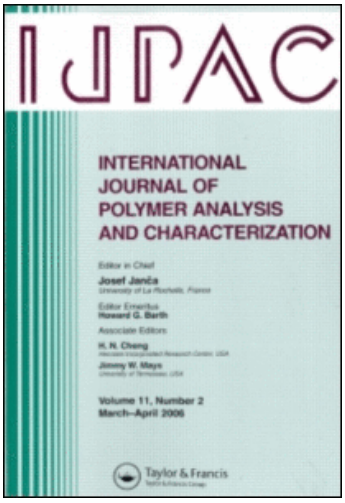

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HPLC Analysis of Mixtures of Acrylamide and Quaternary Ammonium Cationic Monomers

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The HPLC separation of acrylamide from the quaternary ammonium cationic monomers dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate has been investigated. It was found that a cyano-bonded silica stationary phase provided superior separations relative to an octyldecyl-bonded coated substrate. For either stationary phase, a binary mixture of acetonitrile and water gave far improved elution characteristics to a methanol-water mobile phase. An optimum acetonitrile-water ratio of 50:50 vol% was identified for the CN-coated sorbents. Dibutylamine was also used as an additive to reduce the adsorption of the cationic monomer, with a concentration of 0.01 M providing the best chromatograms. The mobile phase pH, and the acid used to adjust the pH, were also found to influence the peak quality. The optimized method can be used for rapid data acquisition. The method was demonstrated for the determination of residual monomer concentration in an inverse-emulsion copolymerization.

KEY WORDS Acrylamide, quaternary ammonium monomers, HPLC, inverse-emulsion, copolymerization

INTRODUCTION

The copolymer composition of cationic polyelectrolytes is usually determined by colloid titration [1–3], conductiometric titration [4], or silver nitrate titration [5]. Colloid titrations were developed by Terayama [6] based on observations of stoichiometric complexes formed between high molecular weight polyanions and polycations. The formation of these symplexes has been verified by measuring the chemical shift displacement in ^{13}C NMR [7]. Colloid titration is volumetric, incorporating a metachromatic end point detection [8] which provides a steeper gradient than potentiometric detection. To titrate positively charged macromolecules, potassium poly(vinyl alcohol sulfate) (PVSK) is usually used as a negative colloid, with toluidine blue (a cationic dye) as the indicator [9,10]. A distinct color change from blue to reddish-purple, and the precipitation of the polyelectrolyte, are observed at the end point. However, these titrations are affected by trace levels of multivalent salts and have very slow symplex formation. Furthermore, they are not sto-

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ichiometric for chain lengths below approximately three hundred [11]. Other means of end-point detection such as ion-selective electrodes [12], conductivity [13] and turbidimetry [14] have also been used, but offer similar accuracy to colorimitry.

In this research our goal was to develop analytical methods to quantify the composition of reaction mixtures involving acrylamide and quaternary ammonium monomers, such as dimethylaminoethyl acrylate (DMAEA) and dimethylaminoethyl methacrylate (DMAEM). Both of the cationic monomers were quaternerized with methyl chloride.

A recent review of the estimation of comonomer composition for the determination of reactivity ratios [15] concluded that chromatographic techniques, specifically gas and liquid chromatography, provide the most accurate measurements of residual monomer concentration. While gas [16–18] and liquid [19–21] chromatographic methods have been employed for several years in the detection of acrylamide, only one procedure has been reported for the acrylamide-quaternary ammonium system [22]. This involved the use of a mobile phase which consisted of a 50:50 vol% mixture of acetonitrile-water with 0.005 mol/L of dibutylamine phosphate. The stationary phase was a silica column with 9% CN groups bonded to the surface.

The objective of this present investigation was the evaluation and optimization of alternative mobile and stationary phases for this separation. In particular, the substitution of acetonitrile with less expensive solvents, the effect of pH, the concentration of the dibutylamine additive, the type of acid employed for the pH adjustment and the stationary phase were studied.

EXPERIMENTAL

Hardware

The HPLC system consisted of a Hitachi L6000 isocratic pump (Hitachi Instruments, Tokyo, Japan), a Hitachi L4000H variable wavelength UV detector operating at either 210 or 214 nm, and a Rheodyne 7725i injector (Cotati, CA). For all analyses the mobile phase flow rate was kept at 2.0 mL/min [22]. A stainless-steel filter and a CN precolumn (Waters, Millford, MA) were in-line between the pump and the column. The columns used were housed in a Waters Radial Pak TM cartridge, operating at a nominal pressure of 180 kg/cm^2. Two columns were investigated. The CN column had an 8 mm I.D. and was packed with 10 μm particles (mean pore size 125 Å), with a 6% carbon load bonded to a μ-Porasil (silica) substrate. The C_{18} column had an 8 mm I.D. and was packed with 5 μm particles (mean pore size 125 Å), with a 10% carbon load bonded to the μ-Porasil substrate.

Chromatograms were collected on either a HP Vectra 286 or a 486 computer running Viscotek GPC PRO Version 4.01 software (Houston, Texas).

Mobile Phases

The principal mobile phase investigated consisted of combinations of acetonitrile, water and dibutylamine. The dibutylamine was used to suppress undesired interactions of the cationic monomer with the sorbent surface and thereby influence the retention volume and peak separation. The acetonitrile-water ratio was varied between 50 to 90 vol % acetonitrile with the dibutylamine concentration varied between 0.005 and 0.1 mol/L. The mobile phase

pH was varied between 3.3 and 8.0. Phosphoric, hydrochloric and nitric acids were utilized for the pH adjustments. In certain separations the acetonitrile was replaced with methanol. The methanol to water ratio was systematically varied between 60 and 98 vol % methanol.

