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Journal of Chromatography A, 739 (1996) 327-331

JOURNAL OF
CHROMATOGRAPHY A

Retention behavior of methylamines, ethylenediamine and N-methyl-substituted ethylenediamines on a cation-exchange resin having a polycarboxylic acid as the functional group

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Abstract

The retention behavior of ethylenediamine and N-methyl-substituted ethylenediamines on a polycarboxylic acid-type cation-exchange resin was investigated. These diamines were retained as 2+ cations on the polycarboxylic acid-type cation-exchange resin using nitric acid solution as the eluent. The capacity factor of the N-methyl-substituted ethylenediamines increased with increasing number of methyl groups. The retention of these diamine compounds was only slightly affected by adding CH_3CN to the eluent. On the other hand, the retention of methylamines was strongly affected. This result would be due to the difference in the hydrophobic effect of the methyl group for the hydration state of the amines.

Keywords: Stationary phases, LC; Polycarboxylic acids; Methylamines; Ethylenediamines; Amines

1. Introduction

Amines are important compounds in the biological, pharmaceutical, and other various fields including the chemical industries. At the same time, amines are also known as difficult compounds to analyze. One of the reasons for the difficulty in amine analysis is their high adsorptive activity toward the stationary phases. In recent years, cation-exchange resins having di- or polycarboxylic acid as the functional group have been developed. These resins are mainly used for the simultaneous analysis of alkaline and alkaline earth metals, and also useful for the analysis of alkylamines. The character of polycarboxylic acid as an ion-exchange functional group will provide an advantage for separating the amine compounds. Though separation of some biological

polyamines [1,2] or ethylenediamine [3-5] using various separating modes have been reported, studies on the retention behavior of simple diamines, such as ethylenediamine or its derivatives are few [6]. The investigation of the retention behavior of diamines is important and useful for developing more advanced analytical procedures of more complex polyamines. This investigation will also be useful for clarifying the ion-exchange functional property of polycarboxylic acid. We report here on the retention behavior of N-methyl-substituted ethylenediamines on a polycarboxylic acid-type cation-exchange resin.

2. Experimental

2.1. Instrumentation

A model IC7000 Ion Chromatographic Analyzer (Yokogawa Analytical Systems, Tokyo, Japan) with

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a conductivity detector and a model WS 7000 Data Station were used.

2.2. Column and eluent

A hydrophilic polymethacrylate gel with a 6 μm diameter was used as the base material for the cation-exchange resin. Benzenetricarboxylic acid was introduced as the cation-exchange functional group. This cation-exchange resin was packed into a PEEK (polyether ether ketone) column pipe (150 mm \times 4.6 mm I.D.). The column and detector were kept at 40°C using an oven.

6–12 mM Nitric acid solution was used as the eluent. CH_3CN was added to the eluent in the range of 2–20% (v/v). The eluent flow-rate was 1.0 ml/min.

2.3. Reagents

Nitric acid and CH_3CN (Wako Pure Chemicals, Osaka, Japan) were used for the eluents. A standard stock solution of monomethylamine (MMeA), dimethylamine (DMeA), trimethylamine (TrMeA), tetramethylammonium hydrochloride (TetMeA), ethylenediamine (EDA), N-methylethylenediamine (N-MeEDA), N,N-dimethylethylenediamine (N,N-

DMeEDA), N,N'-dimethylethylenediamine (N,N'-DMeEDA), N,N,N'-trimethylethylenediamine (TrMeEDA) and N,N,N',N'-tetramethylethylenediamine (TetMeEDA) were prepared by dissolving the appropriate amount of free amines (reagent grade, Tokyo Kasei Kogyo, Tokyo, Japan). Samples were prepared by diluting stock solutions with purified water. The purified water was obtained using a Millipore Milli-Q water reagent system (Nippon Millipore, Tokyo, Japan).

