

## A COMPUTATIONAL METHOD FOR THE DETERMINATION OF DISSOCIATION CONSTANTS OF NITRILOTRIACETIC ACID

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Presented by Ü. Lille

Received October 19, 1993; accepted November 2, 1993

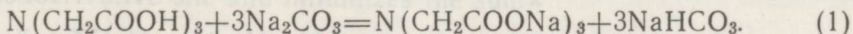
**Abstract.** A computational method is presented for the calculation of the  $pK_2$  and  $pK_3$  values of nitrilotriacetic acid (NTA). This method makes use of NTA and sodium carbonate mixtures with measured pH values. The  $pK$  values of carbonic acid and the complex formation between NTA and  $Na^+$  ions ( $\log K_{MX}=1.22$ ) were taken into account. It was found that the  $pK_2$  and  $pK_3$  values of NTA are  $2.87\pm 0.03$  and  $10.06\pm 0.01$ , respectively.

**Key words:** dissociation constants, nitrilotriacetic acid, computational methods in chemistry.

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### INTRODUCTION

Nitrilotriacetic acid (NTA) is a classical chelating agent [1]. Recently its application in ion chromatography with its mixtures with sodium carbonate used as eluents has been suggested for the determination of common anions [2]. This application has drawn our attention to the pH calculations of the  $NTA+Na_2CO_3$  mixtures used in ion chromatography. As a result, a computational method for calculating  $pK_2$  and  $pK_3$  values of NTA has been developed. The reaction between NTA and  $Na_2CO_3$  can be presented as follows:



### METHOD OF CALCULATION

The pH of aqueous solutions containing NTA and  $Na_2CO_3$  depends on the NTA concentration,  $C_{NTA}$ , as well as on the ratio  $a=C_{Na_2CO_3}/C_{NTA}$ , where  $C$  stands for the respective analytical molar concentrations. In the aqueous solutions suggested to be used in ion chromatography,  $0.5 \leq a \leq 3$ . Denoting the NTA as  $XH_3$  and neglecting the activity coefficients, we can write

$$K_1 = C_{\text{H}^+} \cdot C_{\text{XH}_2^-} / C_{\text{XH}_3}, \quad (2)$$

$$K_2 = C_{\text{H}^+} \cdot C_{\text{XH}^{2-}} / C_{\text{XH}_2^-}, \quad (3)$$

$$K_3 = C_{\text{H}^+} \cdot C_{\text{X}^{3-}} / C_{\text{XH}^{2-}}, \quad (4)$$

$$KA_1 = C_{\text{H}^+} \cdot C_{\text{HCO}_3^-} / C_{\text{H}_2\text{CO}_3}, \quad (5)$$

$$KA_2 = C_{\text{H}^+} \cdot C_{\text{CO}_3^{2-}} / C_{\text{HCO}_3^-}, \quad (6)$$

$$KK = C_{\text{NaX}^{2-}} / C_{\text{Na}^+} \cdot C_{\text{X}^{3-}}, \quad (7)$$

$$K_{\text{W}} = C_{\text{H}^+} \cdot C_{\text{OH}^-}, \quad (8)$$

$$C_{\text{NTA}} = C_{\text{XH}_3} + C_{\text{XH}_2^-} + C_{\text{XH}^{2-}} + C_{\text{X}^{3-}}, \quad (9)$$

$$C_{\text{Na}_2\text{CO}_3} = C_{\text{CO}_3^{2-}} + C_{\text{HCO}_3^-} + C_{\text{H}_2\text{CO}_3}, \quad (10)$$

$$C_{\text{H}^+} + C_{\text{Na}^+} = C_{\text{OH}^-} + C_{\text{XH}_2^-} + 2C_{\text{XH}^{2-}} + 3C_{\text{X}^{3-}} + C_{\text{HCO}_3^-} + 2C_{\text{CO}_3^{2-}} + 2C_{\text{NaX}^{2-}}, \quad (11)$$

$$C_{\text{Na}^+} = 2C_{\text{Na}_2\text{CO}_3}. \quad (12)$$

The values for all the constants involved in Eqs. (2)–(12) may be found in the literature:  $pK_1=1.89$  [3],  $pK_2=2.49$  [3],  $pK_3=9.73$  [3],  $KA_1=4.45 \cdot 10^{-7}$  [4],  $KA_2=4.69 \cdot 10^{-11}$  [4],  $\log KK=1.22$  [5],  $K_{\text{W}}=1.0 \cdot 10^{-14}$  [4].

