DETERMINATION OF ETHANOLAMINES IN AQUEOUS SOLUTIONS BY GAS CHROMATOGRAPHY

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The method of the separation and quantitative determination of mono-, di- and tris(2-hydroxyethyl)amines (ethanolamines, MEA, DEA and TEA) in aqueous solutions is described. 1% of OV-17 on Chromosorb G-AW, DMCS served as the packing of the column and the programmed temperature was used. The standard deviations $s_{y,x}$ for MEA, DEA and TEA were 14·91, 5·4 and 1·12% rel. respectively.

In the analysis of ethanolamines (mono-, di- and tris(2-hydroxyethyl)amines) the procedures are mostly used which have already proved[1,2] to be convenient for the determination of individual components in the primary, secondary and tertiary aliphatic amine mixtures. First of all the total amount of basic compounds is determined in aqueous and non-aqueous medium by the acid–base volumetric analysis, the determination of strongly basic tertiary amines is then carried out after the conversion of primary and secondary amines (in the non-aqueous medium) to slightly basic acetamides. The contents of mono- and di(2-hydroxyethyl)amine can be determined by oxidimetric titration with periodate[3]. Also the volumetric or manometric method according to van Slyke[1] can be used for determining primary amines. The amount corresponding to the individual components can be calculated from the difference of the several titrations in question. Also procedures based on liquid chromatography[4–6] were proposed for the identification and determination of single ethanolamines in their mixtures. As far as gas chromatography was employed the anhydrous mixtures of ethanolamines were needed because of the subsequent conversion of individual components to sufficiently volatile trifluoroacetyl[7] derivatives. Vacuum gas chromatography[8] which has been relatively little tested up to the present time was also used.

In the present work an attempt was made to determine individual ethanolamines without any pre-column modification of the sample contained both in non-aqueous mixtures and aqueous solutions. By using the linear programmed temperature gas chromatographic column containing 1% of OV-17 on Chromosorb G-AW, DMCS we found the conditions at which a total separation of mono-, di- and tris(2-hydroxyethyl)amines was achieved and the separation of methyl (2-hydroxyethyl)amine from di(2-hydroxyethyl)amine was satisfactory.

EXPERIMENTAL

Apparatus and materials. The apparatus used for the present study was PYE Heated Dual Flame Ionisation Detector Programmed Chromatograph, Model 64 (Series 104, Cambridge,

Great Britain). It was equipped with a recorder 0 —1 mV (Honeywell, model Electronik 194). The column employed was a 170 × 0·4 cm I.D. glass tube. Nitrogen was used as the carrier gas at the flow rate approximately of 30 ml/min. The sample solutions in ethanol were introduced with 10 μl Hamilton microsyringe. The injection port and the detectors were maintained at 170°C and 180°C, respectively. The linear increase of oven temperature was used from 50 to 220°C at 3°C/min. The column was packed with 80—100 mesh Chromosorb G-AW, DMCS (Johns-Manville) coated with 1% OV-17. The packing was prepared by dissolving the stationary phase in chloroform and coating the support in the usual manner. The column was preconditioned at 250°C for 12 hours with a carrier gas flow. The method of the internal standardization was employed for the quantitative determination of hydroxyethylamine, phenol being found to be the most convenient internal standard. The direct calibration was used for the determination of (2-hydroxyethyl)amine and tris(2-hydroxyethyl)amine.

Chemicals. 2-Hydroxyethylamine (monoethanolamine, MEA, pure, Merck, Darmstadt) and bis(2-hydroxyethyl)amine (diethanolamine, DEA, pure, Lachema, Brno) were purified by distillation in the nitrogen atmosphere in the vacuum apparatus without a ground glass joint. The vacuum of 20 and 6 Torr was applied to monoethanolamine and diethanolamine respectively. The purity of individual fractions was checked by gas chromatography. The purest diethanolamine fractions were diluted with water so as to provide approximately 10% solutions which were subsequently purified by ion exchange chromatography (cation exchanger Amberlit IR-120, 25 × 2 cm, the total volume 78 ml, the total exchange capacity approximately 15 mval). The elution was carried out by the 1M aqueous solution of ammonium carbonate. Fractions of 15 ml were taken, the purity of which was after concentration through the evaporation to sirupy consistency on a water bath checked by gas chromatography. Methyl bis(2-hydroxyethyl)amine (methyl diethanolamine, MDEA, pure, BASF, Leverkusen) contained 4% of water and its purity was checked by gas chromatography. Tris(2-hydroxyethyl)amine (triethanolamine, TEA) was obtained from triethanolamine hydrochloride (reagent grade, Lachema, Brno) which was first crystallized repeatedly from ethanol in the presence of active carbon. Then pure triethanolamine was prepared by the ion exchange from aqueous solution on strong-base anion exchanger Zerolit FF (column 38 × 0·8 cm, the volume 20 ml, the total column exchange capacity 26 mval) which was converted in advance into the hydrocarbonate form by $NaHCO_3$ solution and then washed successively by 2M-NH_3 and water. The individual 15 ml fractions taken during elution were concentrated through evaporation to sirupy consistency on a water bath and the residues were checked by gas chromatography. The calibration solutions *Ia*, *Ib* and *Ic* for monoethanolamine determination were prepared in such a manner as to possess values of about 5 : 1, 3 : 1 and 2 : 1 respectively of the mass concentration ratio of MEA/phenol. Therefore, the amounts of 0·52170 g of MEA and 0·11440 g of phenol (*Ia*), 0·29975 g of MEA and 0·10205 g of phenol (*Ib*) and 0·19755 g of MEA and 0·08709 g of phenol (*Ic*) were weighed always into a 10 ml volumetric flask and made up to the mark by ethanol. The calibration solutions *II* and *III* for the determination of diethanol- and triethanolamine respectively were prepared from 0·49375 g of DEA (*II*) and 0·56655 g of TEA (*III*), always inserted into 10 ml flask and made up by ethanol.

