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Ion-exclusion chromatography of ethanolamines on an anion-exchange resin by elution with polyols and sugars

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Abstract

Ion-exclusion chromatography of mono-, di- and triethanolamines of different basicity (pK_b) and hydrophobicity was investigated on a polystyrene–divinylbenzene (PS–DVB)-based strongly basic anion-exchange resin in the OH^- form. Conductivity detection and UV detection at 200 nm were used. When water was as an eluent, the ethanoamines were separated from strong base (NaOH) but the resolution was low and some peaks were fronted. This is due mainly to adsorption as a side-effect in the ion-exclusion chromatography. To improve the peak shape and the peak resolution, aqueous eluents containing polyols or sugars with 1–8 alcoholic OH groups (methanol, ethylene glycol, glycerol, erythritol, xylitol, fructose, sorbitol and sucrose) were tested for the ion-exclusion chromatographic separation of ethanolamines. When aqueous eluents containing polygols or sugars were used, peak fronting was decreased drastically by increasing a number of OH groups in the polyols and sugars. This is due mainly to the increase in the hydrophilicity of the PS–DVB surface by the OH groups. When an aqueous fructose eluent was used, fructose was strongly adsorbed on the resin surface. By this permanent coating method, the ion-exclusion chromatographic separation of ethanolamines was accomplished successfully by elution with water with reasonable resolution and highly sensitive UV and conductimetric detection.

Keywords: Mobile phase composition; Stationary phases, LC; Ethanolamines; Polyols; Sugars

1. Introduction

Ion-exclusion chromatography is a useful technique for the separation of organic and inorganic weak bases such as ammonium and aliphatic and aromatic amines [1–3]. Generally, a polystyrene–divinlybenzene copolymer (PS–DVB)-based high-capacity strongly basic anion-exchange resin in the OH^- form is used in ion-exclusion chromatography.

Haddad et al. [3] reported in the ion-exclusion chromatography of a large number of organic and inorganic basic compounds by elution with sodium hydroxide on an anion-exchange resin in the OH^- form. They mentioned that hydrophobic adsorption and steric exclusion as side-effects in ion-exclusion chromatography are predominant for the separation of aliphatic and aromatic amines with a hydrophobic nature.

On the other hand, we have reported that in ion-exclusion chromatography with elution with water, although mono-, di and triethanolamines are separated successfully from strong base (NaOH) depending on the pK_b and the hydro-

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phobicity, the resolution is low and the peaks show leading depending on the hydrophobicity [4]. Therefore, to achieve high-resolution ion-exclusion chromatographic separations of ethanolamines by depressing the hydrophobic adsorption effect with the PS–DVB-based anion-exchange resin, we used glycerol–water as the eluent. By using this eluent, highly sensitive UV detection and reasonable resolution for ethanolamines were accomplished.

A major goal of this research was to demonstrate the effectiveness of polyols- or sugar–water mixed eluents that gives sharp chromatographic peaks and highly sensitive UV and conductivity detection for ethanolamines showing hydrophobicity.

To improve the peak shape, the resolution and the detection sensitivity, aqueous eluents containing polyols or sugars with 1–8 alcoholic OH groups (methanol, ethylene glycol, glycerol, erythritol, xylitol, fructose, glucose, sorbitol and sucrose) with a hydrophilic nature were tested for the ion-exclusion chromatography of ethanolamines on PS–DVB-based strongly basic anion-exchange resin in the OH form with UV detection at 200 nm and conductivity detection with and without conductivity enhancement columns. It is shown that excellent resolution and highly sensitive UV and conductivity detection for ethanolamines is accomplished on an anion-exchange resin column coated dynamically with fructose with water as the eluent.

2. Experimental

2.1. Apparatus

The ion chromatograph consisted of a JASCO (Tokyo, Japan) Familic HPLC eluent delivery pump at a flow-rate of 1 ml/min equipped with a Reodyne Model 7125 sample injector with a 100-μl loop.

UV detection at 200 nm for detecting OH^- from ethanolamines in aqueous eluents was carried out with a JASCO Uvidec-100-IV spectrophotometer [4].