This allows us to calculate the pH of the solutions applied, using the iterative step-by-step procedure described below. We have first to calculate the estimated  $C_{\text{H}^+}$  value by Eq. (13) derived by combining Eqs. (2)–(12):

$$C_{\text{H}^+} = (4C_{\text{Na}_2\text{CO}_3} \cdot C_{\text{X}^{3-}}) / (1 + KK \cdot C_{\text{X}^{3-}}) + K_{\text{W}} / C_{\text{H}^+} - 2C_{\text{Na}_2\text{CO}_3} + C_{\text{Na}_2\text{CO}_3} \cdot B / Q + A \cdot C_{\text{X}^{3-}}, \quad (13)$$

where  $A$ ,  $B$ , and  $Q$  are

$$A = C_{\text{H}^+} / K_2 K_3 + 2C_{\text{H}^+} / K_3 + 3, \quad (14)$$

$$B = KA_1 / C_{\text{H}^+} + 2KA_1 \cdot KA_2 / (C_{\text{H}^+})^2, \quad (15)$$

$$Q = KA_1 / C_{\text{H}^+} + KA_1 \cdot KA_2 / (C_{\text{H}^+})^2 + 1, \quad (16)$$

and the concentration  $C_{\text{X}^{3-}}$  is

$$C_{\text{X}^{3-}} = (-D - T) / 2E, \quad (17)$$

where

$$D = KK(C_{\text{NTA}} - 2C_{\text{Na}_2\text{CO}_3}) - Z, \quad (18)$$

$$E = -Z \cdot KK, \quad (19)$$

$$T = (D^2 - 4E \cdot C_{\text{NTA}})^{0.5}, \quad (20)$$

$$Z = (C_{\text{H}^+})^3 / K_1 K_2 K_3 + (C_{\text{H}^+})^2 / K_2 K_3 + C_{\text{H}^+} / K_3 + 1. \quad (21)$$



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  $pH = 1.0$  and calculated  $C_{H^+}$  (13) with this  $pH$  value.

If now  $C_{H^+}$  (13)  $< 10^{-pH}$ , we have to make a step towards higher  $pH$  values:

$$pH(\text{new}) = pH(\text{old}) + \text{STEP}, \quad (22)$$

and calculate  $C_{H^+}$  (13) again. This procedure was repeated with  $\text{STEP} = 1.0$  until  $C_{H^+} > 10^{-pH}$ . Then a reverse step was made to restore the previous  $pH$  value, which still yielded  $C_{H^+} < 10^{-pH}$  and the  $\text{STEP}$  in Eq. (22) was diminished as follows:

$$\text{STEP}(\text{new}) = 0.1 \cdot \text{STEP}(\text{old}) \quad (23)$$

and the whole procedure was continued with the smaller  $\text{STEP}$  (23). So, each time we diminished the  $\text{STEP}$  after  $C_{H^+} > 10^{-pH}$  had been achieved, we calculated the  $pH$  value for the solution concerned with three decimal numbers, i.e. with an error  $< 0.001$ . This  $pH$  value corresponds to the  $\text{NTA} + \text{Na}_2\text{CO}_3$  solution with the fixed values of  $a$  and  $C_{\text{NTA}}$ . The whole iteration procedure takes about a second on a PC with a 286 processor using the respective program in FORTRAN 66.