Purification

Type I water (Continental Water, San Antonio, TX) with a resistivity ≥ 16.7 mΩ-cm was filtered through a 0.2 μm nylon membrane filter (Scientific Resources, Inc., North Brunswick, NJ) and used immediately for analysis. HPLC grade acetonitrile and methanol were purchased from Fisher Scientific (Norcross, GA) and used as received. The dibutylamine (99.9% purity) was obtained from Eastman Kodak (Rochester, NY) and was used without further purification. The mobile phase was prepared by adding the dibutylamine to the water, mixing in the acetonitrile or methanol and adjusting the pH. The nitric acid (Certified ACS Grade, 70% purity), hydrochloric acid (Certified ACS Grade, 36% purity) and phosphoric acid (Certified ACS Grade, 85% purity) were purchased from Fisher Scientific.

The acrylamide monomer was purchased from Cytec (Charlotte, NC) and was purified by recrystallization in chloroform (ACS Reagent Grade, 99.9% pure, Fisher). The DMAEA and DMAEM quaternary ammonium monomers were obtained from CPS Chemicals (West Memphis, AR) as aqueous solutions (75% for DMAEM and 80% for DMAEA) inhibited with approximately 600 ppm of hydroquinone monomethylether. The faster reacting DMAEM was also stabilized with 10 ppm of cupric ions to chelate the monomers. Both of the cationic monomers were quaternerized with methyl chloride. These monomers can be purified by repeated extraction with acetone [22]*, which has the effect of simultaneously removing the water, cupric ions and hydroquinone monomethylether, as well as precipitating the monomer. Following five vigorous extractions (six were required for DMAEA), the quaternary ammonium monomer precipitated as a powder. Further HPLC analysis showed that the precipitated monomers contained less than 0.5 ppm of impurities.

Polymer Synthesis

The reactivity ratios, as well as the drift in the copolymer composition with conversion, are very sensitive to the initial monomer concentration [23]. Therefore, the results obtained in a solution polymerization are not applicable to commercial synthesis which are generally carried out at 50% solids levels in heterophase water-in-oil processes. In this work, all copolymers were synthesized by inverse-emulsion polymerization [24]. This involved the dispersion of the aqueous comonomer mixture (50 vol % water) in an isoparaffinic continuous phase (Isopar-M, Exxon; supplied by ChemCentral, Nashville, TN). The mixture was stabilized with HB 239 or HB 246, nonionic steric stabilizers provided by ICI Americas (Wilmington, DE), and agitated at 400 RPM throughout the reaction. Prior to the synthesis, the aqueous and organic phases were individually sparged with nitrogen (99.9% pure, AL Compressed Gas, Nashville, TN) for 15 min. This lowered the dissolved oxygen concentration to below 1.5 ppm measured with a Ingold dissolved oxygen probe (Wilmington, MA). Azobisisobutyronitrile, a chemical initiator, (Wako, Richmond, VA) was used as received (99.9% purity). Syntheses were performed isothermally at temperatures between 30 and 50 °C. This resulted in a dispersion of small particles (dp approximately 150 nm).

*Other extracts such as benzene, and solid materials such as activated charcoal, were found to be significantly less effective in the removal of the hydroquinone monomethylether.

Syntheses were performed in a 5-L stainless steel reactor [25] equipped with an external heating/cooling jacket. The reactor was computer controlled, using an error-squared proportional-integral-derivative controller, to within 0.3 ± °C throughout the reaction by varying the chilled water-to-steam ratio entering the cooling jacket. The reactor was sparged continually with purified nitrogen to remove any residual oxygen which could consume radicals and interfere with the polymerization.

Sample Handling

Twenty-milliliter aliquots were withdrawn from the reactor at 5–10 min intervals in presterilized 20-mL glass-scintillation vials (Fisher Scientific) containing 100–200 ppm of hydroquinone. The hydroquinone was used to terminate the reaction. These samples were then stored in ice water for the remainder of the reaction and then transferred to a refrigerator where they were maintained at a temperature below 10°C until they were analyzed, usually the next day. A 0.01–0.02 gram sample of this aliquot was added to 10 mL of acetonitrile and agitated until the supernatant was clear. The acetonitrile precipitated the polymer and separated the oil and emulsifier while it simultaneously solubilized the monomers. This method was found to be a much faster means to prepare LC samples as compared to the traditional method of centrifugation, separation and redissolution in water, which required up to one week for sample preparation and has a precision which is limited to approximately ±1%. With the present technique, the supernatant turbidity can be controlled either by time (waiting for separation), centrifugation or filtration. All three methods were employed in this study with the centrifugations performed at 2000 RPM using an IEC centrifuge and the filtrations carried out with a 0.45 μm membrane filter (Scientific Resources, Inc., North Brunswick, NJ).

