	12	32000
T8	28	60	12	38000
T9	30	58	12	42000
T10	32	56	12	45000
T11	34	54	12	42600

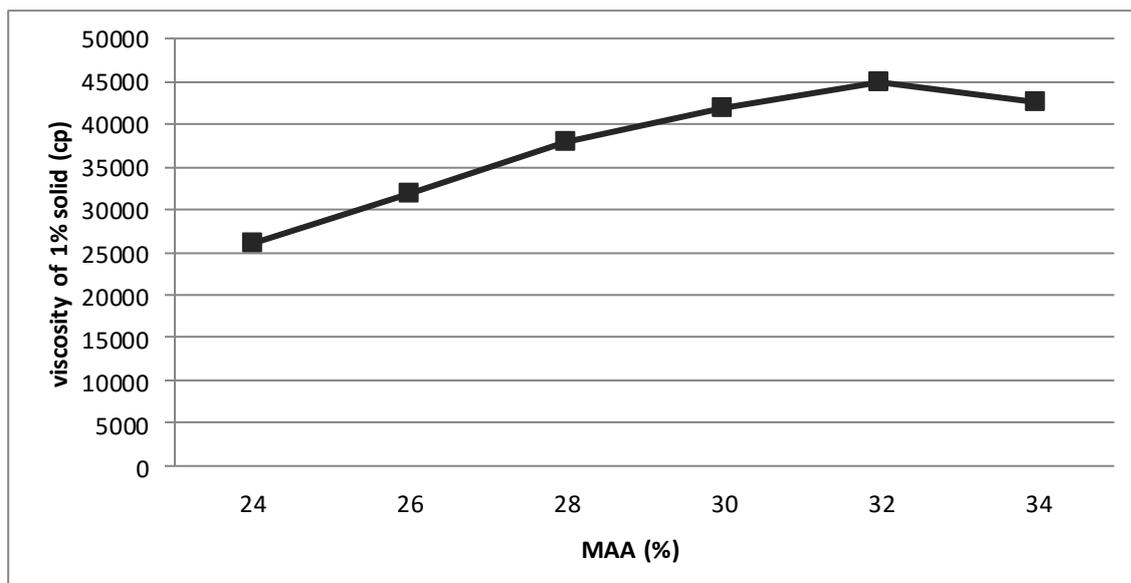


Figure 2: Effect of EA ratio on thickening effect of the product

**Optimum of cross-linker NMA ratio**

The data listed in table (3) figure (3) indicate that , the best ratio of N-methylol acrylamide to get the best viscosity effect was 1.2 g per 1 kg batch , where the thickening effect change from 45000 cp ( 0 NMA ) to 65000 cp. ( 1.2 NMA) The increase of NMA ratio over 1.5 gram per 1 kg batch increase the precipitate largely. The optimum NMA ratio that give higher viscosity that contains 300 gram monomer mixture of EA , MAA and (AS-25 MA) with the weight ratio (56 : 32 : 12 ) , thus the polymer of code number T15 is involved in comparative study with another type of thickener. The optimum EA:MAA: (AS-25 MA) ratio that give higher viscosity is 56:32,12 with 1.2 g NMA per 1Kg thickener thus the polymer of code number T15 is involved in comparative study with other types of thickener. Addition ammonium compound enhanced the stability of obtained polymer due to their antimicrobial activity in addition to formation of H-bond between carboxyl groups and amides in NMA [26-28].

Table 3: Effect of NMA ratio on the thickening effect at constant amount of other monomer

Monomer polymer code	MAA (g per 1kg batch)	EA (g per 1kg batch)	(AS-25 MA) (g per 1kg batch)	NMA (g per 1kg batch)
T7	96	168	36	0
T8	96	168	36	0.5
T9	96	168	36	0.8
T14	96	168	36	1
T15	96	168	36	1.2
T16	96	168	36	1.3

Figure 3: Effect of NMA ratio on thickening effect at constant amount of other monomer

