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Poly (DADMAC-co- VEMEA): Synthesis and Flocculation Properties

Abstract: Flocculants are widely investigated chemicals, which can be utilized to remedy or purify waste water from industries including petroleum, fabric, mining. Although many types of flocculants have been explored, each flocculant has it's merits and demerits. Thus, we investigated poly (N,N-diallyl-N,N-dimethylammonium chloride) cationic flocculants. This work reports a novel flocculant which was developed based on the widely used flocculant, poly (N,N-diallyl-N,N-dimethylammonium chloride) (DADMAC) cationic polymers. This newly developed flocculant has not only enhanced flocculant performance, but also provided reusability of this polymer with insertion of crosslinking groups. The new developed copolymer, Poly (DADMAC-co- VEMEA), was synthesized via random radical polymerization approach and characterized by NMR and FTIR. The flocculation performance for these polymers were evaluated and studied by turbidity experiments and zeta-potential measurements. Their flocculation performance over poly (DADMAC) homopolymer can be improved by adding a VEMEA unit to the polymer chain and partially crosslinking the copolymer. This newly developed flocculant can provide new direction in developing flocculants potentially.
Key words: Flocculant, DMDAAC, VEMEA, Zeta potential, Turbidity

Introduction

The supply of pure water is still one of many urgent matters which our society faces worldwide at present [1-3]. For example, based on the United Nation's statistics, one out of seven people do not have a proper clean water source to use [4]. Water contamination is the main obstacle to accessing a pure water source, which is mainly caused by waste water from fabric factories and petroleum oilfields, and leakage from mining and other industry failures [5]. Thus, water purification techniques have been developed based on the concept of distillation [6], filtration [7], reverse osmosis [6], and electrodialysis [3]. All treatment techniques can be utilized in terms of the nature of the contaminants. However, due to physical chemical properties of the contaminates, filtration membranes or permeable active barriers can be easily contaminated by different types of contaminates [6]. For examples, filtration membranes are easily blocked and lose performance due to the attachment of positively or negatively charged organic pollut-ants. Therefore, it is very important to precipitate or remove via coagulants[8, 9] before filtration.

Polyelectrolytes have been broadly explored to neutralize colloidal contaminants or pollutants via a coagulation process [10]. The principle is that organic or inorganic colloidal contaminants can be precipitated from waste water via addition of flocculants, which have high affinity to remove colloidal contaminates with physical forces such as electrostatic and other forces. This binding between colloidal contaminates and flocculants creates large particles of flocs, which further induce the precipitation of the pollutants. This treatment is usually applied before filtration of industrial waste water and other water treatment [10, 11]. In recent years, cationic flocculants like poly (N,N-diallyl-N,N-dimethylammonium chloride) (DADMAC) have been explored [8-9, 12]. This flocculant is widely used in the treatment of pulp and paper mill industrial wastewater [13] .

In this work, to increase the flocculation performance of P(DADMAC), we plan to synthesize a copolymer of N,N-diallyl-N,N-dimethylammonium

chloride (DADMAC) and vinyl ether of monoethanolamine (VEMEA) (Scheme 1) and improve water purification performance based on the hypothesis that copolymers containing double amine groups can provide better flocculation properties (Scheme 2), and at the same time self-crosslinking between monomers further improve flocculation quality (Scheme 1). Regarding this, Cationic polystarch flocculant was investigated for flocculating activity, which was improved until the optimal degree of crosslinking [14]. We used random radical polymerization techniques to synthesize copolymers of Poly (DADMAC-co-VEMEA) under different conditions, including varying monomer ratio, and characterized them using FTIR and NMR. The resulting polymers are further applied to test waste water containing bentonite. Flocculation performance was further evaluated and explained via turbidity measurements and zeta potential approaches.

Materials and Methods

Materials

N, N-Diallyl, N, N-dimethyl ammonium chloride (65 wt % in water), ammonium persulfate (APS, 99.7 wt% purity), Silver Nitrate (99.8 wt % purity), Sodium Chloride (97 wt %), Hydrochloric Acid (37 wt %) were purchased from Sigma Aldrich Inc., (USA) and used without any further purification. The co-monomer VEMEA was provided by JSC "Carbit" (Kazakhstan). Before use, it was purified by distillation at temperature range 112-116ºC and its refractive index was recorded as 1.4382 at 298 K. Acetone was purchased from "Labchimprom" Ltd. (Kazakhstan) and used as it is. Ultra-high pure (99.995 wt %) purging gas, Argon was owned from "Ikhsan" Ltd. (Kazakhstan). During all synthesis and purification process of polymers, the Mili-Q water with resistivity at least 15 M$\Omega \times$ cm at 298 K was used. For flocculation experiments Bentonite, main component of which is montmorillonite (90-100% conc.) was purchased from Sigma Aldrich Inc., (USA).