Once the supernatant was clear, a 100-μL aliquot was removed with a glass syringe (Hamilton Co., Reno, NV) and injected into the HPLC. Although the injection solvent was pure acetonitrile and the mobile phase was an acetonitrile-water mixture, system peaks were not found to interfere with the chromatogram for either the acrylamide or the quaternary ammonium monomers. In all cases the reaction mixtures contained less than 200 ppm of acrylamide and 500 ppm of the quaternary ammonium monomers since these were the corresponding limits for Beer's law. Residual monomer concentrations were determined from calibration curves between 0 and 500 ppm for the DMAEA and DMAEM and 0 and 100 ppm for the acrylamide. These were prepared each day prior to analysis and duplicated at the end of the analysis. Samples from a given experiment were always analyzed together within a 10 hour period.

RESULTS AND DISCUSSION

C_{18} Column

Mobile Phase Optimization: Substitution of Methanol for Acetonitrile

The interaction of quaternary ammonium monomer with silica is usually too strong to permit the application of silica based sorbents for chromatographic characterization. This adsorption can be mitigated to some extent through the appropriate selection of a, usually binary, mobile phase. Hunkeler [22] succeeded to separate acrylamide from DMAEM,

DMAEA and diallydimethylammonium chloride (DADMAC) using a mixture of acetonitrile and water. Since methanol has similar solvent properties to acetonitrile, and is much less expensive, it was considered as an alternative constituent of the mobile phase. A screening was performed where the methanol-water ratio was varied between 60 and 98 vol % methanol with an optimum found at 90% methanol. Figure 1 shows a chromatogram of an acrylamide-DMAEM sample. It is evident that the DMAEM is strongly retained on the C_{18} column and the peak is highly skewed. Additionally, the peak separation between the acrylamide and the DMAEM is too large to render this method acceptable for rapid data analysis. The adsorption of the cationic monomer can be suppressed with dibutylamine, as is reported in a later section. However, no combination of methanol, water and dibutylamine significantly improved the characteristics of the DMAEM peak. These experiments indicated that the combination of a methanol containing mobile phase and a C_{18} stationary phase did not give an acceptable separation. They were not further considered in this investigation.

For the remainder of the experiments with the C_{18} column, an acetonitrile-water ratio of 90/10 vol% was found to give reasonable peaks for both the acrylamide and the DMAEM, as is shown in Figure 2. In Figure 2 the retention volume for acrylamide was 2.68 mL compared with 4.86 mL for DMAEM. These are comparable to the results obtained by Baade et al. [26] with a CN stationary phase. It is important to note that neither Figures 1 nor 2 represent optimized systems; in particular, the peak shape and plate count for the DMAEM is still poor.

Effect of Dibutylamine Concentration

Figure 3 is a capacity factor-concentration plot which illustrates the effect of the dibutylamine concentration in the mobile phase on the chromatograms obtained for the acrylamide-DMAEM system. The capacity factor (k') is defined as $k' = (t_r - t_m)/t_m$, where t_r is the retention time and t_m is the dead time of the column. Clearly, increasing the concentration of the dibutylamine reduces the adsorption of the cationic monomer, as is to be expected. The increased level of the dibutylamine also improved peak shape as can be

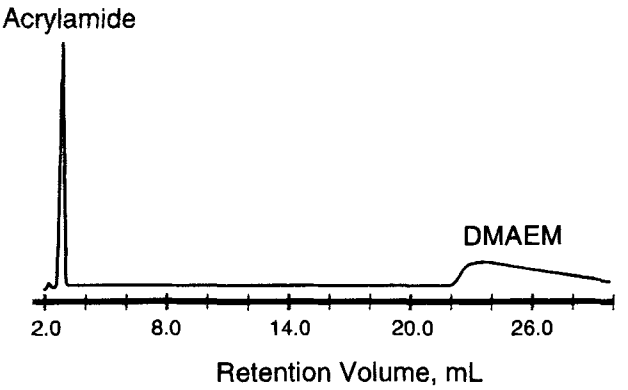


FIGURE 1 The Chromatogram of a mixture consisting of 25.0 ppm of acrylamide and 500 ppm of DMAEM using a C_{18} column. The mobile phase was 90 vol % methanol and 10 vol% water. The pH was adjusted to 3.5 with the addition of hydrochloric acid. Dibutylamine was used as an additive to reduce adsorption at 0.01 M. The peaks were detected at 210 nm.

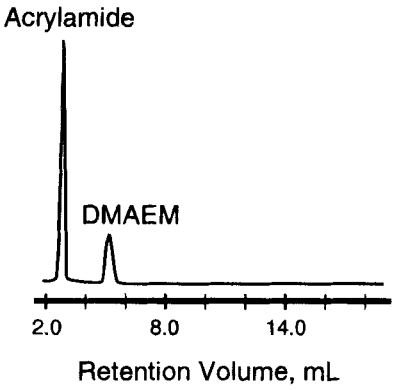


FIGURE 2 Chromatogram of a mixture consisting of 100 ppm of acrylamide and 100 ppm of DMAEM using a C_{18} column. The mobile phase was 90 vol % acetonitrile and 10 vol% water. See Figure 1 for other conditions.