3. Results and discussion

The chromatogram of four methylamines, EDA and four N-methyl-substituted ethylenediamines (NMeEDA) on the polycarboxylic acid-type cation-exchange resin using 10 mM HNO_3 as the eluent is shown in Fig. 1. Methylamines, EDA and NMeEDA were eluted in the order of increasing number of methyl group. N,N-DMeEDA and N,N'-DMeEDA coeluted under this condition. Fig. 2 shows the k' of these amines with 6–12 mM HNO_3 as the eluent. The slopes of k' vs. nitric acid concentration were 0.98–1.02 for methylamines, and 1.98–2.06 for EDA and NMeEDA. This result shows that methylamines

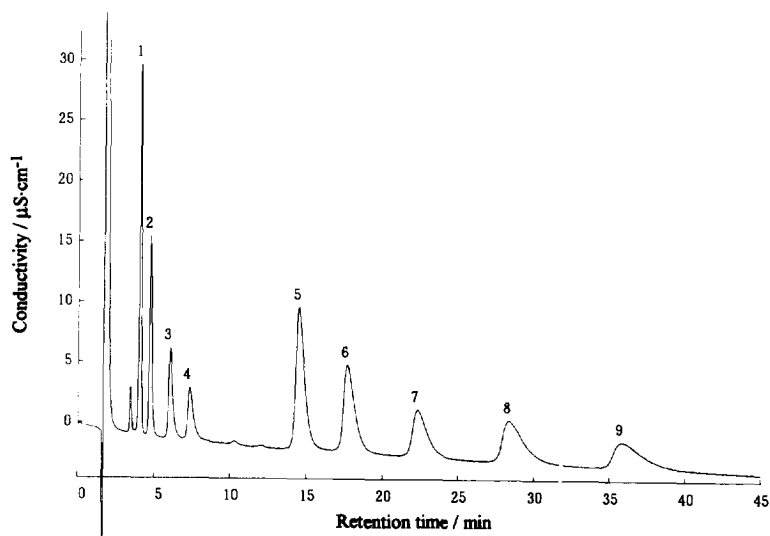


Fig. 1. Chromatogram of methylamines, EDA and NMeEDA using 10 mM HNO_3 as the eluent. Other conditions described in text. Peaks: (1) MMeA; (2) DMeA; (3) TrMeA; (4) TetMeA; (5) EDA; (6) N-MeEDA; (7) N,N'-DMeEDA; (8) TrMeEDA; (9) TetMeEDA.

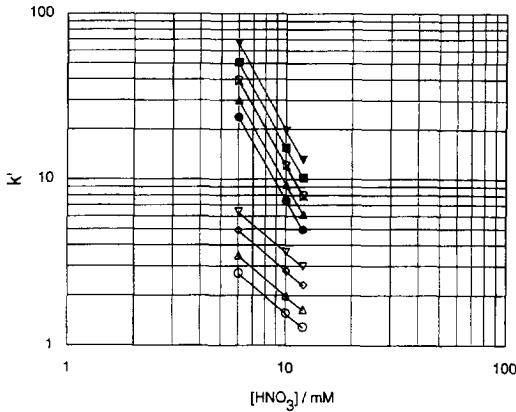


Fig. 2. Effect of nitric acid concentration on the k' value of the amines. Conditions described in text. Symbols: (○) MMeA; (△) DMeA; (◇) TrMeA; (▽) TetMeA; (●) EDA; (▲) N-MeEDA; (□) N,N-DMeEDA; (×) N,N'-DMeEDA; (■) TrMeEDA; (▼) TetMeEDA.

existed as +1 cation and EDA and NMeEDA existed as +2 cation in 6–12 mM HNO_3 .

For investigating the hydrophobic effect of the methyl group on the retention mechanism, the retention behavior of methylamines, EDA, NMeEDA and inorganic cations, was examined with eluent containing CH_3CN . A chromatogram of 10 mM HNO_3 containing 20% of CH_3CN is shown in Fig. 3.