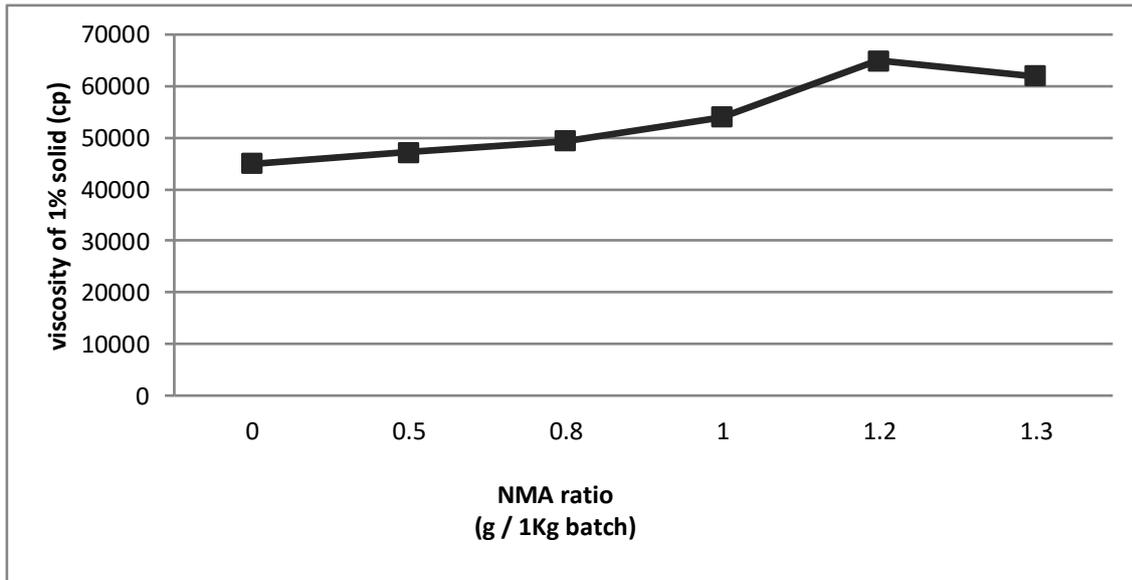


Figure 3: Effect of NMA ratio on thickening effect of the product

**Comparative study on thickening effect of different commercial thickener samples**

Table (4) and figure (4) show that, the thickening effect of different type of thickener T15 and EBCA THICK 30 and Acrysol RM 7 in distilled water at different concentrations using spindle 4 at 3 rpm. The results clearly show that T15 thickener give higher thickening effecting in water than EBCA THICK 30 and Acrysol RM 7 thickeners at all concentration and thus can be used for thickening of aqueous base medium (such as aqueous paint, textile printing, liquid detergents and shampoos) instead of them and even at lower concentration.

Table 4: The thickening effect of different sample of thickener

Sample \ Concentration % solid	thick30	acrysol rm-7	T 15
0.2	420	530	820
0.4	2000	2800	4500
0.6	9900	13500	22700
0.8	21600	26000	45400
1	30500	36000	65000

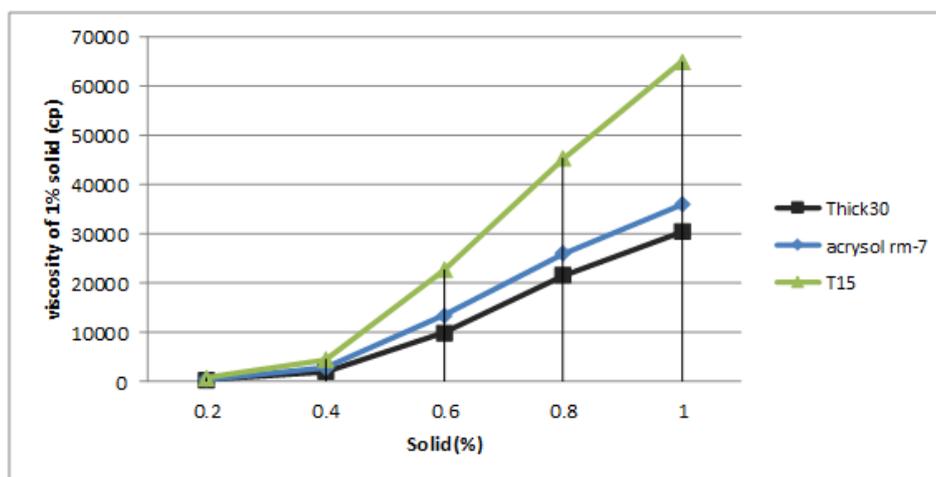


Figure 4: Comparison between thickening effect of different thickener samples.