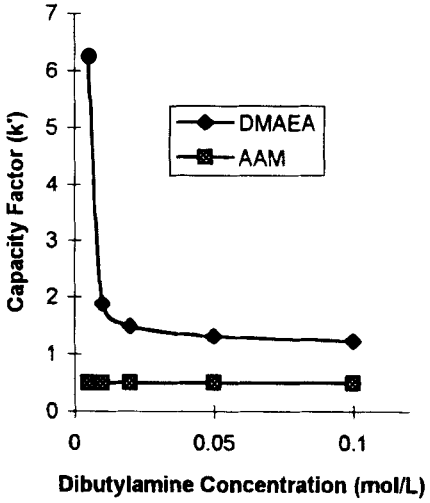


FIGURE 3 Capacity factor k' vs. concentration plot illustrating the effect of the dibutylamine concentration on the retention time of the DMAEM. The experimental conditions are the same are listed in Figure 2.

seen by comparing the chromatograms in Figures 2 and 4. A dibutylamine concentration of 0.1 M was found to be optimal and was used throughout the remainder of this study. Marginally lower levels of dibutylamine (e.g. 0.01 and 0.05 M) also yielded good chromatograms as defined by the shape of the DMAEM peak. Therefore, the elution behavior is not extremely sensitive to the dibutylamine level, and any concentration between 0.01 and 0.1 M would give acceptable results and nondistorted peaks.

Effect of Mobile Phase pH

The mobile phase pH has no effect on the elution of the acrylamide; however, it did strongly influence the retention of the DMAEM, as is illustrated in Table I. The capacity factor was high in either highly acidic or basic solutions; however, between a pH of 3.5 and 7.0, the adsorption of the cationic monomer was strongly reduced. Clearly, the opti-

TABLE I

The effect of mobile phase pH on the capacity factor k' and the peak height of DMAEM*.

pH	Capacity Factor (k')	DMAEM Peak Height (mV)
3.3	0.95	0.54
3.5	0.87	0.63
5.5	0.83	0.67
7.0	0.80	0.71
8.0	1.35	0.28

*The mobile phase was buffered with 0.05 M dibutylamine. DMAEM was injected at 100 ppm, and peak detected at 210 nm.

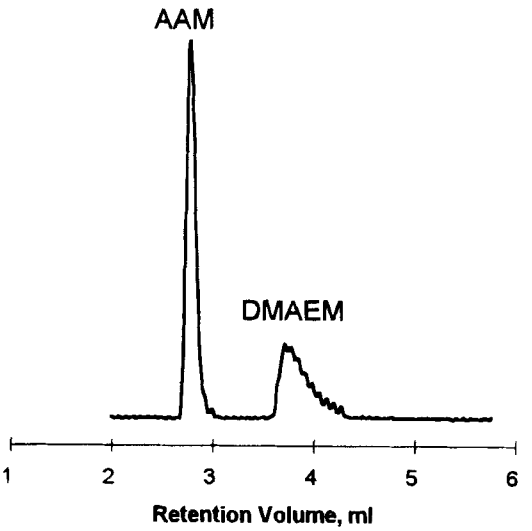


FIGURE 4 Chromatogram of a mixture consisting of 100 ppm of acrylamide and 100 ppm of DMAEM using a C_{18} column. The 'optimal' mobile phase for the C_{18} stationary phase consisted of a mixture of 90 vol % acetonitrile and 10 vol % water. The pH was adjusted to 7.0 with the addition of hydrochloric acid. Dibutylamine was used as an additive to reduce adsorption at 0.1 M. The peaks were detected at 210 nm.

mum peak height and capacity factor occur at a pH of 7.0. While these results are presented for DMAEM, the separations are very similar with the more hydrophilic DMAEA as is seen in Figure 5. The peak quality for DMAEA was not very good using the C_{18} sorbent. For both cationic monomers, the calibration curves were linear up to 500 ppm, while for acrylamide the extinction coefficient was constant up to 200 ppm, in agreement with ref [22].

For both DMAEA and DMAEM the best results which were obtained on the C_{18} stationary phase with a mobile phase consisting of a mixture of 90/10 vol % acetonitrile-water, dibutylamine concentration between 0.01 and 0.1 M and a pH between 3.5 and 7.0. More specifically, the capacity factor was minimized at a neutral pH and a dibutylamine concentration of 0.1 mol/L. This would represent an 'optimal' mobile phase with the C_{18} stationary phase.

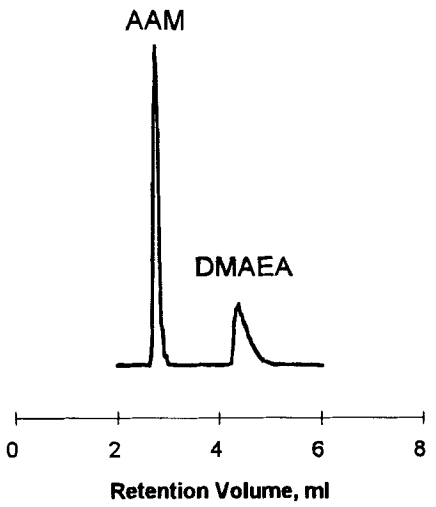


FIGURE 5 Chromatogram of a mixture consisting of 100 ppm of acrylamide and 100 ppm of DMAEA using a C_{18} column. See Figure 4 for other conditions.

CN Column

The separation of mixtures of acrylamide with DMAEM, DMAEA, and DADMAC using a CN coated silica stationary phase has been studied by Hunkeler [22], who found that the optimum mobile phase was a 50:50 vol % mixture of acetonitrile and water adjusted to a pH 3.0. Given these results, the present investigation focused on adjusting the dibutylamine concentration in order to control the retention volume of the cationic peak. Additionally, we examined various strength acids to determine if the acid selection significantly influenced the quality of the chromatograms.