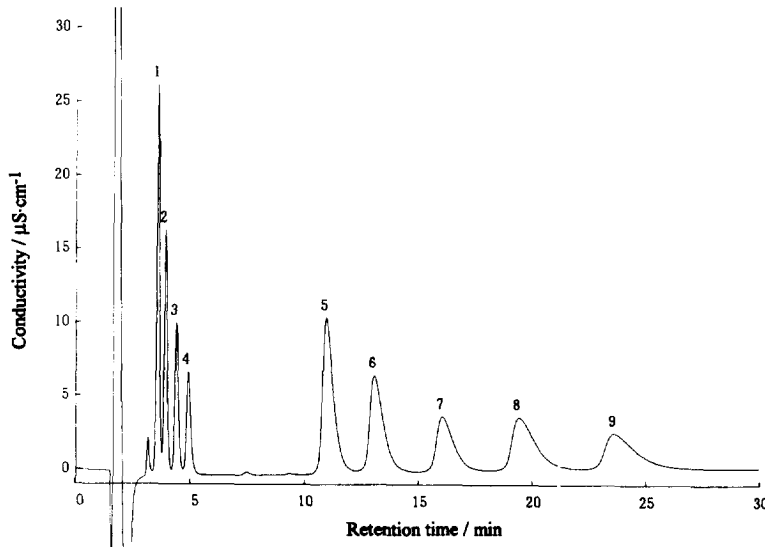


Fig. 3. Chromatogram of methyl amines, EDA and NMeEDA with 10 mM HNO_3 - CH_3CN (80:20) as the eluent. Other conditions described in text. Peaks: (1) MMeA; (2) DMeA; (3) TrMeA; (4) TetMeA; (5) EDA; (6) N-MeEDA; (7) N,N'-DMeEDA; (8) TrMeEDA; (9) TetMeEDA.

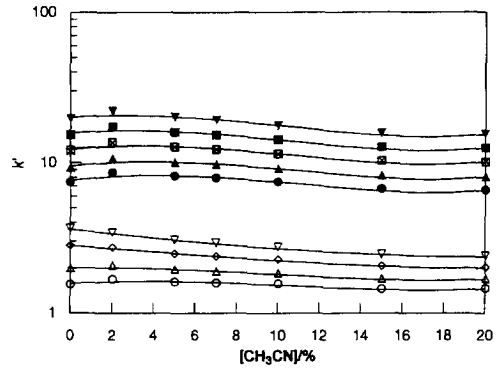


Fig. 4. Effect of acetonitrile in the eluent on the k' of the amines. Conditions described in text. Symbols: (○) MMeA; (△) DMeA; (◇) TrMeA; (▽) TetMeA; (●) EDA; (▲) N-MeEDA; (□) N,N-DMeEDA; (×) N,N'-DMeEDA; (■) TrMeEDA; (▼) TetMeEDA.

The variations of k' for methyl amines, EDA, NMeEDA are shown in Figs. 4–7 shows the effect of CH_3CN concentration on the selectivity for EDA and NMeEDA, methylamines and inorganic cations, respectively. In these figures, selectivity was calculated by $(k' \text{ of target cation}) / (k' \text{ of Li}^+)$. The vertical axis is normalized by the values when CH_3CN was 0%. EDA and NMeEDA showed almost the same behavior. This behavior was similar to Mg^{2+} and Ca^{2+}

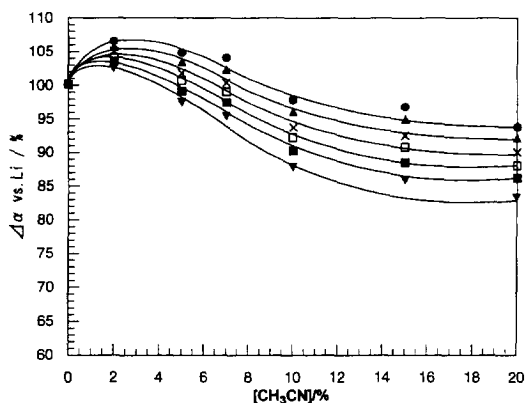


Fig. 5. Effect of acetonitrile in the eluent on the selectivity (α) of EDA and NMeEDA. $\alpha = (k' \text{ of EDA or NMeEDA}) / (k' \text{ of Li}^+)$. Eluent was 10 mM $\text{HNO}_3 + \text{CH}_3\text{CN}$. Other conditions described in text. Symbols: (●) EDA; (▲) N-MeEDA; (□) N,N-DMeEDA; (×) N,N'-DMeEDA; (■) TrMeEDA; (▼) TetMeEDA.

in Fig. 7. By adding CH_3CN to the eluent, the hydration state of Mg^{2+} and Ca^{2+} could be changed, and the solvation of CH_3CN to Mg^{2+} and Ca^{2+} would occur. Therefore, the retention capabilities of Mg^{2+} and Ca^{2+} on the cation-exchange resin should be changed. This process would be the same in the case of EDA and NMeEDA. The difference in the influence on selectivity of EDA and NMeEDA would mainly result from the hydrophobic effect of the methyl group. In this case, the hydrophobicity of the methyl group will affect both the solvation of