### Characterization of prepared acrylic thickner T15

#### Zeta potential

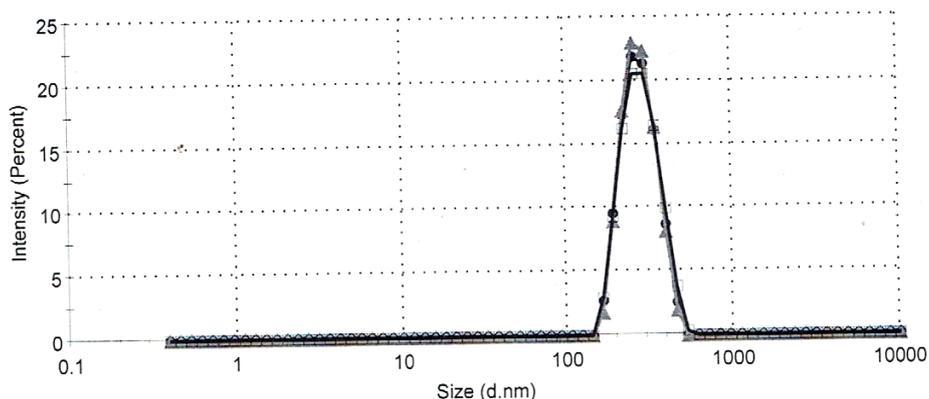
The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent Zeta potential [mV] Stability relationship can be shown as the following behavior of the colloid

- from 0 to  $\pm 5$ ,                      Rapid coagulation or flocculation
- from  $\pm 10$  to  $\pm 30$                 Incipient instability
- from  $\pm 30$  to  $\pm 40$                 Moderate stability
- from  $\pm 40$  to  $\pm 60$                 Good stability
- more than  $\pm 61$                     Excellent stability [Hanaor, D.A.H 2012].

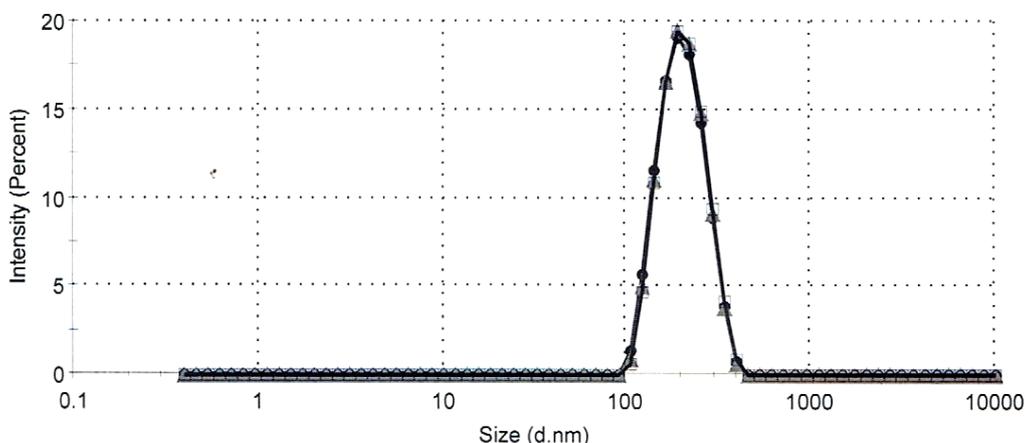
The particle size of the two thickeners T15 and Acrysol RM 7 was measured by the Malvern instrument Ltd. Table (5) ,figure(5)and figure(6) shows the results of the two thickeners which show that T15 emulsion is more stable than Acrysol emulsion.

**Table 5: zeta potentials and particle sizes of the two thickeners T15 and Acrysol RM 7**

Test Sample	zeta potentials	Average particle sizes
T15	48.6	191.7
Acrysol RM 7	44.2	266.8



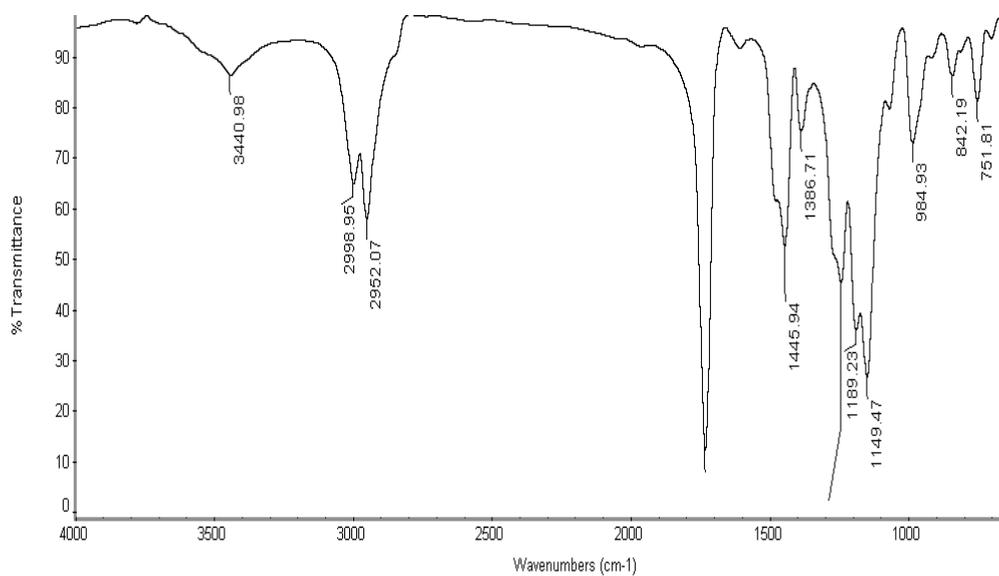
**Figure 5: Particle size of Acrysol RM 7**



