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# APPLICATION OF ELUENTS CONTAINING PHTHALIC ACID AND PROTONATED ETHOXYAMINES IN SINGLE COLUMN ION CHROMATOGRAPHY

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**Abstract**. Possibilities of using eluents made from phthalic acid and ethoxyamines in single column ion chromatography are discussed. These eluents proved to be useful in single column ion chromatography.

**Key words**: ion chromatography, single column, phthalic acid, protonated ethoxyamines.

## INTRODUCTION

Eluents containing phthalic acid are widely used in single column ion chromatography. The only problem is which basic component should be added in order to make the phthalic acid dissociate into phthalate ions.

The basic components usually applied are:

1. Aqueous solutions of NaOH [1] or $Na_2CO_3$. The chromatographic properties of eluents made with NaOH and $Na_2CO_3$ are not equal because the carbonate ions are also involved in the chromatographic separation process if they are present [2].

2. N-methyldiethanolamine has been used as the basic component in some cases when vanillic acid has been used instead of phthalic acid [3, p. 16].

A comparison of the use of NaOH and $Na_2CO_3$ for these purposes shows that $Na_2CO_3$ should be preferred as it may be heated and used as a pure substance, exactly corresponding to its formula. If aqueous NaOH is used, the problem of its correspondence to the formula arises. Therefore, the carbonate content in solid NaOH should be also taken into account.

3. Other basic compounds besides NaOH, $Na_2CO_3$, and N-methyldiethanolamine may in principle also be applied as components of eluents for single column ion chromatography. For instance, organic amines may be used for this purpose. The only problem with the organic amines is their unpleasant smell. As a result, their use in eluents has been avoided. Therefore, eluents containing alkoxy groups are certainly preferable, because they do not smell, are easily available, and are not expensive.

## EXPERIMENTAL

A model IVK-11 ion chromatograph with a conductometric detector JD-1, both from the Design Office of the Estonian Academy of Sciences, Tallinn, were used. Chromatograms were recorded on a Servogor S recorder (Goerz, Germany). The analytical columns (4 × 250 mm) were packed with Spheron 100 000: 0.025–0.040 mm (Lachema Ltd., Brno). Before packing Spheron was coated with aqueous solution (2.0% w/w) of water soluble anionite BA-2 from Olaine Chemical Co. Ltd. (Olaine, Latvia) and heated at 85 °C for 48 h. The capacity of the columns used was 0.0519 mequiv./$cm^3$. The concentrations of phthalic acid and amine were varied in the range 2–5 mM (see Tables 1–3). The eluent flow rate was 1.5 ml/min and the loop volume used was 0.221 ml.

*Table 1*

**Measured (numerator) and calculated* (denominator) pH values for phthalic acid and monoethanolamine eluents**

| Concentration of phthalic acid, mM | Concentration of monoethanolamine, mM | | | |
|---|---|---|---|---|
| | 2.0 | 3.0 | 4.0 | 5.0 |
| 2.0 | 4.30 / 4.25 | 5.43 / 5.34 | 6.66 / 6.50 | 9.27 / 9.19 |
| 3.0 | 3.61 / 3.42 | 4.26 / 4.33 | 5.08 / 5.09 | 5.51 / 5.72 |
| 4.0 | 3.27 / 3.22 | 3.61 / 3.58 | 4.17 / 4.23 | 4.88 / 4.95 |
| 5.0 | 3.09 / 3.05 | 3.34 / 3.31 | 3.52 / 3.65 | 4.11 / 4.23 |

* taking phthalic acid $pK_1 = 2.95$ and $pK_2 = 5.41$ [4].

*Table 2*

**Measured (numerator) and calculated* (denominator) pH values for phthalic acid and diethanolamine eluents**

| Concentration of phthalic acid, mM | Concentration of diethanolamine, mM | | | |
|---|---|---|---|---|
| | 2.0 | 3.0 | 4.0 | 5.0 |
| 2.0 | 4.10 / 4.23 | 5.23 / 5.36 | 6.60 / 6.73 | 8.45 / 8.58 |
| 3.0 | 3.31 / 3.40 | 4.11 / 4.20 | 4.98 / 5.06 | 5.50 / 5.63 |
| 4.0 | 3.05 / 3.08 | 3.37 / 3.43 | 4.08 / 4.10 | 4.65 / 4.78 |
| 5.0 | 2.95 / 2.98 | 3.12 / 3.25 | 3.54 / 3.67 | 4.10 / 4.23 |