Conductimetric detection of ethanolamines was carried out with a Tosoh (Tokyo, Japan) CM-8000 detector.

The computing integrator was a Shimadzu (Kyoto, Japan) Chromatopac-R6A.

2.2. Column

The separation column was a Tosoh glass column (300 mm × 8 mm I.D.). The column was packed by the slurry packing technique after regeneration with 1 *M* sodium hydroxide and equilibrated thoroughly with the eluent before each chromatographic run.

2.3. Resin

A Tosoh TSKgel SAX PS–DVB-based strongly basic anion-exchange resin in the OH^- form with a particle size of 5 μm and an exchange capacity of 3.7 mequiv./g was used as a separation column in all chromatographic runs.

2.4. Reagents and solutions

Standard solutions of ethanolamines and sodium hydroxide were prepared from analytical-reagent grade chemicals without further purification.

The aqueous eluents containing polyols and sugars were prepared by dissolving the polyols (methanol, ethylene glycol, glycerol, erythritol, xylitol and sorbitol) and sugars (glucose, fructose and sucrose) in distilled, deionized water. Methanol, ethylene glycol and glycerol were obtained from Wako (Osaka, Japan) and the other compounds from Nikken Kasei (Tokyo, Japan).

3. Results and discussion

3.1. Effect of eluent composition on the separation of ethanolamines

As described in a previous paper [4], although ethanolamines are separated from each other by elution with water based on the differences in the pK_b values of monoethanolamine (4.5), diethanolamine (5.1) and triethanolamine (6.2) and/

or in the hydrophobicities of these ethanolamines, the resolution is very low and the peak is fronted, primarily owing to the hydrophobic adsorption effect as a side-effect in the ion-exclusion chromatography. In an attempt to reduce peak fronting, polygols and sugars were tested and the elution and detection performance were compared for the ion-exclusion chromatographic separation of ethanolamines. As shown in Table 1, these polyols and sugars have different numbers of alcoholic OH groups in the molecules with a hydrophilic nature.

Fig. 1A shows a complete ion-exclusion chromatographic separation of a strong base (NaOH) and mono-, di- and triethanomines with water as the eluent. As expected from the results in previous papers on fundamental ion-exclusion chromatographic studies of weak bases [1,2,4] and acids [5–10] on a PS–DVB ion-exchange resin, the separation time of ethanolamines was very long and the peaks were fronted, especially for hydrophobic ethanolamines such as triethanolamine. This is a consequence of an adsorption effect.

Fig. 1B–J show the ion-exclusion chromatographic separation of sodium hydroxide and ethanolamines obtained by elution with polyol–water or sugar–water mixtures of concentration 0.2 *M* each. As can be seen from the peak shape of triethanolamine, fronting was dramatically decreased by increasing the number of OH groups in the polyols or sugars. This means that the hydrophobicity of the PS–DVB-based anion-exchange resin surface decreased by the adsorption of polyols or sugars. Hence, it is possible to modify the polarity of the PS–DVB-based anion-exchange resin surface by adsorption with polyols and sugars, especially those with more than three alcoholic OH groups. Reasonable resolution and detection were obtained for the eluents of polyols or sugar with 3–8 alcoholic OH groups, except for fructose.

As described below, the low UV detection sensitivity of ethanolamines on elution with fructose is caused by the high eluent background absorbance. Therefore, when considering the UV detector response and the resolution for ethanolamines, polyols or sugars with 3–8 alcoholic OH groups seem to be suitable eluents.

Table 1
Characteristics of polyols and sugars tested as eluents in ion-exclusion chromatography on an anion-exchange resin column in the OH^- form for the separation of ethanolamines

Polyol or sugar	Formula	No. of alcoholic OH groups
Methanol[a]	CH_3OH	1
Ethylene glycol[a]	$C_2H_6O_2$	2
Glycerol[a]	$C_3H_8O_3$	3
Erythritol[a]	$C_4H_{10}O_4$	4
Xylitol[a]	$C_5H_{12}O_5$	5
Fructose[b]	$C_6H_{12}O_6$	5
Glucose[b]	$C_6H_{12}O_6$	5
Sorbitol[a]	$C_6H_{14}O_6$	6
Sucrose[b]	$C_{12}H_{22}O_{11}$	8

[a] Alcohols (polyols).
[b] Sugars.