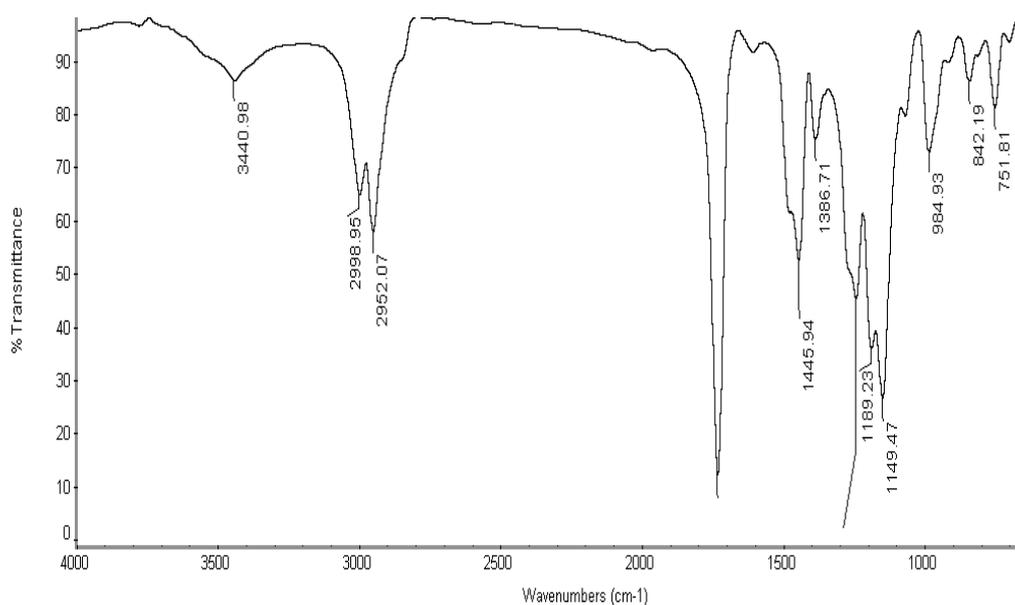
**Figure 6: Particle size of T15**

**FTIR spectra**

The chemical composition of the surfmer sample can for instance be determined by Fourier transform infrared (FTIR) spectroscopy Figure (5) and figure (6). FTIR spectrum in the region from 4000 to 500  $\text{cm}^{-1}$  were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, and then removing the film from the glass using TENSOR 27 Mid FT-IR spectrophotometer made by BRUKER Optics Ettlingen-Germany [29]. IR spectra of the modified polymer (T15) sample give band at 3420  $\text{cm}^{-1}$  that is characteristic of carboxyl [OH] group of methacrylic acid, band at 1638  $\text{cm}^{-1}$  that is characteristic of ester or carboxyl [C=O] group of ethyl acrylate or methacrylic acid, band at 1129  $\text{cm}^{-1}$  that is characteristic of ether [C-O] group of ethoxylate groups and give band at 2992  $\text{cm}^{-1}$  that is characteristic of aliphatic [CH] groups. FTIR spectrum of the EMULDAC-AS-25-SC-Methacrylate (A25M) surfmer in the region from 4000 to 500  $\text{cm}^{-1}$  was recorded. The peaks at 2800-2900, 1751, 1465 and 1170  $\text{cm}^{-1}$  were associated with C-H of alkane, C=O, and C=C stretching frequencies of the ethoxylated fatty alcohol methacrylate surfmer, respectively. A broad band having a medium value at 3440  $\text{cm}^{-1}$  characteristic for CH aliphatic methylene and methine coupled with that of OH of carboxylic group and that of H<sub>2</sub>O [30].



