

Low-temperature synthesis of allyl dimethylamine by selective heating under microwave irradiation used for water treatment

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Abstract

Low-temperature synthesis of allyl dimethylamine (ADA) by selective heating under microwave irradiation (MI) used for water treatment is investigated. The effect of MI, ultrasound irradiation (UI) and conventional heating on yield of ADA, reaction time and the flocculation efficiency of polydiallyl dimethylammunion chloride (PDADMAC) prepared from ADA were studied. The results show that by selective heating at low temperature, MI not only increases yield of ADA and reduces reaction time, but also greatly enhances the flocculation efficiency of PDADMAC.

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Keywords: Microwave irradiation; Low temperature; Selective heating; Flocculation; Allyl dimethylamine

1. Introduction

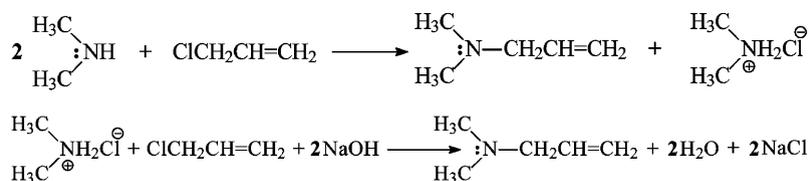
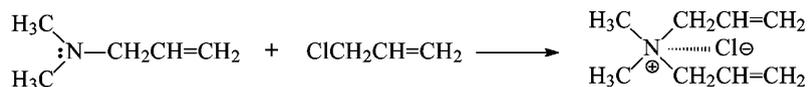
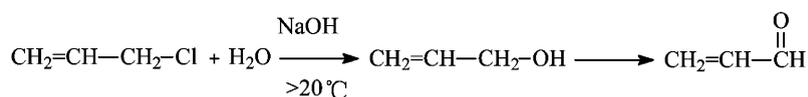
Microwave irradiation (MI) has gained increasing interest in recent years, and has been used more and more as an activation method for a number of organic synthesis (Berlan, 1995; Chen et al., 2004; Caddick, 1995; Fini and Breccia, 1999). The main benefits of performing reactions under MI are the significant rate-enhancement and the higher product yields. However, MI is generally not effective for organic synthesis at low temperature, while most microwave-assisted organic syntheses were carried out at high temperatures by using the thermal action of MI (Dollington et al., 1991; Cherng, 2002). To our knowledge, only few papers on organic syntheses under MI at low temperature have been reported. Bose et al. (1991), Sun et al. (1988) and

Lewis et al. (1992) reported the athermal action of MI on organic synthesis at low temperature. Huang et al. (1996a,b) studied the kinetics theory of MI on chemistry synthesis at different temperatures. The results showed that the acceleration of chemical reaction with MI is caused by not only the dielectric heating, but also the athermal action. MI can cause the variation of activation energy and pre-exponential factor. But these early reports have been discounted as merely thermal effects. Because it is clear that when irradiating organic materials in a microwave, even the frequency of the radiation (2.45 GHz) does not “activate” specific bonds in a molecule. It has been agreed that microwave heating will not lead to any kinetic differences compared to any other form of heating (Caddick, 1995).

Allyl dimethylamine (ADA) is an intermediate in the reaction process of preparing diallyl dimethylammunion chloride (DADMAC), whose polymers have potential applications in various fields (Wandrey et al., 1999; Mastsumoto, 2001; Ren et al., 2001) (Scheme 1). In reference to the literatures (Wandrey et al., 1999;

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Step I (forming ADA)**Step II (quaterisation)****Side reaction**

Scheme 1. Synthesis of diallyldimethylammonium chloride.

Brain, 1995; Butler and Angelo, 1958; Butler and Bunch, 1949; Negi et al., 1967) as well as our previous works (Zhao et al., 2002; Chang et al., 2000), synthesis of ADA is a key step for producing higher molecular weight polymers of DADMAC (PDADMAC) as a flocculant. In the conventional methods, the yields of ADA at both high temperature and low temperature are too low and reaction time is long so that yield of high-purity DADMAC is lower than 57% and reaction time is longer than 6h. This problem seriously inhibits the application of higher molecular weight polymer of DADMAC as a highly efficient flocculant.