Calculations. From the results of measuring the calibration solutions *Ia*, *Ib* and *Ic* a graph was constructed by plotting the ratios of the retention curve areas of MEA/phenol *versus* the ratios of their weighed amounts. A similar graph was obtained from the measurement of the solutions *II* and *III* by plotting the retention curve areas *versus* the corresponding weighed amounts. The best straight lines were calculated by the least square method and the standard deviations $s_{x,y}$ for MEA, DEA and TEA were 14·91, 5·4 and 1·12% rel., respectively.

RESULTS AND DISCUSSION

The chemical methods of determining the individual components in the MEA, DEA and TEA mixtures using the acid–base titrations or combined with oxidimetric procedures are basically capable of discriminating among all aliphatic tertiary, secondary and primary amines. With regard to small differences of the pK_a values of the single components of these mixtures (25°C, TEA 7·76; DEA 9·0; MEA 9·51 and MDEA 8·28 (ref.[9]) it is hardly possible to determine the individual ethanolamines by the successive acidimetric titration. The combination of the chemical methods mentioned in the introductory part of this paper is less reliable because it does not make it possible to determine the individual components directly. All calculations are based on the result differences of various determinations carried out by different techniques and subject to different kind of errors. The reliability of the results obtained can be disputable especially when the mutual representation

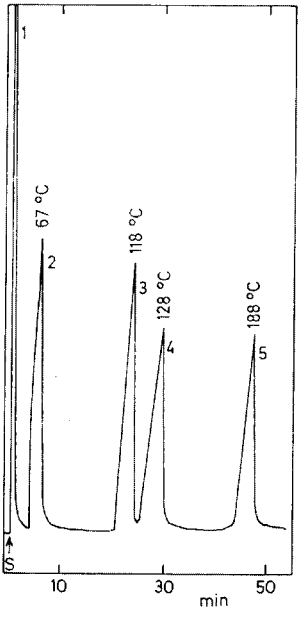

FIG. 1

Separation of the Synthetic Mixture of Ethanolamines

Column 170 × 0·4 cm I. D., 1% of OV-17/ /Chromosorb G-AW, DMCS, 80—100 mesh; N_2 30 ml/min; the temperature program 50—220°C, 3°C/min. 1 Ethanol, 2 monoethanolamine, 3 methyl diethanolamine, 4 diethanolamine, 5 triethanolamine.

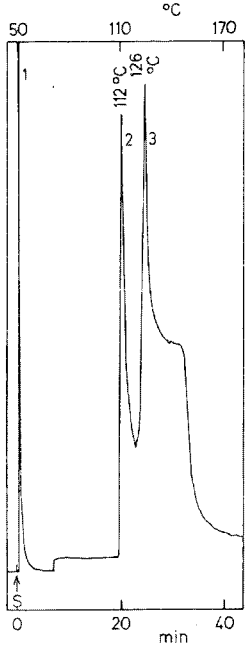

FIG. 2

Separation of the Synthetic Mixture of Methyl Diethanolamine and Diethanolamine For the conditions see Fig. 1. 1 Ethanol, 2 methyl diethanolamine, 3 diethanolamine.

of individual components in the mixture is unfavourable and when the analysed mixture may contain not only ethanolamines but also other basic compounds. Moreover, some determinations have to be performed in non-aqueous medium and for this reason they are not convenient for the analyses of aqueous ethanolamine solutions.

With regard to relatively small differences in the basicities of the individual ethanolamines the ion-exchange liquid chromatography is also hardly feasible. Differential refractometry or a quite pretentious technique of measuring the ^{14}C-labelled compounds activity has to be used for the detection of the eluted fractions. A flow-through UV-detector equipped with a mercury lamp is also inapplicable because no ethanolamine absorbs light at 254 nm. Relatively successful separation of ethanolamine mixtures by strong-acid cation exchangers or weak-base anion exchangers in the Ni(II) form can also be performed by radioactive detection only.

Although gas chromatographic technique is of considerable advantages it does not appear to have been used successfully for the dirrect determination of individual ethanolamines in aqueous solutions. Apprehension of their deep decay at temperatures needed to attain complete and momentaneous sample evaporation was apparently the most serious obstacle for the extension of the method in question. The conversion of individual ethanolamines to easy volatile trimethylsilyl and trifluoroacetyl[7] derivatives is unfeasible as far as the analysis of aqueous solution is concerned. For the analysis of ethanolamine aqueous solutions by gas chromatograpby the stationary phase had to be chosen in such a manner as to cause both a sufficiently large retention volume of MEA under the given conditions and a satisfactory separation of DEA and MDEA without an excessive sorption of the high-boiling components (TEA). Fig. 1 and 2 show the separation of the ethanolamine mixtures. Large dilution of the sample by ethanol permitted to shorten the time and to lower the temperature necessary for its evaporation. With regard to the great differences of the boiling points (MEA b.p. 170°C/760 Torr, DEA b.p. 270°C/748 Torr; TEA b.p. 277°C/150 Torr) of the determined compounds it was possible to use a low-polar stationary phase the low content of which on the support caused a relatively small retention also for TEA; in addition, the separation efficiency remained sufficient for all the components being determined. The use of two different temperatures in the run of the analysis was reported[8] for vacuum gas chromatography. In this work we have chosen the linear temperature increase from relatively low values in order to obtain the chromatogram convenient for the quantitative evaluation.

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