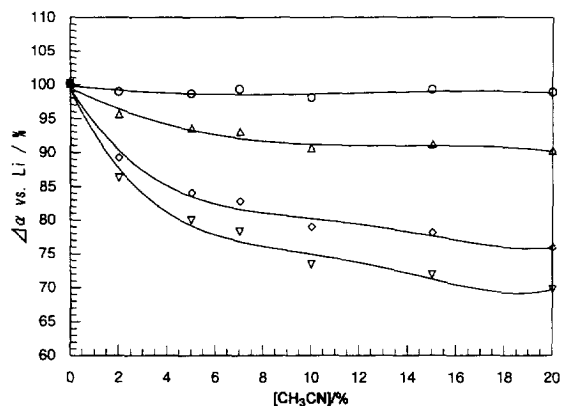


Fig. 6. Effect of acetonitrile in the eluent on the selectivity (α) of methylamines. $\alpha = (k' \text{ of methylamines}) / (k' \text{ of Li}^+)$. Eluent was 10 mM $\text{HNO}_3 + \text{CH}_3\text{CN}$. Other conditions described in text. Symbols: (○) MMeA; (△) DMeA; (◇) TrMeA; (▽) TetMeA.

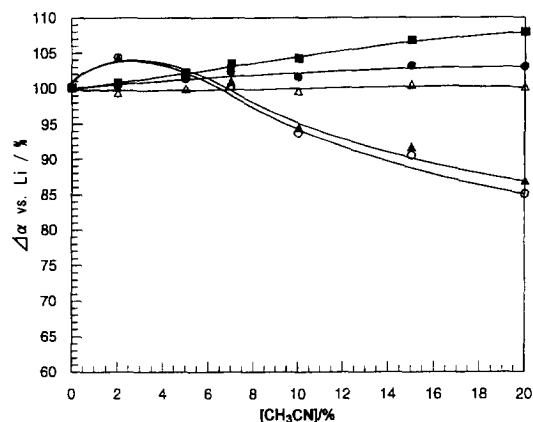


Fig. 7. Effect of acetonitrile in the eluent on the selectivity (α) of inorganic cations. $\alpha = (k' \text{ of inorganic cations}) / (k' \text{ of Li}^+)$. Eluent was 10 mM $\text{HNO}_3 + \text{CH}_3\text{CN}$. Other conditions described in text. Symbols: (●) Na^+ ; (△) NH_4^+ ; (■) K^+ ; (○) Mg^{2+} ; (▲) Ca^{2+} .

CH_3CN and the interaction with the cation-exchange resin. Additionally, the elution order of EDA and NMeEDA would be due to the size of the molecules and was not affected by the presence of CH_3CN . From the results in Figs. 5 and 7, the hydrophobic interaction between NMeEDA and the cation-exchange resin used this study will only slightly affect the retention behavior.

In the case of the methylamines (Fig. 6), the effect of CH_3CN on the selectivity is different from NMeEDA. While MMeA was slightly affected, a remarkable effect appeared on DMeA, TrMeA and TetMeA, especially on TrMeA and TetMeA. This result is due to the specific hydration state of such amines. TrMeA and TetMeA are weakly hydrated so that these amines are strongly retained on cation-exchange resins. When CH_3CN is added to the eluent, TrMeA and TetMeA would be more strongly solvated by CH_3CN than MMeA and DMeA. As a result of the solvation by CH_3CN , the retention of TrMeA and TetMeA would become weaker with increasing concentration of CH_3CN to the eluent. Over 15% CH_3CN , solvation of CH_3CN would be constant, so that the change in retention strength would be small. Of course, the hydrophobic effect of the methyl group would influence the retention behavior, however, this hydrophobic effect will only slightly affect the retention behavior of the methylamines.

4. Conclusions

The retention behavior of methylamines, EDA and NMeEDA on the polycarboxylic acid-type hydrophilic cation-exchange resin was surveyed. Methyl amines exist as +1 cations, and EDA and NMeEDA exist as +2 cations in HNO₃ solutions over 6 mM. Though the k' of the diamines was only slightly affected by adding CH₃CN to the eluent, the selectivity of the diamines referenced to Li⁺ was more influenced by CH₃CN, and it was similar to Mg²⁺ and Ca²⁺. The k' and selectivity of the methylamines were more affected by CH₃CN than diamines. This result would be mainly due to the difference in hydration state between the methylamines and NMeEDA.

For the polycarboxylic acid-type hydrophilic cation-exchange resin, the influence of CH₃CN on the retention strength and selectivity was mainly concerned with the hydration state of the ions, and

little concerned with the hydrophobic interaction between the solute ions and cation-exchange resin. A further survey of the retention mechanism of ions on the ion-exchange resins using a mixed solvent will necessary.

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