3.2. UV detection and separation of ethanolamines by elution with polyols and sugars on an anion-exchange resin column

In order to determine the optimum concentration of polyols or sugars with 3–8 alcoholic OH groups, the effect of the concentration of xylitol (five alcoholic OH groups) in the eluent on the resolution and UV detection of ethanolamines was studied using concentrations of 0.01–0.4 *M*.

As shown in Fig. 2A, a reasonable resolution of ethanolamines without fronting was obtained with concentrations above 50 m*M* xylitol–water. However, the eluent background was noisy owing to high background absorbance (ca. 0.25 AU).

Similar results to those with the xylitol eluent were also obtained on elution with the other polyols and sugars with 3–8 alcoholic OH groups.

3.3. UV detection and separation of ethanolamines by elution with water on a fructose-coated anion-exchange resin column

As described above, 50 m*M* xylitol seems to be a suitable eluent for the ion-exclusion chromato-

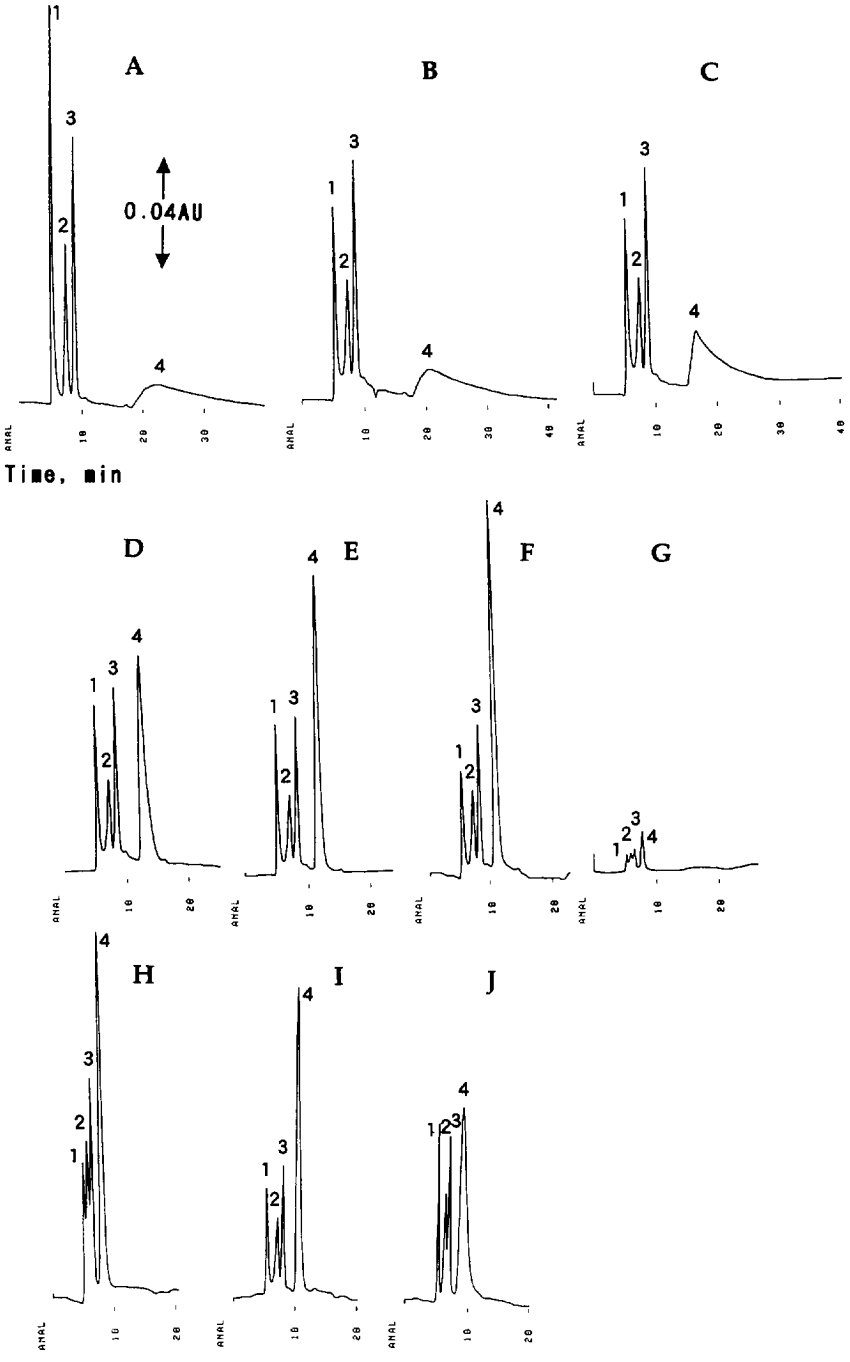

Fig. 1. Effect of eluent composition on ion-exclusion chromatographic separation and UV detection of strong base and ethanolamines. Eluent: (A) water; (B) 0.2 *M* methanol–water; (C) 0.2 *M* ethylene glycol–water; (D) 0.2 *M* glycerol–water; (E) 