**Figure 7: IR spectra of the modified polymer (T15) sample**



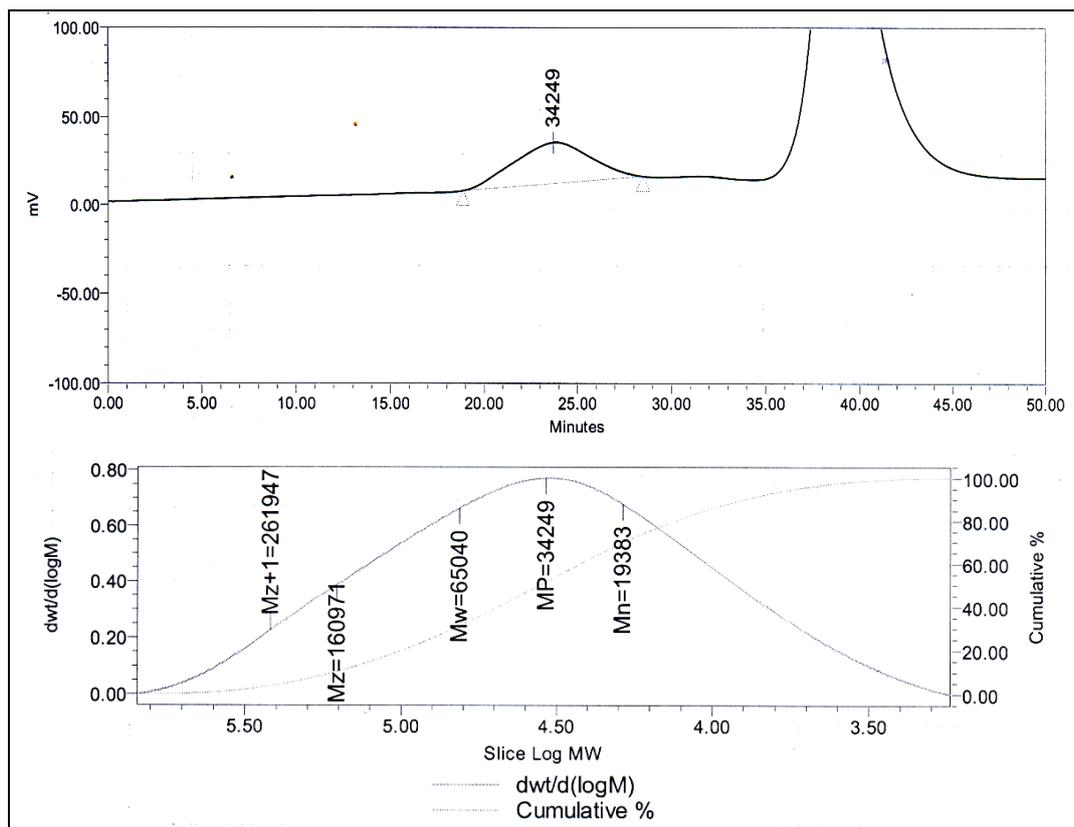
**Figure 8: FTIR spectrum of the EMULDAC-AS-25-SC-Methacrylate (A25M) surfmer.**

**Gell Permeation chromatography (GPC) analysis**

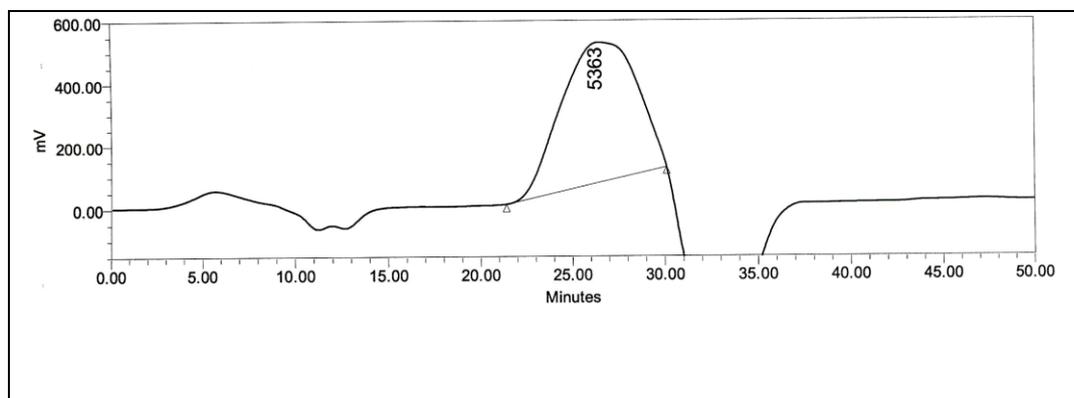
SEC spectra of modified P(AA) homopolymer (the weight average (Mw), number average (Mn), and polydispersity for acryzol and T15 are given in table (6) , figures (7) and figure (8).