In this paper, we wish to report a novel process: low temperature synthesis of ADA under microwave irradiation in order to prepare high molecular weight PDADMAC as a highly efficient flocculant. The work presented is mainly aimed at reducing reaction time and improving the yield of ADA. Though there seems a paradox between microwave irradiation and low temperature, it may be explained as a result of selective heating within the heterogeneous reaction. In order to study the reaction mechanism, the effects of MI, ultrasound irradiation (UI) and the conventional heating on the process were investigated. The flocculation efficiency of high molecular weight PDADMAC prepared by the products from this method was studied. The results showed that this novel reaction procedure is highly efficient and affords higher yield and shorter reaction time. Compared with conventional methods, the results clearly show a significant effect of microwave on a heterogeneous reaction by selective heating at low temperature.

2. Experimental part**2.1. Apparatus**

The self-improved domestic microwave oven, LG Korea, is used. Its irradiation power is from 75 to 750 W. In the modified microwave oven, the reactor is a 50 ml flask placed in a beaker containing 500 ml ice-water (8:2) mixture for controlling the reaction temperature. This flask is attached to a four-way tube connected with a reflux condenser, stirring apparatus and a filling tube. This system allows for different adding methods of NaOH (the addition of the NaOH solution or the solid NaOH) under microwave irradiation at low temperature.

The sonochemical experiments and the tradition synthesis were carried out in a Branson S3200 (50 kHz, 150 W, USA) ultrasonic cleaning bath and in magnetic mixer (YY 90-3, China) under ice water bath, respectively.

2.2. Materials

Allyl chloride, dimethylamine and sodium hydroxide are chemically pure. All the reagents are domestic products and are used without further purification. Distilled water is used for the preparation of all solution.

2.3. General procedures of synthesis of ADA by MI, UI and conventional heating

To investigate the effect of MI, UI and the conventional heating on reaction of forming ADA, conversion

of dimethylamine determined by a fashion in which thymolphthalein was used as an indicator (Butler and Angelo, 1958; Hunter, 1979; Chang et al., 2000). After the 33% aqueous solution of dimethylamine (0.1 mol) was charged into the flask from the filling tube and cooled to 5 °C under ice–water bath and stirring. Then allyl chloride (0.1 mol) was added and cooled. Finally, $\frac{1}{10}$ of 40% aqueous solution of sodium hydroxide or solid sodium hydroxide (0.1 mol) was added. The microwave oven (or ultrasound reactor) was started up with the power of 150 W under stirring until the blue color disappeared. The reaction time was recorded in order to draw the curve of the conversion of dimethylamine. Then another $\frac{1}{10}$ NaOH solution/solid NaOH was added and the reaction time was recorded again when the blue color disappeared. The process was repeatedly carried out until the blue color did not disappear after adding NaOH for long time.

Yields of tertiary amine are calculated from high-purity DADMAC yield. The concentration of produced DADMAC aqueous solution was measured by the precipitation titration using sodium tetrphenylboron.

2.4. The flocculation test

For the flocculation tests, a total of 1 L of water was transferred to a 1 L beaker. Under rapid stirring conditions, 15 ml of the stock kaolin suspension (100 g/L) was added by using a micropipet, giving a clay concentration of 1500 mg/L. The flocculation experiments were conducted at room temperature (20–23 °C). Prior to the addition of flocculants, the target pH was adjusted by adding a predetermined amount of NaOH or HCl into the kaolin suspension, with rapid stirring. The flocculant was added using a micropipet. After being dosed, 1 min of rapid mixing at 300 rpm was applied, followed by 10 min of slow stirring at 40 rpm. The flocs were allowed to settle for 30 min, and the residual turbidity (RT) was measured using a HACH 2100N Turbidimeter (Hach, Loveland, Co).

Throughout the mixing and coagulation periods, the suspension was continuously sampled by peristaltic pump and monitored by a photometric dispersion analyzer (PDA 2000; Rank Brothers Ltd.) to obtain a flocculation index (FI).