0.2 *M* erythritol–water; (F) 0.2 *M* xylitol–water; (G) 0.2 *M* fructose–water; (H) 0.2 *M* glucose–water; (I) 0.2 *M* sorbitol–water; (J) 0.2 *M* sucrose–water. Detection, UV at 200 nm; eluent flow-rate, 1 ml/min; column, Tosoh TSKgel SAX strongly basic anion-exchange resin in the OH^- form (300 mm × 8 mm I.D.); column temperature, 30°C; sample concentration, 1 m*M* each; sample injection volume, 100 μl. Peaks: 1 = strong base (sodium hydroxide) [V_R of sodium hydroxide = column void volume (complete ion exclusion)]; 2 = monoethanolamine; 3 = diethanolamine; 4 = triethanolamine.

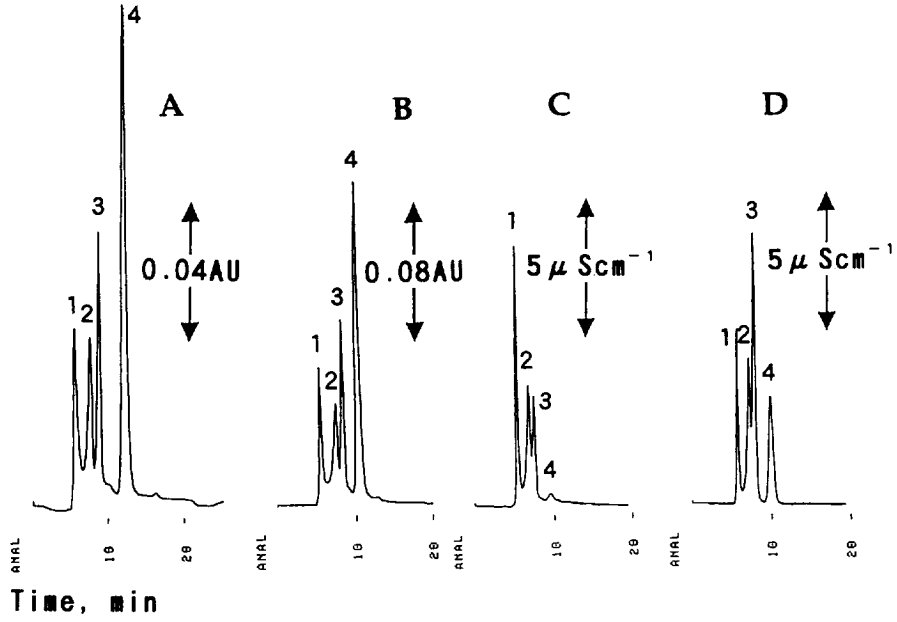

Fig. 2. Ion-exclusion chromatogram of strong base and ethanolamines on anion-exchange resin columns coated with fructose or uncoated under different elution and detection conditions. (A) UV detection, elution with 50 m*M* xylitol on anion-exchange resin column; (B) UV detection, elution with water on fructose-coated anion-exchange resin column; (C) conductivity detection, elution with water on fructose-coated anion-exchange resin column; (D) conductivity detection with conductivity enhancement column, elution with water on fructose-coated anion-exchange resin column. Other chromatographic conditions and peak identifications as in Fig. 1.