Effect of Acid Type Used for Mobile Phase pH Adjustment

Figures 6a-c illustrate the effect of the acid used to adjust the pH of the mobile phase on the chromatograms. Separations performed using either H_3PO_4 (Figure 6a) or HCl (Figure 6b) gave better peak shapes than when HNO_3 was employed (Figure 6c). In particular, as is seen in Figure 6a, the DMAEA peak is nonskewed and very symmetric with H_3PO_4, while with HNO_3 the sensitivity of the UV detection was strongly reduced (Figure 6c). Even though HCl provided a better selectivity, H_3PO_4 was selected for the mobile phase pH adjustment for subsequent measurements, since it provided improved peak symmetry and, as a result, also higher plate counts for both acrylamide and DMAEA.

Effect of Dibutylamine Concentration

Figures 6a and 7 illustrate the effect of the dibutylamine concentration on the peak separation for the acrylamide-DMAEA system. The concentration of dibutylamine in the mobile phase was either 0.005 or 0.01 mol/L while the other chromatographic conditions remained the same. As was observed with the C_{18} column (Figure 3), the adsorption, and hence the retention volume, of the cationic monomer was reduced as the dibutylamine concentration was increased. Clearly the dibutylamine is competitively blocking active surface sites where the cationic monomer could adsorb. At an optimum dibutylamine con-

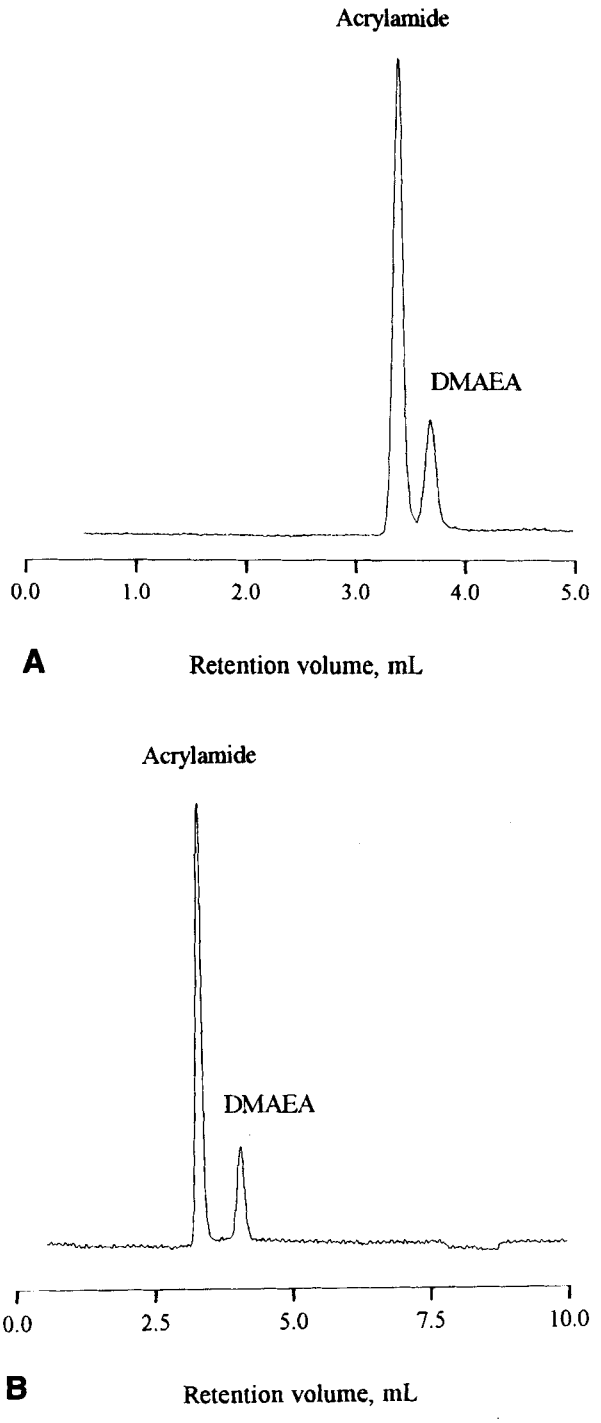


FIGURE 6 Chromatogram of a mixture consisting of 53.0 ppm of acrylamide and 214.4 ppm of DMAEA using a CN column. The mobile phase was 50% acetonitrile and 50% water. Dibutylamine used as an adsorption reduction additive at 0.01 M. The pH was adjusted to 3.0 using a) 1.0 M H_3PO_4, b) 1.0 M HCl, c) 1.0 M HNO_3. The peaks were detected at 214 nm.