3. Results and discussion

3.1. Synthesis of ADA by conventional heating at different temperature

Fig. 1 shows that variations of dimethylamine conversion with reaction time by conventional method at different temperatures. Results in Fig. 1 indicate that the conversion of dimethylamine increases obviously

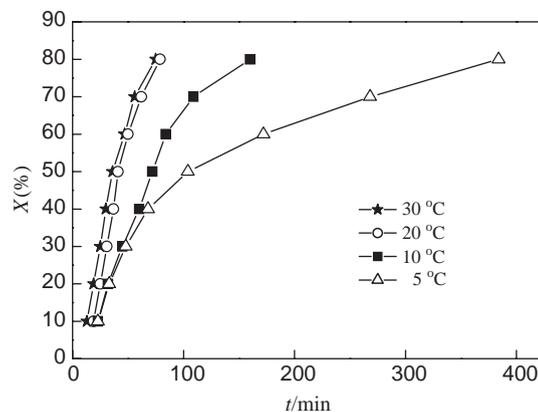


Fig. 1. Variation of dimethyl amine conversion with reaction time using conventional method.

with increasing the reaction temperature. However, from Table 1, it is found that the yield of ADA is not improved with an increase of the reaction temperature, especially all these yields at different temperatures are lower than 60%, though the reaction time at the optimum point can be reduced with increasing reaction temperature. The cause is that with increasing reaction temperature by conditional heating, reaction rates of side reaction and the quaterization reaction are more obviously accelerated than reaction rate of forming ADA (Boothe, 1969; Hunter, 1979; Zhao et al., 2002).

3.2. Synthesis of ADA by MI, UI and conventional heating at low temperature

Table 2 illustrates different yields of ADA by MI, UI and conventional heating at low temperature. It is found that MI, UI or the addition of solid NaOH has a significant effect upon yields of ADA at low temperature. In particular, under the condition of MI and using the addition of solid NaOH, the optimum yield of ADA is improved to 71% and reaction time is only 7 min.

In order to better understand the reaction mechanism of forming ADA by MI, UI and conditional heating at low temperature, variations of dimethylamine conversion with reaction time by MI, UI and conventional heating at low temperature are shown in Fig. 2. The figure shows that MI has a significant effect upon the conversion of dimethylamine, especially in the region where conversion of dimethylamine is higher than 40%. It is highly probable that the reaction system consists of two phases: water phase and oily phase. The reaction of forming ADA is carried out at the interface of two phases, while the reaction of producing DADMAC is carried out in the oily phase. MI heating can rapidly heat water phase whose dielectric constant is large, whereas oily phase whose dielectric constant is small do not couple and therefore is not heated with MI although

Table 1
Yields of ADA by conventional method

Different temperatures	Yields of tertiary amine (%)				
	30 min	60 min	120 min	240 min	480 min
5 °C	10.7	18.9	35.2	57.8	57.5
10 °C	17.8	43.6	58.9	59.2	58.5
20 °C	40.6	58.2	57.6	57.1	56.9
30 °C	45.3	60.2	58.5	57.8	57.5

Table 2
Yields of ADA by MI, UI and conventional method at low temperature (5 °C)

Different methods	Yields of tertiary amine (%)			
	3 min	7 min	11 min	15 min
Adding 40% NaOH solution	Trace	1.8	3.6	5.1
UI, adding 40% NaOH solution	1.8	3.6	5.7	8.9
MI, adding 40% NaOH solution	2.1	4.4	6.3	9.8
Adding solid NaOH	16.3	28.2	41.5	46.5
UI, adding solid NaOH	18.2	28.9	42.3	47.8
MI, adding solid NaOH	37.0	71.0	70.2	70.5

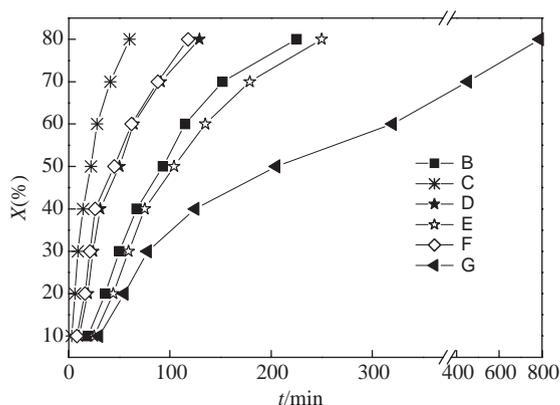


Fig. 2. Variations of dimethyl amine conversion with reaction time by MI, UI and conventional method at low temperature (5 °C). (B): MI, 40% NaOH solution; (C): MI, solid NaOH; (D): solid NaOH; (E): UI, 40% NaOH solution; (F): UI, solid NaOH; (G): 40% NaOH solution.

it is of course heated by heat transport from water phase. At low temperature, MI can accelerate reaction rates of forming ADA by selective heating and accelerating mass transport in the water phase. At the same time, reaction rates of producing byproducts and DADMAC can be observably inhibited at low temperatures of the system and the oily phase. Therefore, reaction rate, yield and purity of ADA are remarkably increased. The most interesting phenomenon can be

found that conversion of dimethylamine and the yield of forming ADA are dramatically increased under MI heating and by using the addition method of solid NaOH. All these results seem to suggest that at low temperature, dissolution heating generated from water phase, as MI heating, also can selectively heat water phase to accelerate reaction rate of forming ADA at the phase interface and mass transport of dimethylamine in water phase. In conclusion, the selective heating at low temperature is significantly enhanced by MI heating and using addition of solid NaOH together.