graphic separation of ethanolamines. However, since the eluent background level was relatively high, the UV detection sensitivity was therefore relatively low. Accordingly, water with an extremely low absorbance (ca. 0 AU) was tested as the optimum eluent for the ion-exclusion chromatographic separation of ethanolamines with UV detection.

As can be seen from Fig. 1G, when 0.2 *M* fructose was used as the eluent, although the resolution of ethanolamines was reasonably good, as with xylitol as the eluent, the UV detection sensitivity was very low because the eluent background absorbance was extremely high (>2 AU). However, fortunately, the fructose was adsorbed strongly and specifically on the anion-exchange resin surface. Hence water seems to be a useful eluent.

When water was used as the eluent in the ion-exclusion chromatography of ethanolamines on the anion-exchange resin column coated dynamically with fructose with UV detection, the resolution obtained was reasonably good, like that with the xylitol eluent. Additionally, since the eluent background absorbance level on elution with water was very low (ca. 0 AU), stable and reproducible chromatograms were obtained, as shown in Fig. 2B.

3.4. Conductimetric detection of ethanolamines by elution with water on a fructose-coated anion-exchange resin column

Generally, it is well-known that UV detection at 200 nm is subject to interference from co-existing UV-absorbing organic compounds. Since this ion-exclusion chromatographic method uses water as the eluent, conductivity detection was therefore applied to achieve the highly sensitive detection of ethanolamines without interference from UV-absorbing substances.

Fig. 2C and D show the chromatograms of

ethanolamines with conductivity detection and conductivity detection with the conductivity enhancement column [11–13], respectively. In the conductivity enhancement method, a column packed with anion-exchange resin in the Cl^- form (TSKgel SAX; 50 mm × 8 mm I.D.) was connected in series after the fructose-coated anion-exchange resin separation column. Since the eluent background conductivity level on elution with water was very low (ca. 0 $\mu S\ cm^{-1}$), stable and reproducible chromatograms were obtained with conductivity detection both with and without the conductivity enhancement column.

3.5. Reproducibility of ion-exclusion chromatographic separation of ethanolamines on a fructose-coated anion-exchange column

The long-term reproducibility and stability of the fructose-coated anion-exchange resin column was studied in terms of the resolution and the UV and conductivity detection sensitivity for ethanolamines.

There was no variation of the resolution for ethanolamines obtained with UV detection during the course of repeated chromatographic runs for at least 380 h.

Further, there was no variation (<2.2%) of the peak areas for all of the ethanolamines with repeated sample injection ($n = 20$) of 1 m*M* standards with UV detection for at least 380 h.

Regarding the reproducibility and stability, very similar results to those with UV detection were also obtained with conductivity detection of ethanolamines both with and without the conductivity enhancement column.

The above results suggest that the adsorption of fructose on the resin surface is very strong and stable. Accordingly, the desorption of fructose from the resin surface was possible only by washing with water after the formation of a fructose–borate complex with sodium borate. Such an adsorption behaviour was not observed on a PS–DVB-based un-functionalized resin and observed only with the combination of fructose and anion-exchange resin in the OH^- form. The details of this adsorption mechanism are unclear.

As described above, the selection of the kind of sugar eluent and base polymer is a very important factor for understanding the adsorption mechanism. Therefore, more detailed investigations, on the use of hydrophilic polymeric resins and other ketoses will be subject of future work.