**Table 6: Gell Permeation chromatography Data for Acrisol RM 7 and T15**

Sample	Retention Time	Mn(g/mol)	Mw(g/mol)	MP	MZ (Daltons)	MZ+1 (Daltons)	Mw/Mn (polydispersity)
Acryzol	23.700	19383	65040	34249	160971	261947	3.355
T15	26.283	2424	9609	5363	27598	47922	3.963



**Figure 9: Gell Permeation chromatography Data for Acryzol**



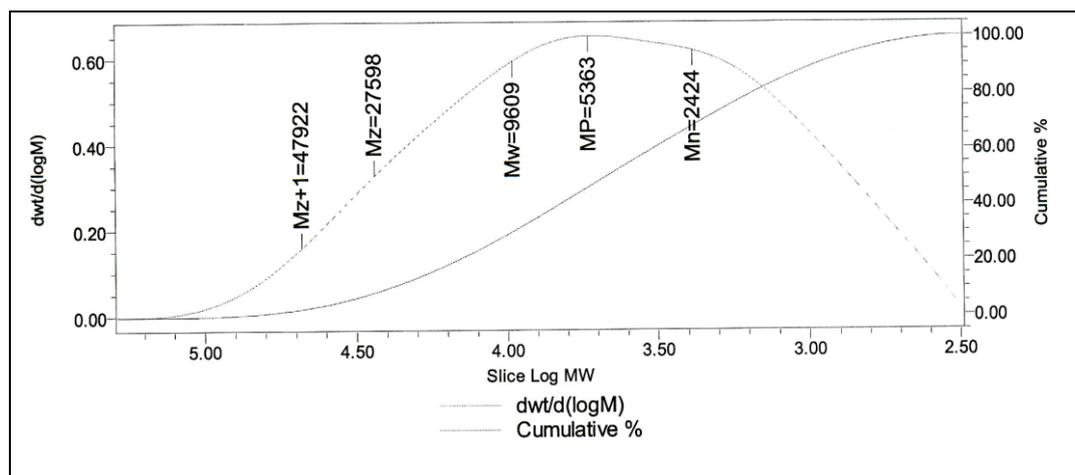


Figure 10: Gell Permeation chromatography Data for Acryzol and T15

**Application of prepared acrylic thickener in printing**

**Pigment printing**

In this type of printing the thickener is added to water at high stirring rate (2000 rpm), then pH is adjusted at 7-8 to obtain maximum viscosity. Then the binder and pigment are added forming printing past which applied over cotton cloth. After that the cloth species is dried at 160 ° -170 ° C and subjected to color fastness to rubbing test and color strength.

**Color fastness to rubbing test**

The results of dry and wet tests for rubbing test of T15 and EBCA print 38 thickeners (already used as thickener for pigment printing) are shown in the table (10).

The table (7) shows that the T15 thickener nearly gives the same results that obtained by EBCA print 38 in dry test and in wet test but give better result than.

Table 7: Fastness Properties of pigment printed samples for T15 and EBCA print 38

Sample	Fastness to Washing		Fastness to Rubbing		
	Dry	Wet	Alt.	SC	SW
Print 38	3-4	3	4-5	4-5	4-5
Thick 30 CL	3-4	3	4-5	4-5	4-5

**Color strength test**

Table (8) shows the value of K/S for T15 and EBCA print 38. Table (8) shows nearly similar K/S results for EBCA print 38 (13.37) and T15 (13.41) thickeners and low ΔE result.

Table 8: Colour strength and colour coordinates of pigment printed samples for T15 and EBCA print 38

Sample	K/S						
	λmax. (600 nm)	L*	a*	b*	C*	h	ΔE
Print 38	13.41	28.74	4.32	-31.28	31.57	277.87	--
Thic 30 CL	13.37	28.83	4.71	-31.86	31.86	278.49	0.67

**Cost evaluation** for 100kg printing past made by the two types of thickener.

The two printing pasts formulas of T15 and EBCA print 38 are shown in table (12).

The calculations indicate there are lowering in cost by 1.7 \$ for each 100 kg. in case of T15 printing past.

**Reactive dye printing**

In this type of printing the thickener (sodium alginate or T15) is added to water and stirred by high speed stirrer (2000 rpm), pH is adjusted at 11-12 with sodium carbonate where the thickening water prepared by sodium alginate is stored for 24 hrs. to obtain maximum swelling. Urea and reactive dye is added and then this printing paste is applied over cotton cloth ,after that the cloth species is dried at 160 ° -170 ° C to make fixation for the color. The printed samples then evaluated with color fastness to rubbing test and color strength test.

**Color fastness to rubbing**

Table (9) shows the result of Color fastness to rubbing of printed species by T15 and sodium alginate thickener. Table (9) shows that the T15 thickener gives nearly similar result as sodium alginate that already used as thickener for reactive dye printing

**Table 9: Fastness Properties of reactive dye printed samples for T15 and sodium alginate.**

Sample	Fastness to Washing		Fastness to Rubbing		
	Dry	Wet	Alt.	SC	SW
Alg.	4-5	4	4-5	4-5	4-5
Thick 30 CL	4-5	4	4-5	4-5	4-5

**Color strength test**

Table (10) shows the values of K/S for T15 and sodium alginate. Table (10) shows nearly similar results for sodium alginate (22.75) and T15 (23.15) thickeners.