Synthesis and purification of polymers

Copolymers of DADMAC and VEMEA were synthesized at different monomer molar ratios and different initiator molar concentrations as mentioned in previous publications [1]. Initially the solution of monomers was purged for 15 minutes with ultra-high pure argon, which was sealed in a glass ampoule after adding a specific amount of initiator. The ampoule was kept in a water bath heated at 60°C for 5 hours. After 5 hours the ampoule was cooled immediately, and the product was precipitated with fresh acetone. After drying in the vacuum oven, the solid mass was placed in dialysis tubing with a molecular weight cut-off of 1200 Da for further analysis such as FTIR, NMR, and flocculation. Dialysis tubing with polymer was kept in water for three days while being stirred with a magnetic stirrer at 400 rpm. The water was replaced with pure water thrice a day. This part of the work was described in more detail in our previous publication[15]. For this work only two samples of polymers were selected: with initial monomer ratio DADMAC: VEMEA 80:20 and DADMAC: VEMEA 95:5 and with molar concentration of initiator 0.2% and 0.03% accordingly.

FTIR

FTIR was carried out in a Vertex 70 FTIR using diffuse reflectance Fourier transform spectroscopy (DRIFT) mode where scan time was 64, and resolution was 4. Samples for this analysis were prepared in a 1:200 mass ratio where KBr is the diluent. The FTIR spectra was detected in the spectral range between 400 cm^{-1} and 4000 cm^{-1}. The sample was characterized in a powder state in the atmosphere of nitrogen gas.

^{1}H and ^{13}C-NMR

The ^{1}H and ^{13}C NMR analysis were performed using a Varian Unity INOVA 500 in D2O media at 298 K. The solvent contained reference standard 1 wt. % DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid). The concentrations of sample were 10 mg and 30 mg of sample per 1 g of solvent for ^{1}H-NMR and ^{13}C-NMR analysis accordingly.

Flocculation Measurements

For flocculation experiments, a 0.5 wt. % solution of bentonite with effective diameter 158.43 nm was prepared. The commercial bentonite received from Sigma Aldrich Inc. has following composition (Table 1):

Table 1 – Composition of Sigma-Aldrich bentonite

Components	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	MnO	CaO	K_2O	MgO	Na_2O	P_2O_5	SO_3
Wt. %	21	60.5	0.153	3.83	0.009	1.02	0.318	2.76	2.11	0.04	0.74

Flocculants were purified by using dialysis tubing with a MW cut-off 1200 Da. Flocculation of suspensions were done in 40 ml graduated cylinders. Suspension of bentonite was tested at 3 different acidic pH's (2, 3, 4) and with original polymer without adding acid. For analysis two polymers were selected with initial monomer concentrations of 80:20 (0.2% APS) and 95:5 (0.03% APS). Dosage of flocculant solution varied from 1 ml to 7 ml per 40 ml of bentonite solution, where polymer concentration was 0.1 wt. %. All flocculation experiments lasted 4 hours before measurement of residual turbidity and zeta potential of supernatant of treated suspension.

Residual Turbidity of supernatants of treated suspension was measured by recording optical density before treatment and after treatment. For performing this experiment, the spectrophotometer Genesys 6 (USA) was set for 740 nm wavelength and deionized water was used as a reference standard. The residual turbidity of treated samples was found using the following formula (1):

$$RT = \frac{OD_{740s}}{OD_{740i}} * 100\%, \qquad (1)$$

where OD_{740s} is optical density of supernatant and OD_{740i} is optical density of initial suspension.

Determination of zeta-potentials of treated solutions

Zeta potentials of both suspension and supernatant of treated samples were measured in Brookhaven Nano Omni. An eluent solution of potassium chloride (0.1M) was used. The sample for zeta-potential measurement was prepared by adding one drop of supernatant to the 20 ml eluent which was filtered with a 0.1-micron syringe filter. The mixture was homogenized by sonicating for about 10 seconds. Afterwards, 3 ml of this mixture was placed in a plastic BI-SCP cell which was rinsed with the same mixture twice beforehand. All zeta potential measurements were performed at 298.15 K. The zeta potential of bentonite which was received from Sigma Aldrich doesn't change significantly with the changing suspension pH [16].