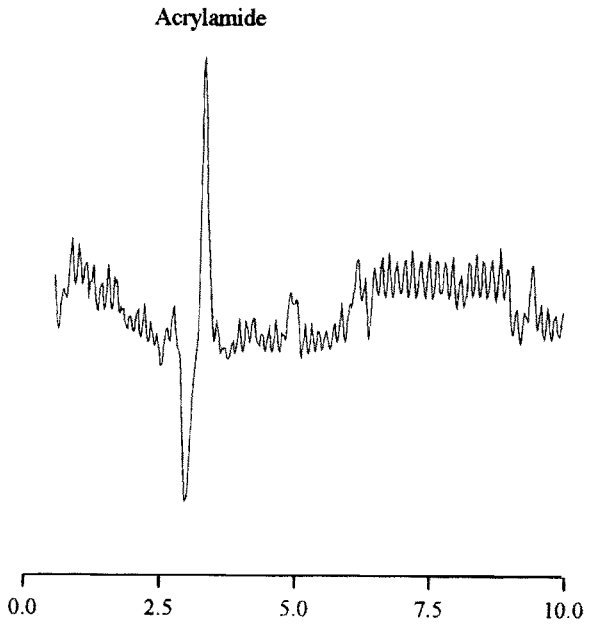


FIGURE 6 (*Continued*)

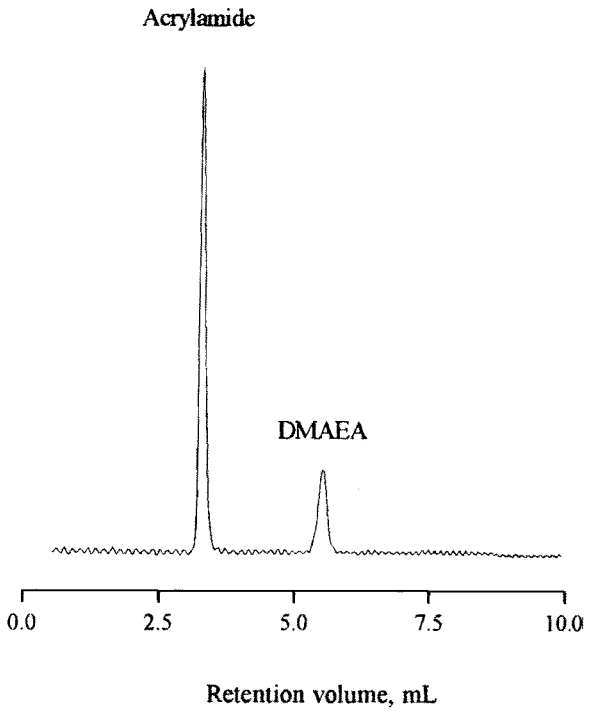


FIGURE 7 Chromatogram of a mixture consisting of 72.5 ppm of acrylamide and 201.4 ppm of DMAEA using a CN column. The mobile phase was 50 vol % acetonitrile and 50 vol % water. The pH was adjusted to 3.0 with the addition of phosphoric acid. Dibutylamine was used as an adsorption reduction additive at 0.005 M. The peaks were detected at 214 nm.

centration (0.01 M), sharp, well-defined and nonskewed DMAEA peaks are observed (Figure 6a). Two advantages of the CN stationary phase are the improved plate count for the cationic monomer peak (12,500/m) and the lower level of the acetonitrile in the mobile phase required for the separation. Figure 8 shows the separation of acrylamide and DMAEM using the optimal mobile phase. The peak height for the DMAEM is much larger than for DMAEA due to its high UV absorbance at 214 nm [22].

The optimal HPLC conditions are a CN stationary phase with a 50–50 vol % acetonitrile-water mobile phase containing 0.01 M dibutylamine and a pH of 3.0 adjusted with phosphoric acid. The calibration curve for acrylamide is illustrated in Figure 9, while Figure 10 shows the corresponding curve for the two cationic monomers.

Applications

Figure 11 shows a plot of the concentration of acrylamide and DMAEA as a function of reaction conversion. The corresponding calculated cumulative copolymer composition drift ($\bar{F}_1$) with conversion is shown in Figure 12. Given that these are relatively standard polymerization procedures, the smooth trend in the concentration-conversion plot shows that this method can be applied to commercially relevant inverse-emulsion syntheses.

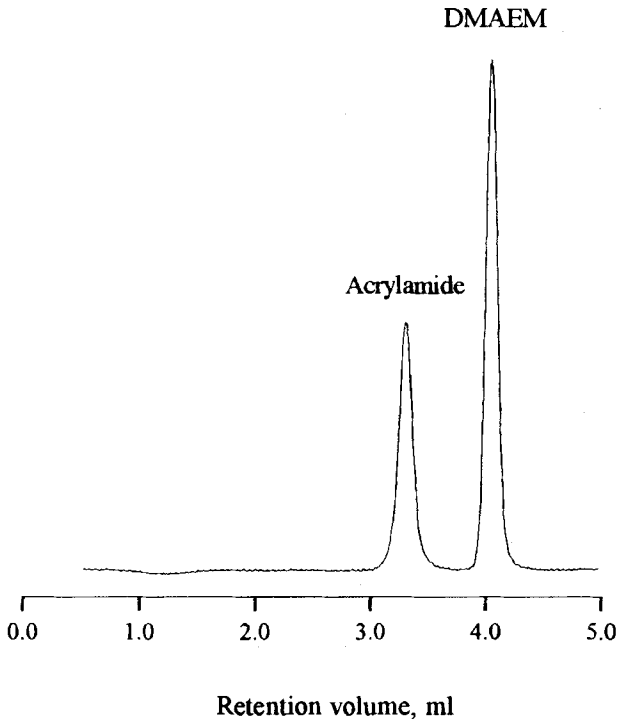


FIGURE 8 Chromatogram of a mixture consisting of 53.0 ppm of acrylamide and 214.4 ppm of DMAEM using a CN column. The mobile phase was 50 vol % acetonitrile and 50 vol % water. The pH was adjusted to 3.0 with the addition of phosphoric acid. Dibutylamine was used as an adsorption reduction additive at 0.01 M. The peaks were detected at 214 nm.