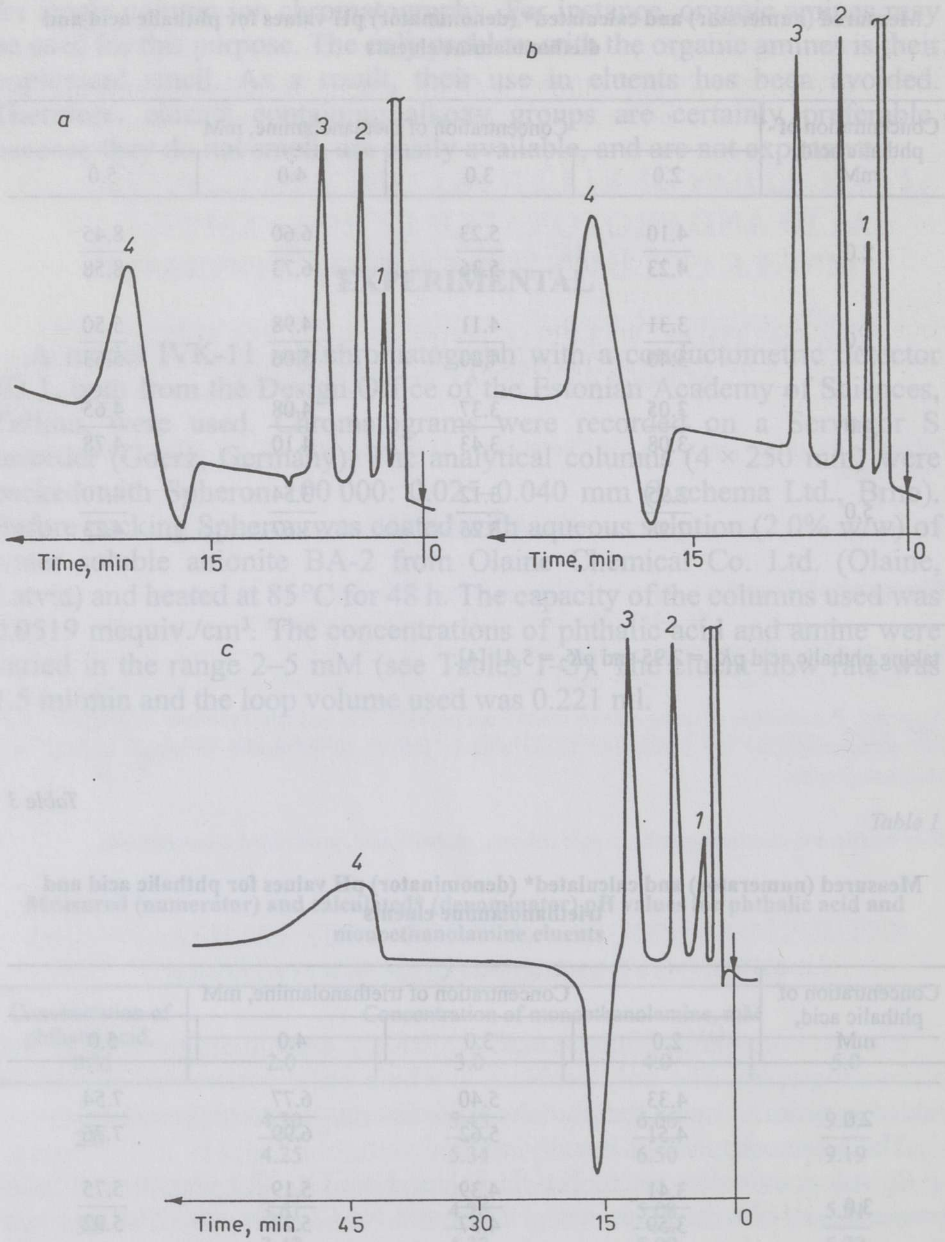
* taking phthalic acid $pK_1 = 2.95$ and $pK_2 = 5.41$ [4].