Since the zeta potential of bentonite changes with pH, it is essential to find out its zetapotential and isoelectric point for flocculation tests (2-4). The zeta potential of samples was calculated using the Smuluchovski model which has following formula (2):

$$\xi = \frac{\mu_e \eta}{\epsilon}, \qquad (2)$$

where μ_e is electrophoretic mobility, ϵ is permittivity of vacuum and η is viscosity of liquid.
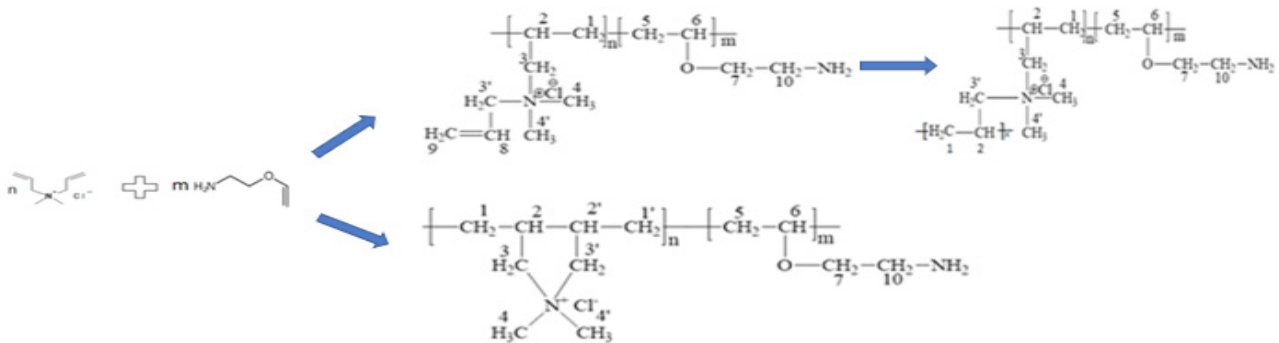
Scheme 1 – Possible reactions in the copolymerization of DADMAC with VEMEA

Scheme 2 – Interaction of amine group of the copolymer with hydrochloric acid

Results and Discussion

We plan to synthesize a copolymer of DAD-MAC and VEMEA which not only provides densely-packed positive ions, but also increases the collection efficiency of flocculants based on our hypothesis mentioned previously (scheme 1 and 2). As mentioned in our previous publication [15], the copolymer based on DADMAC and VEMEA may have two possible molecular structures where DADMAC polymerizes either by forming a five-membered cycle or a pendant group with double bond (Scheme 1). In the latter case, the pendant group with a double bond at high temperature can cause partial cross-linkage [17]. Additionally, the cross-linking degree increases with increasing initiator concentration in the initial reaction mixture.

The resulting copolymers from the above reaction were further characterized by both NMR and FTIR. For the ^{1}H-NMR, ^{13}C-NMR and FTIR spectra analyses, the copolymer with initial monomer ratio of 80:20 with 0.2 wt.% initiator was selected. The