From the above results, water was judged to be the most suitable eluent for the high-resolution ion-exclusion chromatographic separation and highly sensitive UV and conductivity detection of ethanolamines on the fructose-coated anion-exchange resin column.

3.6. Effect of column temperature on the retention of ethanolamines

The effect of column temperature on the retention volumes (V_R) was studied between 10 and 50°C.

The values of V_R for mono-, di- and triethanolamines decreased with increasing column temperature. This means that the present method is based mainly on the hydrophobic adsorption mechanism as a side-effect of ion-exclusion chromatography.

The UV background level for the water eluent increased at temperatures above ca. 40°C. This increase might be due to the formation of UV-absorbing substances by slight decomposition of the anion-exchange resin and also slight desorption of fructose from the resin phase at elevated temperature.

Since the resolution of ethanolamines on elution at an elevated temperature (50°C) was similar to those at 10–20°C, it was confirmed that the adsorption of fructose on the resin surface is very strong and stable.

From the above results, the optimum column temperature was judged to be ca. 30°C for the ion-exclusion chromatography of ethanolamines.

3.7. Calibration graphs of ethanolamines with UV and conductivity detection

Calibration graphs were obtained by plotting peak height against ethanolamines concentration in the range 0–5 m*M* under the four different

separation and detection conditions described below.

The calibration graph for ethanolamines obtained on the anion-exchange resin column with 50 m*M* xylitol as eluent with UV detection was linear up to ca. 3 m*M*, as shown in Fig. 3A.

The calibration graph of ethanolamines obtained with water eluent by the UV detection on the fructose-coated anion-exchange resin column was linear up to ca. 3 m*M*, as shown in Fig. 3B.

The calibration graph for ethanolamines obtained with water as eluent on the fructose-coated anion-exchange resin column with conductivity detection was non-linear over the concentration range 0–5 m*M*, as shown in Fig. 3C. This is due mainly to the decrease in the degree

