

ION CHROMATOGRAPHY USING GLYCINE–SODIUM CARBONATE ELUENTS: A RELATIONSHIP BETWEEN ELUENT COMPOSITION AND ITS ALKALINITY

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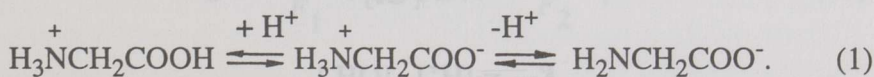
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Abstract. A computer program is described for calculating the pH values of an ionchromatographic eluent containing glycine and sodium carbonate. The calculated pH values are compared with the respective measured ones and the differences between them are estimated (mean root square error ± 0.015 pH units at 14 degrees of freedom).

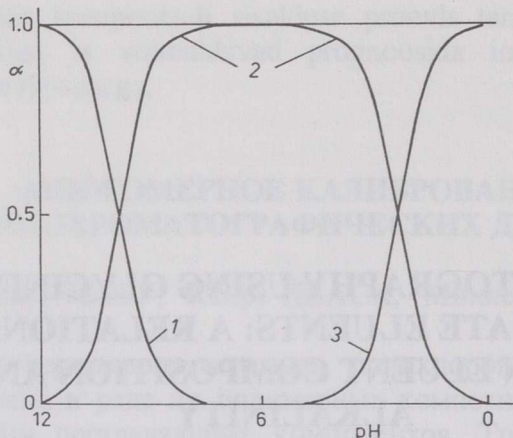
Key words: ion chromatography, glycine, pH values of eluents.

INTRODUCTION

Aqueous solutions of glycine containing sodium carbonate have been suggested for use as eluents in suppressed ion chromatography [1]. The eluent under study contains four anions ($\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$, $\text{H}_2\text{NCH}_2\text{COO}^-$, HCO_3^- , and CO_3^{2-}), acting as eluting ions for the sample anions. Glycine exists in these eluents in the form of three ions [2]:



The equilibria between these ions are presented in the Figure using $\text{p}K_1 = 3.532$ [2] and $\text{p}K_2 = 4.289$ [2].



Equilibria in aqueous glycine solutions: 1 - $\text{H}_2\text{NCH}_2\text{COO}^-$, 2 - $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$, 3 - $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$. $\alpha = i/(1 + 2 + 3)$, where i is 1, 2, or 3.

METHOD OF CALCULATION

Frequently, SiO_2 -based ion exchangers are used. These sorbents are alkaline-sensitive (i.e., they will be destroyed by OH^- ions). Therefore, it seems useful to calculate the eluent's pH values before its use. In the present study, we employed a rather simple method of approximation for this purpose. All the activity coefficients were taken to be equal to 1.000. The errors between calculated and measured pH values were estimated.

The pH of the aqueous solutions containing glycine and Na_2CO_3 depends both on the glycine concentration (CGI) and the Na_2CO_3 concentration (CSODA). If the activity coefficients are ignored, we can write

$$K_1 = \frac{[\text{H}^+] \cdot [\text{GI}]}{[\text{H}^+\text{GI}]}, \quad (2)$$

$$K_2 = \frac{[\text{H}^+] \cdot [\text{GI}^-]}{[\text{GI}]}, \quad (3)$$

$$K_w = [\text{H}^+] \cdot [\text{OH}^-], \quad (4)$$

$$K_{A1} = \frac{[\text{H}^+] \cdot [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}, \quad (5)$$

$$KA_2 = \frac{[H^+] \cdot [HCO_3^{2-}]}{[HCO_3^-]}, \quad (6)$$

$$CGI = [GI] + [H^+GI] + [GI^-], \quad (7)$$

$$[HO^-] + [GI^-] = [H^+GI] + [Na^+] + [H^+], \quad (8)$$

where

$$[Na^+] = 2 \cdot CSODA, \quad (9)$$

$$[GI] = [H_3N^+CH_2COO^-], \quad (10)$$

$$[H^+GI] = [H_3N^+CH_2COOH], \quad (11)$$

$$[GI^-] = [H_2NCH_2COO^-]. \quad (12)$$

The values for all the constants involved in Eqs. (2)–(6) may be found in literature: $pK_1 = 2.35$ [2], $pK_2 = 9.78$ [2], $pK_W = 14.00$ [3], $KA_1 = 4.45 \cdot 10^{-7}$ [4], and $KA_2 = 4.69 \cdot 10^{-11}$ [4].

This allows us to calculate the pH values of the solutions applied using the iterative step-by-step procedure described for nitrilotriacetic acid in [5]. First, we have to calculate the estimated C_{H^+} value from Eq. (13) derived by combining Eqs. (2)–(8):

$$C_{H^+} = \frac{K_W}{[H^+]} - A + B - 2 \cdot CSODA, \quad (13)$$

where A and B are

$$A = \frac{[H^+]^2 \cdot CGI}{K_1 \cdot K_2 \cdot F_1}, \quad (14)$$

$$B = \frac{CGI}{F_1} + CSODA \cdot \frac{F_3 \cdot F_4}{F_2}, \quad (15)$$

where

$$F_1 = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 \cdot K_2}, \quad (16)$$