^{1}H-NMR spectrum (Figure 1) after purification with dialysis tubing still shows multiplet signals at ranges 5.89-5.90 ppm and 5.52-5.60 ppm which belong to hydrogens of carbons with double bonds. As the polymer partially cross-linked, the resulting product usually sophisticated with ability of water absorption and showed the presence of singlet 4.66 ppm which indicates some bound water due to strong interaction of an amine group with D_2O. Multiplets between 3.00-3.18 ppm corresponds to methyl groups which are located at positions 4 and 4'. Peaks at 0 ppm, 0.50 ppm, 1.5-1.64 ppm, and 2.74-2.77 ppm belong to 4,4-dimethyl-4-silapentane-1-sulfonate which is a reference standard as the solvent. As hydrogens in the amine group of the vinyl ether of monoethanolamine are replaced with hydrogens of deuterated water, it is not possible to see hydrogens belonging to the amine group in ^{1}H-NMR spectrum of the copolymer. Another important thing which is worthwhile to mention is the singlet corresponding to 3.69 ppm belongs to the peaks of hydrogens on positions 3 and 3'.
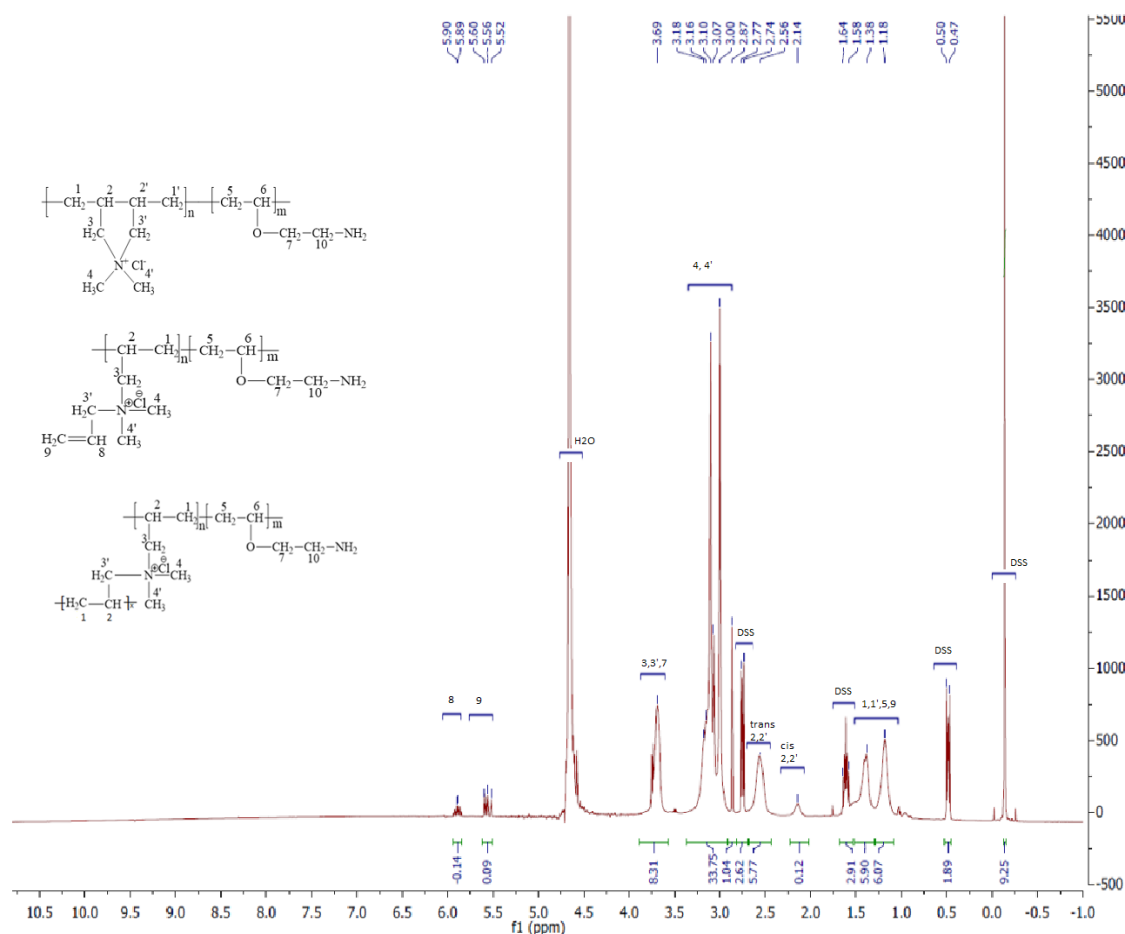