*Table 3*

**Measured (numerator) and calculated* (denominator) pH values for phthalic acid and triethanolamine eluents**

| Concentration of phthalic acid, mM | Concentration of triethanolamine, mM | | | |
|---|---|---|---|---|
| | 2.0 | 3.0 | 4.0 | 5.0 |
| 2.0 | 4.33 / 4.51 | 5.40 / 5.62 | 6.77 / 6.99 | 7.54 / 7.76 |
| 3.0 | 3.41 / 3.59 | 4.39 / 4.57 | 5.19 / 5.28 | 5.75 / 5.92 |
| 4.0 | 3.08 / 3.19 | 3.44 / 3.64 | 4.28 / 4.44 | 4.89 / 4.06 |
| 5.0 | 3.18 / 3.06 | 3.14 / 3.32 | 3.46 / 3.68 | 4.08 / 4.22 |

* taking phthalic acid $pK_1 = 2.95$ and $pK_2 = 5.41$ [4].




Typical chromatograms: *a*, eluent: 227.3 mg/l ethanolamine + 661.9 mg/l $H_2Ft$; *b*, eluent 425.4 mg/l diethanolamine + 749.6 mg/l $H_2Ft$; *c*, eluent 353.0 mg/l triethanolamine + 664.2 mg/l $H_2Ft$. Chromatogram of a mixture: *1*, $F^-$ (30 ppm); *2*, $Cl^-$ (40 ppm); *3*, $NO_3^-$ (60 ppm); *4*, $SO_4^{2-}$ (100 ppm). Separation column: 4 × 250 mm HIKS–1 (capacity 0.0519 mequiv./$cm^3$); flow rate 1.5 ml/min, backpressure 30 kG/$cm^2$, loop 0.221 ml; detector: 0.1 mS full scale 1/40 35.8 μS (*a*), 39.8 μS (*b*), and 41.8 μS (*c*).

## RESULTS AND DISCUSSION

Typical chromatograms obtained using different eluents are presented in the Figure (*a*, *b*, *c*).

It is evident from the Figure that all the eluents tested were appropriate for separating the $F^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ anions in their mixtures. These eluents showed only two system peaks on the chromatograms. The conductivity background of the eluents tested was acceptable for single column ion chromatography.

The pH of the tested eluents containing phthalic acid and ethanolamine depends on the concentrations of the added phthalic acid and amine. The equations used to determine the pH value are presented in the Appendix. Neglecting the activity coefficients, these equations lead to the calculated $[H^+]_{calc}$ value:

$$[H^+]_{calc} = Q_1/F_1 + K_W/[H^+] + K_1 \cdot C_A/F_2 - Q_2/F_3, \qquad (1)$$

where

$$F_1 = [H^+]^2 + [H^+] \cdot K_1 + K_1 \cdot K_2, \qquad (2)$$

$$F_2 = [H^+] + K_1 \cdot K_2/[H^+], \qquad (3)$$

$$F_3 = [H^+] \cdot K_B, \qquad (4)$$

$$Q_1 = 2 \cdot K_1 \cdot K_2 \cdot C_A, \qquad (5)$$

$$Q_2 = [H^+] \cdot C_B. \qquad (6)$$

See the Appendix for $K_1$, $K_2$, $K_W$, $K_B$, $C_A$, and $C_B$.

## APPENDIX

The following equations were used to calculate pH values:

$$K_1 = \frac{[H^+] \cdot [HA^-]}{[H_2A]}$$ (first dissociation constant for phthalic acid);

$$K_2 = \frac{[H^+] \cdot [A_2^{2-}]}{[HA^-]}$$ (second dissociation constant for phthalic acid);

$$K_B = \frac{[H^+] \cdot [B]}{[BH^+]}$$ (dissociation constant for amines conjugated acid);

$C_A = [HA^-] + [A^{2-}] + [HA]$ (stoichiometric balance of acid);

$C_B = [B] + [BH^+]$ (stoichiometric balance of amine);

$[H^+] + [BH^+] = [OH^-] + [HA^-] + 2[A^{2-}]$ (balance of charges), and

$K_W = [H^+] \cdot [OH^-]$ (dissociation constant for water).

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## FTAALHAPET JA PROTONEERITUD ETOKSÜAMIINE SISALDAVATE ELUENTIDE KASUTAMINE ÜHEKOLONNISES IOONKROMATOGRAAFIAS


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On uuritud võimalusi kasutada ftaalhapet ja etoksüamiinist valmistatud eluente ühekolonnises ioonkromatograafias. Need eluendid osutusid kasulikeks.