Fig. 2 also shows that in the present experiments, UI has also significant effect on the conversions of dimethylamine using the addition of 40% NaOH solution, as well as on the yield of forming ADA as shown in Table 2. The reason maybe is that UI can accelerate the reaction rate of the heterogeneous reaction by “hot theory” action and accelerating mass transport (Mason, 1994; Birkin and Susana, 1996). But UI has little effect on conversions of dimethylamine using the addition of solid solution. This phenomenon probably suggests that UI does not selectively affect water phase at low temperature.

3.3. The flocculation test

Homopolymer of high intrinsic viscosity ($\eta = 2.7$) can be prepared from ADA by the two-step method. This value is far higher than that of homopolymer prepared by conventional method, whose intrinsic viscosity is

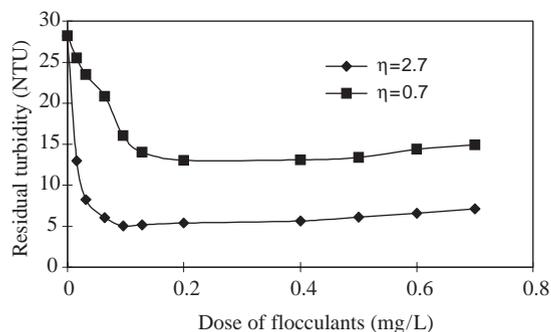


Fig. 3. Effect of different molecular weight PDADMAC on the flocculation of kaolin suspensions.

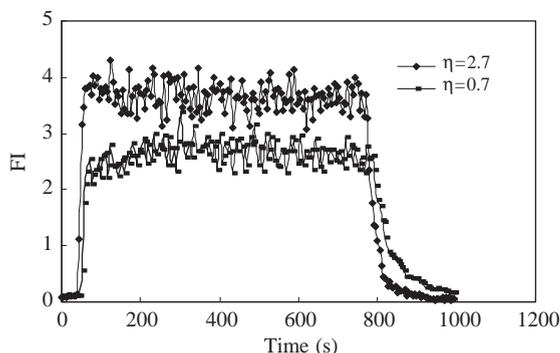


Fig. 4. Effect of different molecular weight PDADMAC on flocculation index at the optimum point for the systems.

about 1.0. Using the above homopolymers as flocculants, the flocculation test was carried out by the jar test. The results are shown in Figs. 3 and 4. Fig. 3 shows that both the optimum dose and the optimum residual turbidity by using PDADMAC of $\eta = 2.7$ as flocculant was smaller than those by using PDADMAC of $\eta = 1.0$. Fig. 4 shows that using PDADMAC of $\eta = 2.7$ as flocculant, the floc size is larger, the floc is more stable and the settling rate is higher. These phenomena indicate that the high intrinsic viscosity ($\eta = 2.7$) PDADMAC prepared from ADA is advantageous in flocculation. It can be suggested by the “bridging action” of flocculants: higher the molecule weight, stronger the “bridging action”. All above results are in favor of low temperature synthesis of ADA under MI.

4. Conclusion

Low-temperature synthesis of allyl dimethylamine by selective heating under microwave irradiation used for water treatment is described. The effect of microwave irradiation, ultrasound irradiation and conventional

heating on the reaction at low temperature was investigated. Compared with conventional methods, the results show that MI has a significant effect on a heterogeneous reaction at low temperature by selective heating. Moreover, the selective heating at low temperature is significantly enhanced by MI heating and addition of solid NaOH together. The results also show that yield of forming ADA is improved from 60% to 71% and reaction time is reduced from 2–6 h to 7 min by selective heating under microwave irradiation and using the addition of solid NaOH. At particular, higher molecular weight polydiallyldimethylammonium chloride prepared from ADA has higher flocculation efficiency.

Acknowledgements

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