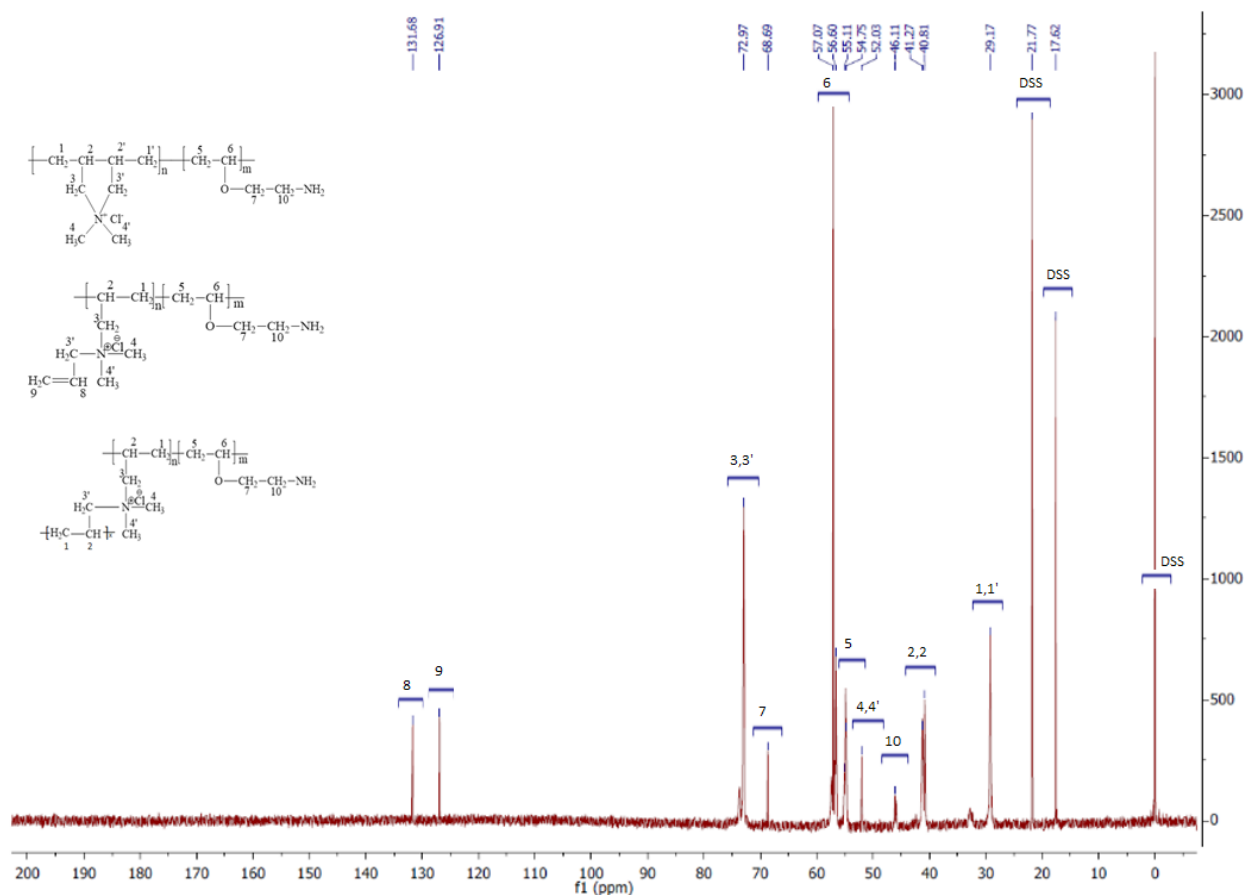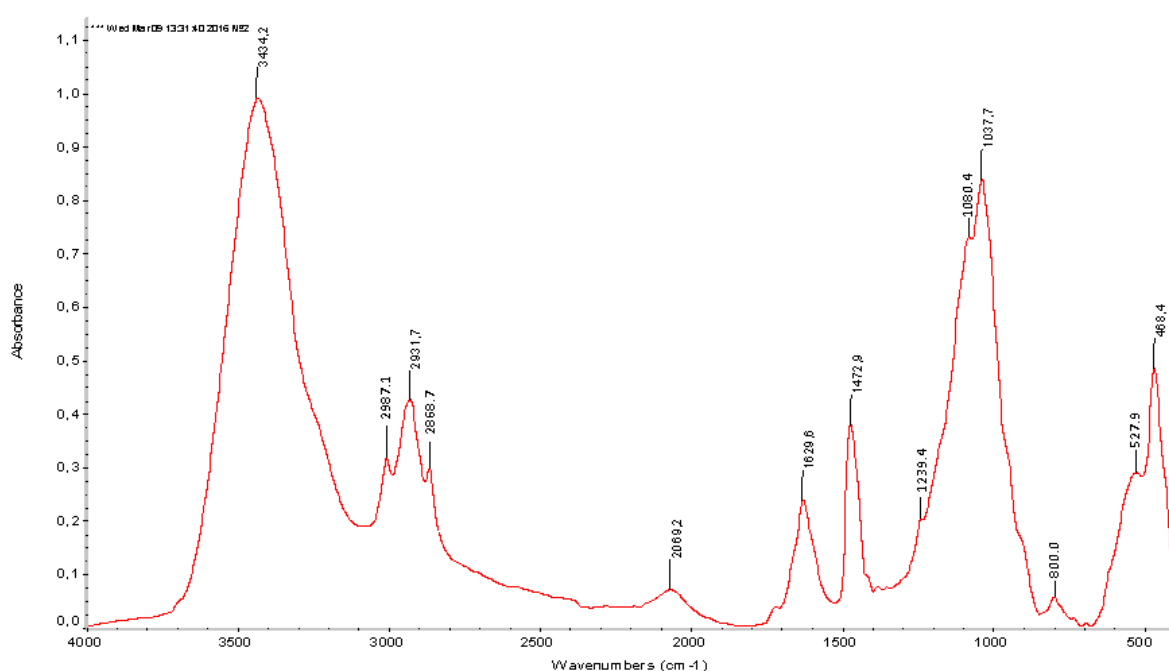**Figure 1** – ^{1}H-NMR spectra of poly (DADMAC-VEMEA 80:20 (0.2% in.))

Figure 2 – ¹³C-NMR spectra of poly (DADMAC-VEMEA 80:20 (0.2% in.))