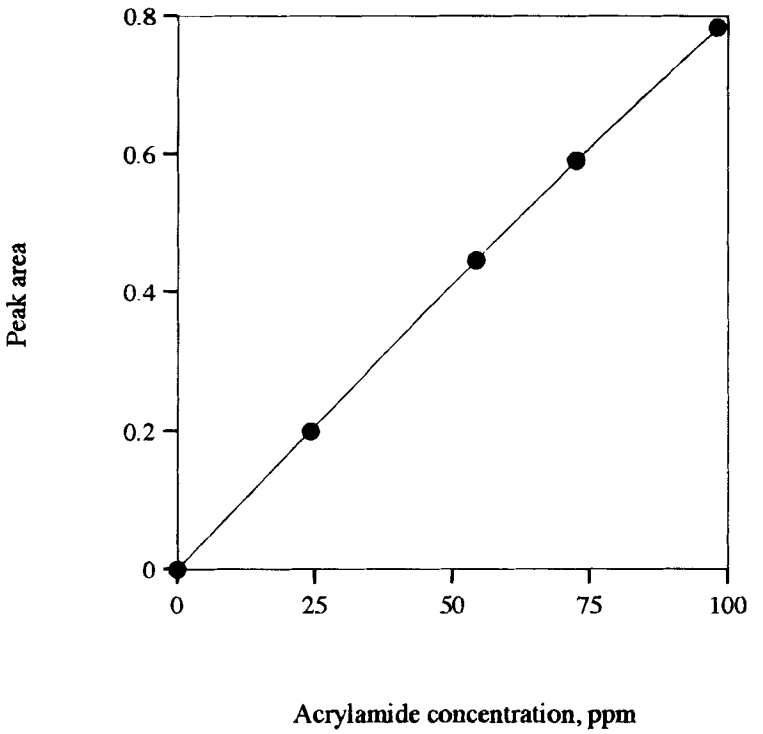
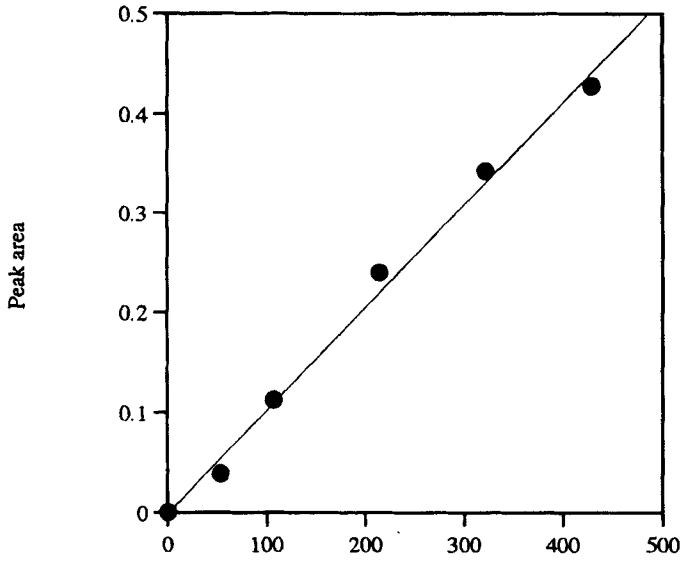


FIGURE 9 Calibration curve for acrylamide with a CN column. The 'optimal' mobile phase consisted of a mixture of 50 vol % acetonitrile with 50 vol % water. The pH was adjusted to 3.0 with the addition of phosphoric acid. Dibutylamine was used as an adsorption reduction additive at a concentration of 0.01 M. The peaks were detected at 214 nm.

Further, with a retention time of less than 2.5 min the technique can be easily adapted and automated for rapid data acquisition.

CONCLUSIONS

The CN-modified silica sorbent was found superior to the C_{18} stationary phase for the separation of acrylamide from either DMAEA or DMAEM. The strength of the acid used to adjust the mobile phase pH influenced the adsorption of the quaternary ammonium cationic monomer onto the sorbent, with phosphoric acid providing high quality peaks as compared with hydrochloric or nitric acids. The dibutylamine concentration in the mobile phase was found to be an effective means to control the peak symmetry of the cationic monomers. The optimal level of dibutylamine in the mobile phase was found to be 0.01 M using the CN sorbent.