$$F_2 = 1 + \frac{KA_1}{[H^+]} + \frac{KA_1 \cdot KA_2}{[H^+]^2}, \quad (17)$$

$$F_3 = \frac{KA_1}{[H^+]}, \quad (18)$$

$$F_4 = 1 + 2 \cdot KA_2/[H^+]. \quad (19)$$

To apply Eq. (13), we have to use some estimated $C_{H^+} = 10^{-pH}$ value in the range of $1 \leq pH \leq 14$. We started with $pH = 1.00$ and calculated C_{H^+} (13) for this pH value. If now C_{H^+} (13) $< 10^{-pH}$, we have to make a step towards higher pH values:

$$pH(\text{new}) = pH(\text{old}) + \text{STEP} \quad (20)$$

and calculate C_{H^+} (13) again. This procedure was repeated applying $\text{STEP} = 1.00$ until $C_{H^+} > 10^{-pH}$ was reached. Then a reverse step was made to restore the previous pH value that still yielded $C_{H^+} < 10^{-pH}$ and the STEP in Eq. (20) was decreased as follows:

$$\text{STEP}(\text{new}) = 0.1 \cdot \text{STEP}(\text{old}). \quad (21)$$

The whole procedure was continued with this smaller STEP (21). So, each time the diminishing of the STEP after $C_{H^+} > 10^{-pH}$ was achieved, we calculated the pH value for the solution concerned with three decimal numbers after the point, i.e. with an error < 0.001 . This pH value corresponds to the glycine and sodium carbonate solution with fixed values of CGI and CSODA.

The whole iteration procedure takes about a second on a computer with a 286 processor using the respective program in FORTRAN 66. The program used is available on request. In order to check the correctness of the equations derived and the computer program written, we measured the pH values for a number of glycine and sodium carbonate solutions (see Experimental and Table).

EXPERIMENTAL

The glycine from Sojuzkhimreaktiv (Moscow) was recrystallized from hot water and dried at 110°C . Sodium carbonate from the same supplier (analytical grade) was dried at 300°C and then used for preparing the solutions. All the solutions were made in CO_2 -free distilled water using

the weighed amounts of glycine and Na_2CO_3 . When Na_2CO_3 was dissolved in glycine solutions no CO_2 gas emission was observed. The pH values were measured on a Russian pH-meter EV-74, previously calibrated, applying the a_{H^+} scale [6].

pH values for the aqueous solutions of glycine-sodium carbonate mixtures

CGI, mM	CSODA, mM	pH, calc.	pH, meas.
6.0	0.6	8.808	9.00
6.0	1.0	9.049	9.10
6.0	2.0	9.400	9.41
6.0	3.0	9.624	9.64
6.0	6.5	10.086	10.06
4.0	0.6	8.996	9.00
4.0	1.0	9.247	9.25
4.0	2.0	9.619	9.65
4.0	3.0	9.856	9.88
4.0	4.5	10.100	10.12
2.0	0.6	9.331	9.26
2.0	1.0	9.605	9.57
2.0	1.6	9.875	9.85
2.0	2.0	10.006	9.95
2.0	2.5	10.135	10.10

RESULTS AND DISCUSSION

The pH data presented in the Table show that the calculated and the measured pH values agree fairly well (the smallest division of the pH-meter used was 0.05 pH units). The differences $d = \text{pH}(\text{calc.}) - \text{pH}(\text{meas.})$ have a mean value of $\bar{d} = 0.0064 \pm 0.035$, which is quite as expected. This result was obtained when all the activity coefficients were taken to be equal to 1.000. It seems unnecessary to take into account the activity coefficients: there is a good agreement between the calculated and the measured pH values in spite of the fact that all these coefficients were taken equal to 1.000. This means that the program yields reliable pH values for glycine-sodium carbonate mixtures in the range of pH values 8.8-10.1.

The pH values measured (Table) show that the eluents studied should be used with polymeric resin-based ion exchangers only because the SiO_2 -based ion exchange materials would be destroyed in aqueous solutions with $\text{pH} > 9$.

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IOONIKROMATOGRAAFIA GLÜTSIINI JA NAATRIUMKARBONAATI SISALDAVATE ELUENTIDEGA: ELUENDI LEELISUSE SÕLTUVUS SELLE KOOSTISEST

Ülo HALDNA, Irina JAKOVLEVA

On tuletatud võrrandid ioonikromatograafias kasutatavate glütsiini ja naatriumkarbonaadi segude vesilahuste pH arvutamiseks. Nende alusel on kirjutatud vastav arvutiprogramm. Arvutustulemused on heas kooskõlas eksperimenti andmetega.

ИОННАЯ ХРОМАТОГРАФИЯ С ЭЛЮЕНТАМИ, СОДЕРЖАЩИМИ ГЛИЦИН И КАРБОНАТ НАТРИЯ: ЗАВИСИМОСТЬ ЩЕЛОЧНОСТИ ЭЛЮЕНТА ОТ ЕГО СОСТАВА

Юло ХАЛДНА, Ирина ЯКОВЛЕВА

Выведены уравнения для расчета значений pH водных растворов смесей глицина и карбоната натрия, предложенных в качестве элюентов при ионохроматографическом анализе смесей анионов. На основе этих уравнений написана программа на языке ФОРТРАН и по ней рассчитаны указанные значения pH, которые затем сравнены с соответствующими экспериментальными данными.