At the same time, it coincides with the peak of hydrogens on position 7, which makes it difficult to prove the involvement of VEMEA in the copolymerization. The rest of the peaks on 1.38 ppm and 1.18 ppm belong to hydrogens at positions 1, 1', 5, 9'. In the case of cyclo-structure of DADMAC, hydrogens in positions 2 and 2' can be located in such a way to form cis-trans isomers of the monomer unit, so the peaks 2.56 ppm and 2.14 ppm correspond to hydrogens which are trans and cis isomers of the monomer accordingly. The peak 2.56 ppm also covers the hydrogens on position 10.

In ¹³C-NMR spectrum (Figure 2), peaks at 0 ppm, 17.62 ppm, 21.77 ppm, and 57.07 ppm belong to the reference standard. The peaks at positions of 29.17 ppm (1 and 1' carbons), 40.81-41.27 ppm (2 and 2' carbons), 52.03 ppm (4 and 4' carbons), and 72.97 ppm (3 and 3' carbons) can be interpreted as signals of the carbons of the DADMAC unit. The copolymer containing carbons with double bonds shows singlets on position 126.91ppm and 131.68 ppm correspond to CH2=CH- group of DADMAC. In the case of the VEMEA monomer, the carbon at position 10 which

is attached to the amine group appears at 46.11 ppm. Other peaks at 56.60-57.07 ppm and 68.69 ppm are characteristic to an ether group, indicating carbons at positions 6 and 7 correspondingly. The last peaks in the range 54.75-55.11 ppm belong to the carbon at position 5.

The FTIR spectrum of the copolymer (Figure 3) is clearer and easier to interpret for proving VEMEA involvement. The broad peak at 3434.2 cm⁻¹ corresponds to the O-H and N-H stretching vibration. As mentioned above, water peaks show up because of material hygroscopicity. The broad peak observed at 1629.6 cm⁻¹ is assigned to the scissoring of amine groups and the stretching vibration of C=C. The signal for the double bond in the copolymer can be observed at peak 800 cm⁻¹, which was identified as the out of plane bending of =CH₂. Peaks at 2868.7 cm⁻¹, 2931,7 cm⁻¹, 2987.1 cm⁻¹ belong to the stretching vibrations of CH₃, CH₂, and CH functional groups. The signal at 1472.9 cm⁻¹ is related to the interaction of counterions in DADMAC unit [18]. The C-O stretching vibration of the VEMEA group corresponds to the broad peak at position 1037.7 cm⁻¹.

**Figure 3** – FTIR spectra of poly (DADMAC-VEMEA 80:20 (0.2% in.))

The selection of copolymer with a different portion of VEMEA monomer is rationalized by the influence of the VEMEA unit on the flocculation ability of the copolymer based on our hypothesis. PolyDADMAC is a very popular flocculating agent in different areas of industry [13, 19-20]. The effect of cross linkage on the flocculating quality of the copolymer is another thing worth mentioning about the copolymer of DADMAC. PolyDADMAC itself is a cationic polymer and is partially cross linked, so it swells at low pH [21]. At the same time, VEMEA reacts with acid-giving cations in aqueous media (Scheme 2). In overall, acidic media is preferred for the flocculation process with synthesized copolymers.

Poly (DADMAC-VEMEA 80:20) (0.2% in.) is characterized with a higher content of VEMEA which gives a better effect at the lowest pH (Figure 4). As initiator amount increases, the resulting copolymer contains higher cross-linkage and a higher content of VEMEA. As bentonite itself is stable at acidic pH, the efficiency of the copolymer at lower pH is only ascribed to the mentioned copolymer behaviors at lower pH. From the graph, it is shown that this copolymer works best at pH 2 in a 4-ml dosage.

Poly (DADMAC-VEMEA 95:5) (0.03% in.) shows the best flocculation performance at pH 4 (Figure 5), which is related to less cross-linkage as the polymer was synthesized with lower initiator concentration with respect to the previous one. Also, it doesn't have much VEMEA, which is sensitive to acid presence. The polymer also has a higher molecular weight because of decreased initiator concentration. This copolymer works best at pH 4 with a 3-ml dosage, which shows that the copolymer with a higher molecular weight is preferred for the flocculation process. It was assumed that this copolymer, because of its higher molecular weight, swells in such a way that during attachment to bentonite particles, it precipitates earlier before becoming neutral.