**Table 10: Colour strength and colour coordinates of reactive dye printed samples for T15 and sodium alginate.**

Sample	K/S (595 nm)	L*	a*	b*	C*	h°	ΔE
Ref	28.36	16.85	-0.57	-7.69	7.71	265.80	--
Print 38	26.83	17.23	-0.82	-7.07	7.12	263.35	0.77

**CONCLUSION**

- The optimum thickening effect is obtained at monomer ratio 32:56:12 for MAA:EA: (AS-25 MA) respectively.
- The optimum thickening effect is obtained at NMA ratio 1.2 g per 300 g monomer mixture with the previous ratios, used to prepare 1 Kg thickener.
- T15 thickener gives nearly similar results as Acrysol RM-7 thickener in glossy and viscosity at the lower dosage in paint application and gives lower cost.
- T15 thickener give nearly similar results as EBCA print 38 in pigment printing on cotton cloth where color strength and rubbing tests for them are nearly similar and give lowering in cost also.
- T15thickener can be used instead of sodium alginate in reactive dye printing where T15 thickener give similar result as sodium alginate in color strength and rubbing test.

## ACKNOWLEDGMENTS

The authors are deeply grateful to the support from EBCA R&D Polymer center and (Egyptian British co. for chemical and auxiliaries), EGYPT.

## REFERENCES

- [1] Wanli Kang, Xianzhong Wang, Xiaoyan Wu, Lingwei Meng, Shuren Liu, Bin Xu, and Xiuhua Shan (2012). Designing water-soluble polymers for enhanced oil recovery, society of plastics Engineer (SPE).
- [2] Glass, J.E., 2001. A perspective on the history of and current research in surfactant-modified, water-soluble polymers. *Journal of Coatings Technology*, 73(913), pp.79-98.
- [3] J. Bock, R. Vara daraj, D. N. Schulz, J. J. Maurer, 1994. Solution Properties of Hydrophobically Associating Water-Soluble Polymers. *Macromolecular Complexes in Chemistry and Biology*, pp 33-50.
- [4] A. Audibert, J. F. Argillier, J. Lecourtier, L. Rousseau, L. Bailey and P. Reid. 1997. Properties of acrylic acid thickeners. *Oil & Gas Science and Technology - Rev. IFP Vol. 52, No.2*, pp. 269-271
- [5] Jassal, M. and Bajaj, P., 2001. Developments in acrylic-based thickeners as substitute of emulsion thickeners for pigment printing. *INDIAN JOURNAL OF FIBRE AND TEXTILE RESEARCH*, 26(1/2), pp.143-155
- [6] Zhang, L.M., 2001. Cellulosic associative thickeners. *Carbohydrate Polymers*, 45(1), pp.1-10.
- [7] Quadrat, O., Horský, J. and Šňupárek, J., 2004. Effect of styrene units in latices of acrylate copolymers with structured particles on the thickening with associative thickeners. *Progress in organic coatings*, 50(3), pp.166-171.
- [8] Horský, J., Mikešová, J., Quadrat, O. and Šňupárek, J., 2004. The effect of (2-hydroxypropyl)- $\beta$ -cyclodextrin on rheology of hydrophobically end-capped poly (ethylene glycol) aqueous solutions. *Journal of Rheology (1978-present)*, 48(1), pp.23-38.
- [9] Taylor, K.C. and NASR-EL-DIN, H.A., 2003. Rheology of Hydrophobically Associating Polymers for Oilfield Applications. *ANNUAL TRANSACTIONS-NORDIC RHEOLOGY SOCIETY*, 11, pp.13-20.
- [10] Biggs, S., Hill, A., Selb, J. and Candau, F., 1992. Copolymerization of acrylamide and a hydrophobic monomer in an aqueous micellar medium: effect of the surfactant on the copolymer microstructure. *The Journal of Physical Chemistry*, 96(3), pp.1505-1511.
- [11] Glass, J.E., 1999. Adsorption of hydrophobically-modified, ethoxylated urethane thickeners on latex and titanium dioxide disperse phases. *Advances in colloid and interface science*, 79(2), pp.123-148.
- [12] Kostansek, E., 2005. Associative polymer/latex dispersion phase diagrams II: HASE thickeners. *Journal of Coatings Technology and Research*, 2(6), pp.417-422.
- [13] Kostansek, E., 2006. Associative polymer/particle dispersion phase diagrams III: Pigments. *Journal of Coatings Technology and Research*, 3(3), pp.165-171.
- [14] Kostansek, E., 2007. Controlling particle dispersion in latex paints containing associative thickeners. *Journal of Coatings Technology and Research*, 4(4), pp.375-388.
- [15] Shay G., 1989. Polymers in Aqueous Media, Performance Through Association, *Advances in Chemistry Series 223*, Glass, J.E. (ed.), American Chemical Society, Washington, D.C., Chapter 25.
- [16] Sperry, P.R., Thibeault, J.C. and Kastanek, E.C., 1987. Flocculation and rheological characteristics of mixtures of latices and water-soluble polymeric thickeners. *Adv. Org. Coatings Sci. Technol*, 9, pp.1-11.
- [17] Thibeault J.T., Sperry P.R., and Schaller E.J., 1986. Water Soluble Polymers :Beauty with Performance, *Advances in Chemistry Series 213*, Glass J.E. (ed.), American Chemical Society, Washington, D.C., Chapter 20.
- [18] Abdel-Wahhab, H., Naser, A.M., Abdel-Hai, F., Mohamed, S.I. and Abdel-Hakim, A., 2011. Preparation and Evaluation of Hydrophobically Modified Alkali-Swellable Emulsion (HASE). *Journal of Applied Sciences Research*, 7(9), pp.1386-1394.
- [19] Hagemycr R.W., iCsye J.p. 1983.(ed), *Pulp and paper chemistry and technology*, vol IV, Wiley Interscience, New york, pp 1013.
- [20] NAGHASH, H.J., Karimzadeh, A., Momeni, A.R., Massah, A.R. and Alian, H., 2007. Preparation and Properties of Triethoxyvinylsilane-Modified Styrene-Butyl Acrylate Emulsion Copolymers. *Turkish Journal of Chemistry*, 31(3), pp.257-269.
- [21] Xue, W., Hamley, I.W. and Huglin, M.B., 2002. Rapid swelling and deswelling of thermoreversible hydrophobically modified poly (N-isopropylacrylamide) hydrogels prepared by freezing polymerisation. *Polymer*, 43(19), pp.5181-5186.
- [22] Magdy A. Zahran, Moneer M. Basuni. 2014; Preparation and evaluation of some lignin graft copolymers and their application in drilling fluid. *International Journal of Academic Research Part A*; 6(3), pp.246-254.
- [23] Kevin C.Taylor, 2003. Rheology of Hydrophobically Associating polymers for oilfield Applications annual transactions of the Nordic Rheology society Vol. 11, 2003