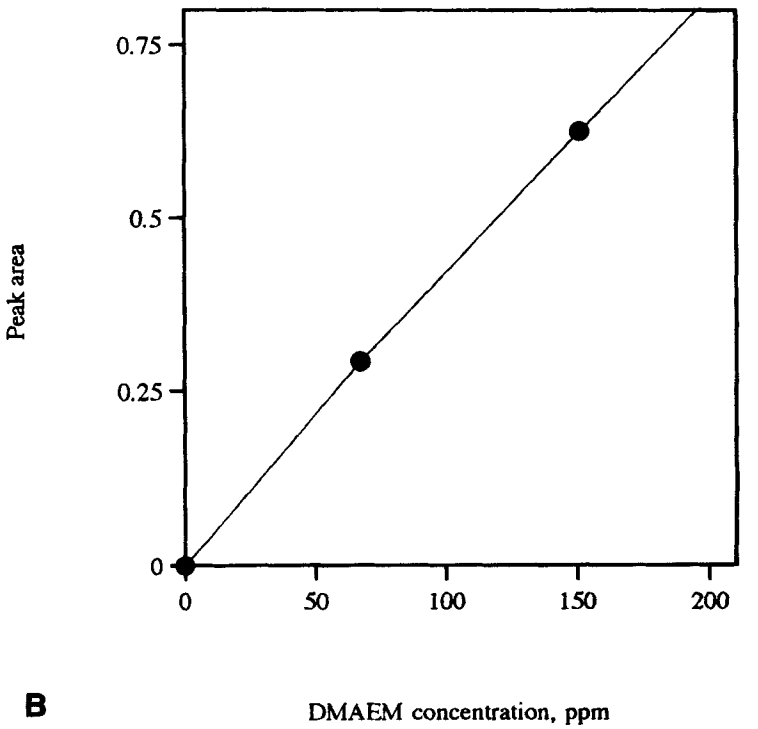


FIGURE 10 Calibration curve for (a) DMAEA and (b) DMAEM with a CN column. The optimal mobile phase conditions are listed in Figure 9. A CN Column with 6% carbon load bonded to a μ-Porasil (silica) substrate was employed as the stationary phase.

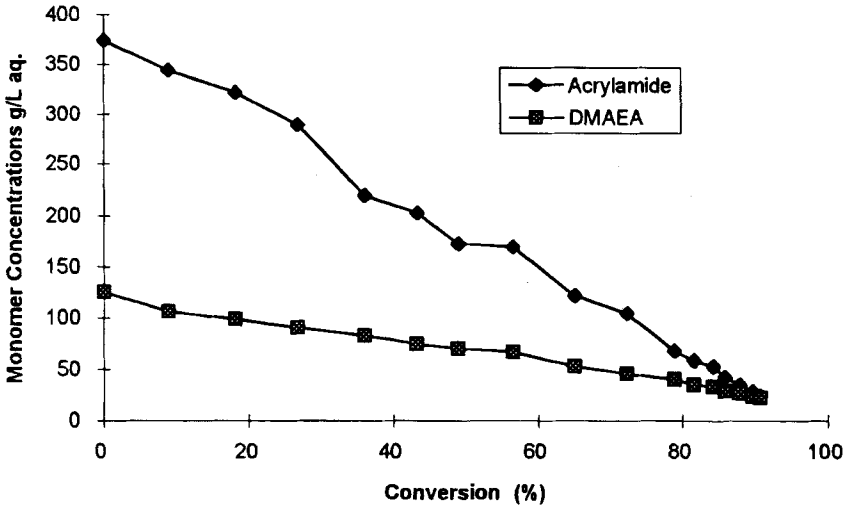


FIGURE 11 Concentration of acrylamide and DMAEA as a function of reaction conversion for an inverse-emulsion polymerization. The reaction conditions were: [monomer] = 5.99 mol/L_{water}, initial acrylamide monomer fraction (f_{10}) = 0.75, [surfactant] = 4.0 wt %, aqueous-to-organic phase ratio = 1:1, Temp.: 35°C.

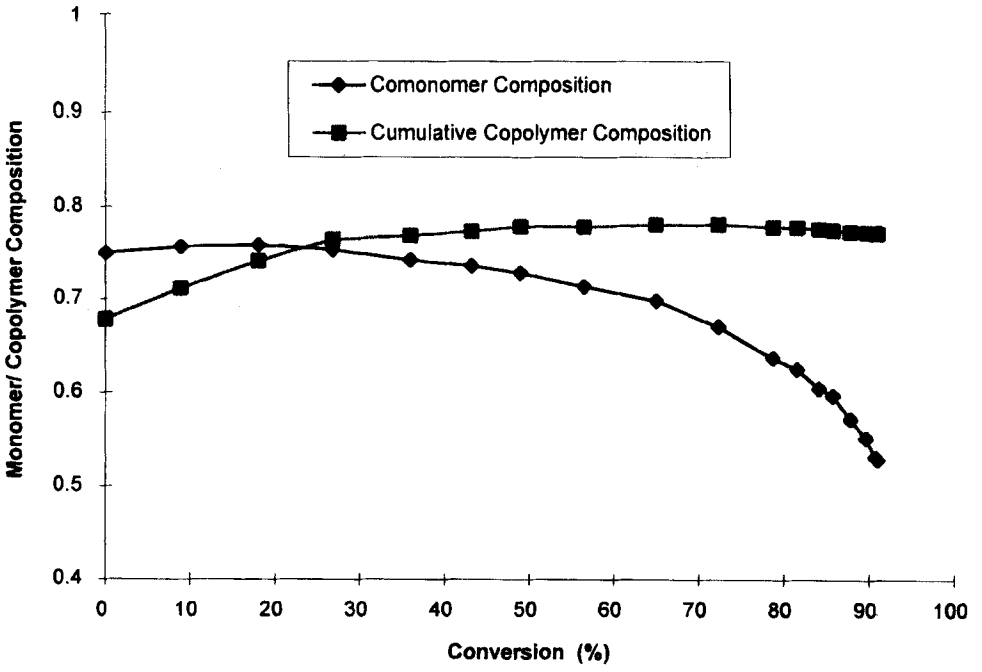


FIGURE 12 Comonomer composition drift and cumulative copolymer composition $\bar{F}_1$ as a function of conversion. The reaction conditions are identical to those listed for Figure 11.

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