Pure solution of the above two copolymers works in the same way, but better efficiency was observed for the second one because of the higher molecular weight. Both samples in the case of pure copolymer solution show destabilization of suspension with a higher dosage of flocculant because of repulsion between copolymers in the solution [25-27, 29, 31]. From the zeta-potential measurements (Figure 6), it becomes clear that Poly (DADMAC-VEMEA 80:20 (0.2% in.)) at pH 2 is more effective in terms of quality of supernatant and dosage amount than the pure solution of Poly (DADMAC-VEMEA 95:5 (0.03% in.)). Consequently, we can be more confident that the copolymer with some degree of cross-linkage and some amount of VEMEA monomer at lower pH works better than the copolymer with less cross-linkage and decreased amounts of theVEMEA unit.
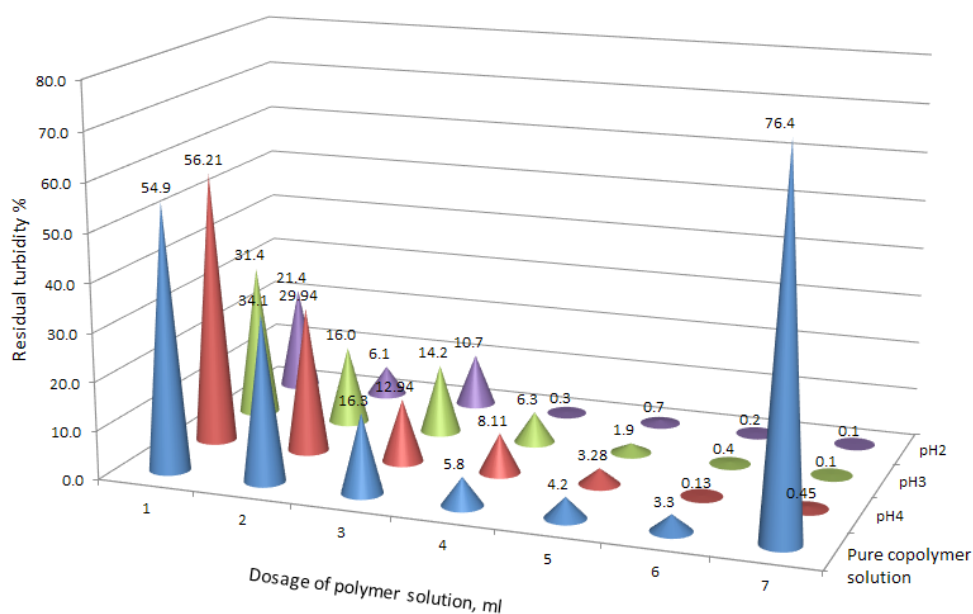
Figure 4 – Flocculation property of poly (DADMAC-VEMEA 80:20 (0.2% in.))
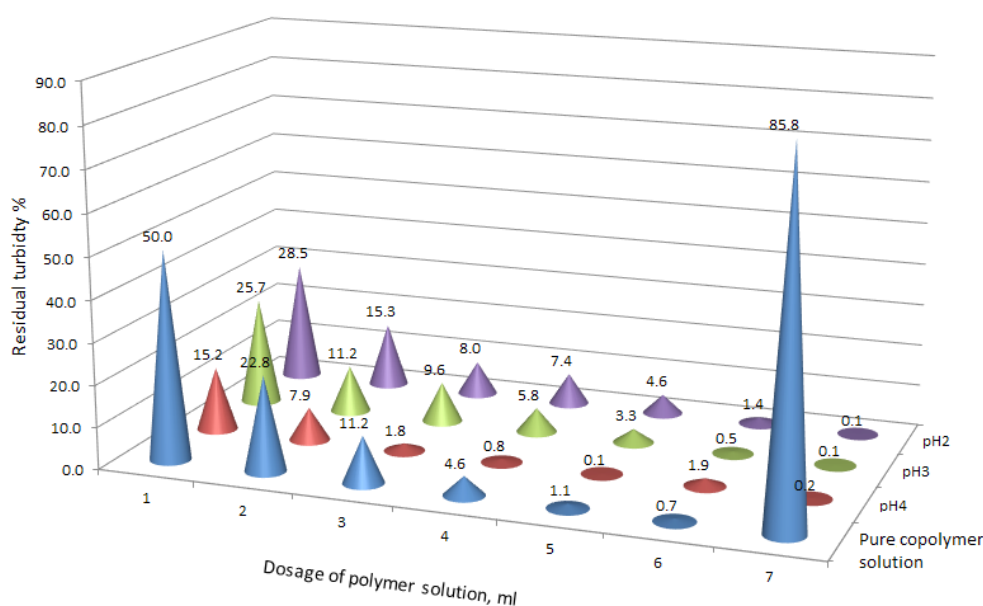
Figure 5 – Flocculation property of poly (DADMAC-VEMEA 95:5 (0.03% in.))