- [24] Abdel, M., Zahran, H. and Basuni, M.M., 2015. Study on Graft-Copolymerization of Sodium Lignosulfonates with Acrylic Monomers. *KGK-KAUTSCHUK GUMMI KUNSTSTOFFE*, 68(9), pp.35-40.
- [25] LI Jian-fa<sup>1, 2</sup>, SONG Zhan-qian<sup>1</sup>, SHANG Shi-bin<sup>1</sup>, LU Jin-hong Study on Graft-Copolymerization of Crude Lignosulfonates with Acrylic-Monomers *MONOMERS Chemistry and Industry of Forest Products* Vol. 24 No. 3 pp1-6. 2004.
- [26] Magdy A. Zahran, Mohammed M.Mohamdy, Moneer M. Basuni, 2014. Study on Lignin Graft Copolymer as Additive agent for the Hydrocarbon Drilling industry, *International Journal of Advanced Scientific and Technical Research*; 4(4)pp.916-932.
- [27] Wu, Y.X., Zhou, J.H., Ye, C.C., Sun, H.Z. and Zhao, R.J., 2010. Optimized synthesis of lignosulphonate-gpoly (acrylic acid-co-acrylamide) superabsorbent hydrogel based on the taguchi method. *Iranian Polymer Journal*, 19(7), pp.511-520.
- [28] M. A. H. Zahran, Osman, A. M. A., Wahed, R. A., Attia, M., Pedersen, E. B., Elnasser, G. A., &Turky, A. S. 2015. Design, synthesis and antimicrobial evaluation of novel carbendazim dithioate analogs. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 6(4), pp. 1084-1092.
- [29] Naghash, H.J., Massah, A. and Erfan, A., 2002. Free-radical crosslinking copolymerization of acrylamide and N, N'-methylenebis acrylamide by used Ce (IV)/polyethylene glycol and Ce (IV)/diethylmalonate redox initiator systems. *European polymer journal*, 38(1), pp.147-150.
- [30] Mallya, P. and Plamthottam, S.S., 1989. Termination rate constant in butyl acrylate batch emulsion polymerization. *Polymer Bulletin*, 21(5), pp.497-504.