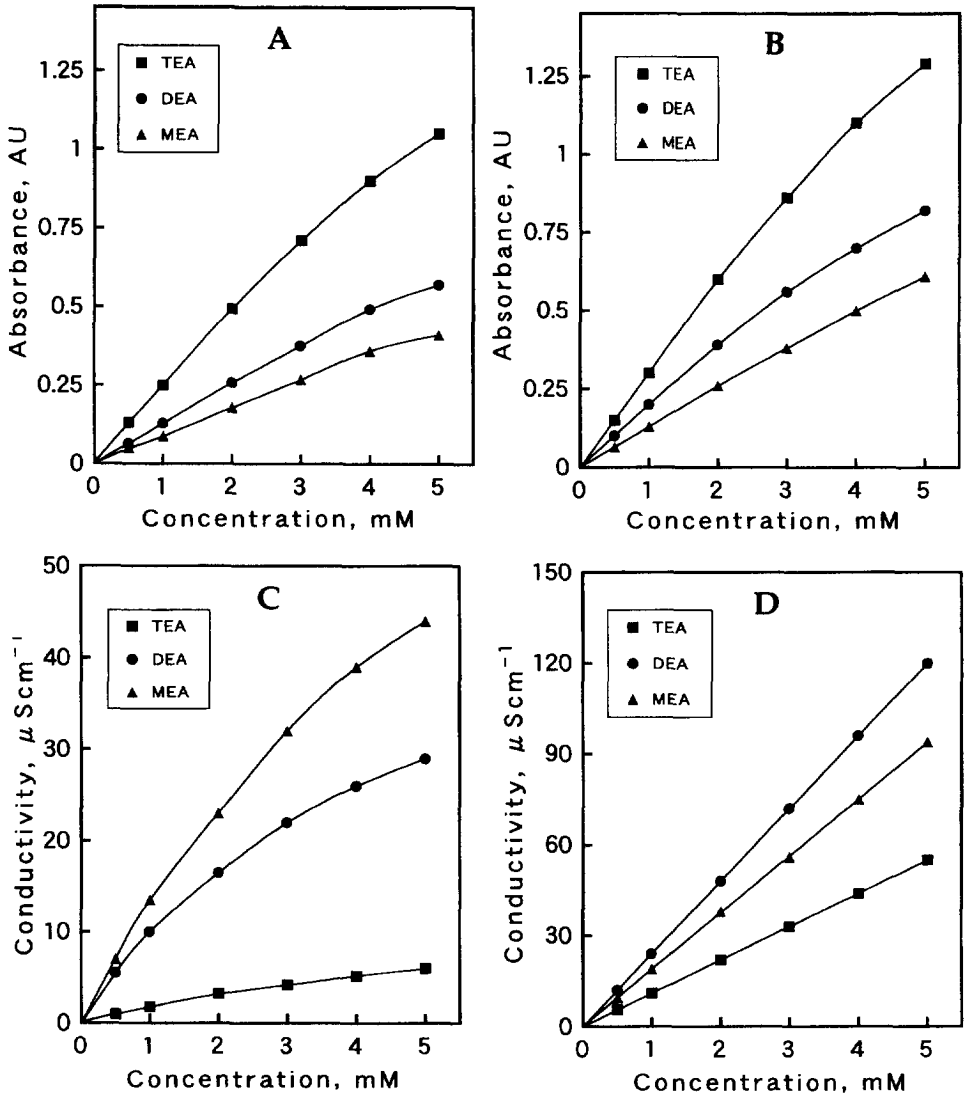

Fig. 3. Calibration graphs of ethanolamines under different elution and detection conditions. (A) UV detection, elution with 50 m*M* xylitol on anion-exchange resin column; (B) UV detection, elution with water on fructose-coated anion-exchange resin column; (C) conductivity detection, elution with water on fructose-coated anion-exchange resin column; (D) conductivity detection with conductivity enhancement column, elution with water on fructose-coated anion-exchange resin column. Other chromatographic conditions and peak identifications as in Fig. 1.

of dissociation of ethanolamines at higher concentration.

When the conductivity enhancement column packed with anion-exchange resin in the Cl^- form was used after the fructose-coated anion-exchange resin separation column, the detection sensitivity was increased for all of ethanolamines and the calibration graph obtained was linear over the concentration range 0–5 m*M*, as shown in Fig. 3D. This improvement in linearity is caused by the complete dissociation of the chloride salt of ethanolamines.

Very similar results to the peak-height method were also obtained by the peak-area method.

From the above results, the optimum detection method for the ion-exclusion chromatography of ethanolamines with elution with water was judged to be conductivity enhancement detection with the fructose-coated anion-exchange column connected in series with the anion-exchange resin column in the Cl^- form.

3.8. Detection limits of ethanolamines with UV and conductivity detection

The detection limits of ethanolamines at $S/N = 3$ with UV detection and with conductivity detection both with and without the conductivity enhancement column were studied.

Table 2 shows a comparison of the detection limits of ethanolamines by ion-exclusion chromatography under four different separation and detection conditions.

Since the other three different ion-exclusion chromatographic methods except for ion-exclusion chromatography with xylitol eluent use water as the eluent, the eluent background level is almost 0 AU and 0 μS cm^{-1}. Therefore, the noise level on the eluent background was extremely low. Although the UV detection of ethanolamines showed relatively high sensitivity, especially with the use of water as eluent, much more highly sensitive detection was achieved with conductivity detection with and without the conductivity enhancement column.

Table 2
Comparison of detection limits of ethanolamines with UV and conductivity detection

Ethanolamine	Detection limit ($S/N = 3$) (μM)[a]			
	A	B	C	D
Monoetholamine	60	0.78	0.016	0.012
Diethanolamine	40	0.42	0.018	0.007
Triethanolamine	20	0.31	0.122	0.017

[a] (A) UV detection, elution with 50 m*M* xylitol on anion-exchange resin column; (B) UV detection, elution with water on fructose-coated anion-exchange resin column; (C) conductivity detection, elution with water on fructose-coated anion-exchange resin column; (D) conductivity detection with conductivity enhancement column, elution with water on fructose-coated anion-exchange resin column. Other chromatographic conditions as in Fig. 1.

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