Considering the above results obtained from flocculation experiments, we can propose a flocculation mechanism. Based on the widely accepted three flocculation mechanisms [22], two mechanisms can be used to explain the flocculation of bentonite suspension with DADMAC-VEMEA copolymer, which are charge neutralization and polymer bridging mechanisms (Figure 7). At low pH the VEMEA unit in the copolymer gains a positive charge in addition to DADMAC, which makes the copolymer more positively charged.

As copolymers are cross-linked in some degree and swell under acidic pH, they overlap the suspended bentonite particles which precipitate due to gravitational force [28, 30].
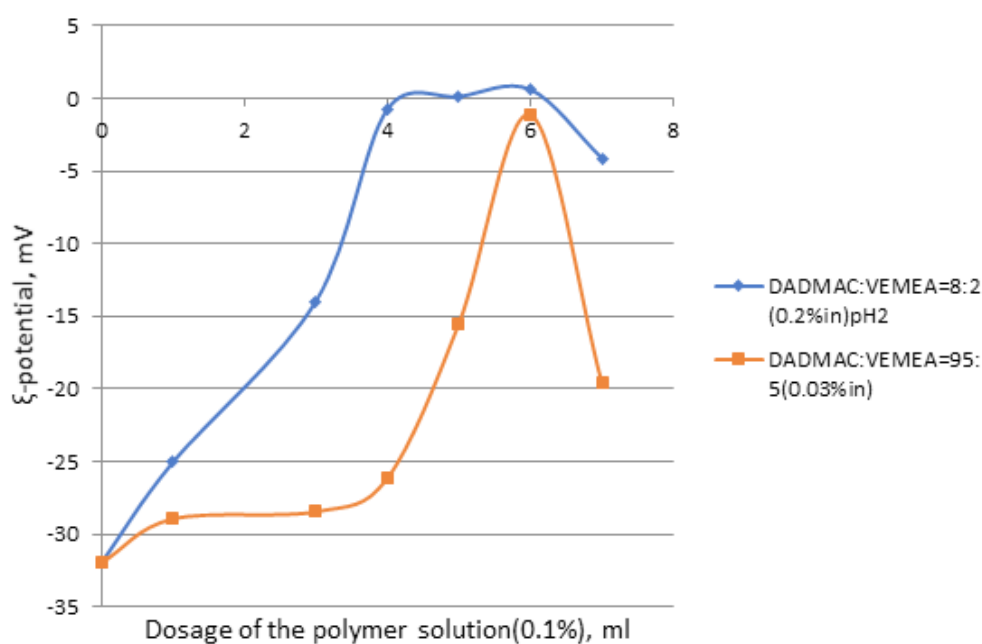
Figure 6 – Zeta potential of supernatants after treatments of copolymers
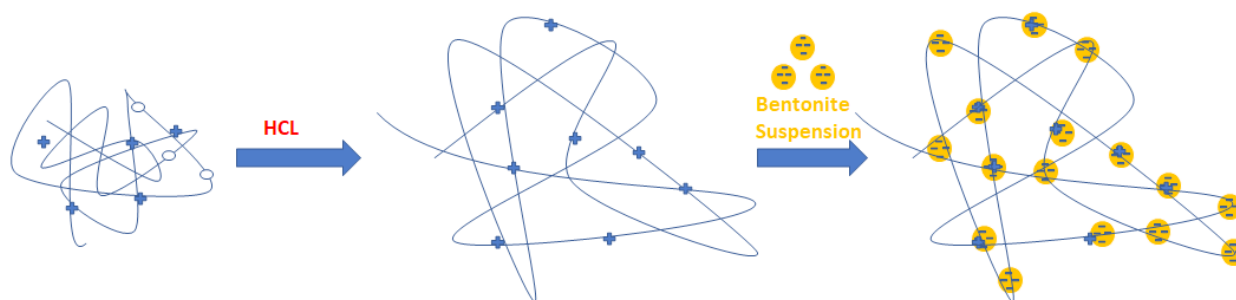

Figure 7 – Suggested flocculation mechanism for treatment of bentonite suspension with poly (DADMAC-VEMEA) copolymer

Conclusion

From the results of performed experiments it can be concluded that the flocculation ability of poly (DADMAC) homopolymer can be improved by adding a VEMEA unit to the polymer chain and making the copolymer partially crosslinked. As mentioned above, the VEMEA monomer becomes positively charged in acidic media, which is preferred in wastewaters containing negatively charged mechanical particles, and the optimized cross linkage degree of the copolymer help to overlap large areas by the flocculant, which initiates flocculation by bridging mechanism. The copolymerization of DADMAC with a VEMEA-containing primary amine has big potential in developing effective flocculants, which can be utilized in the primary steps of wastewater purification, and at the same time partial cross linkage of the copolymers yield purified water with less residual polymer.

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