As pointed out, the procedures described above enable to calculate the  $pH$  using fixed  $a$  and  $C_{\text{NTA}}$  values together with the constant values (Eqs. (2)–(8)) taken from the literature [2–5]. Provided that the  $pH$  data have been measured for a number of  $\text{NTA} + \text{Na}_2\text{CO}_3$  mixtures, we can use them to calculate the best values of the constants involved, or at least a number of these constants. We decided to recalculate the  $pK_2$  and  $pK_3$  values of  $\text{NTA}$ , applying various  $pH$  values (see the Table).

The  $pH$  values measured for 1.0 mM nitrilotriacetic acid solutions with added sodium carbonate

$C_{\text{Na}_2\text{CO}_3}$ , mM	0.05	0.1	0.25	0.5	1.0	2.0	2.2	2.5	3.0
$pH$	2.91	2.94	3.03	3.07	5.06	8.04	9.03	9.58	9.71

It should be noted that the  $pH$  data must be measured for a region in which the constants thus determined have a strong influence on the  $pH$  values. If it is not so, for example, if we had tried to recalculate the  $KK$  value which shows only an insignificant influence on the  $pH$  values measured, every method applied would yield insufficiently unambiguous constant values. As Eqs. (13)–(21) show, the dependence of  $pH$  on the constants is not a linear one. Therefore, we used a non-linear regression algorithm [6, 7] for simultaneous recalculations of  $pK_2$  and  $pK_3$ . This algorithm is similar to that of Hooke and Jeeves [8], i.e. it is a nonderivative one and minimizes the sum

$$Y = \sum (pH_{\text{calc}} - pH_{\text{exp}})^2 \quad (24)$$

using some estimates for the constants under study. The latter are then varied to obtain the lowest possible value of  $Y$  (24). It is important to point out that in the algorithm applied the signs of the parameters adjusted have been given by the researcher.

The mean and the confidence intervals for the  $pK_2$  and  $pK_3$  (at  $P = 0.95$ ) were obtained varying the respective initial guesses using about 3–5 times greater and/or smaller  $pK_1$  and  $pK_2$  values than the literature data. The total number of runs with different guesses was 12.

## EXPERIMENTAL

NTA from Sojuzkhimreaktiv (Moscow) was recrystallized from hot water and dried at 110°C. Sodium carbonate of the same supplier (analytical grade) was dried at 300°C and then used for preparing the solutions. All the solutions were made in CO<sub>2</sub>-free distilled water using weighed amounts of NTA and Na<sub>2</sub>CO<sub>3</sub>. Then Na<sub>2</sub>CO<sub>3</sub> was dissolved in NTA solutions at  $a \leq 3.0$ ; no CO<sub>2</sub> gas emission was observed. The pH values were measured on a Russian-made pH-meter EV-74, previously carefully calibrated, applying the  $a_{H^+}$  scale [9].

## RESULTS AND DISCUSSION

The use of the pH data presented in the Table yielded the following values for NTA:  $pK_2 = 2.87 \pm 0.03$  and  $pK_3 = 10.06 \pm 0.01$  (both with probable errors at  $P = 0.95$  level). These values are quite close to those given in the literature:  $pK_2 = 2.49$  [3],  $pK_2 = 2.94$  [10],  $pK_3 = 9.73$  [3],  $pK_3 = 10.33$  [10],  $pK_3 = 9.15$  [11]. The recalculated  $pK_2$  and  $pK_3$  values together with the values for other constants given above allowed us to reproduce the measured pH values (see the Table) with a mean square root error of  $\pm 0.1$  pH units.

The computer programs were written in FORTRAN 66 and are available on request.

## ACKNOWLEDGEMENT

We acknowledge the financial support provided by the Estonian Science Foundation.

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# NITRILOTRIÄÄDIKHAPPE DISSOTSIATSIIOONIKONSTANTIDE ARVUTAMISE MEETOD

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On esitatud meetod nitrilotriäädikhappe (NTA) kahe dissotsiatsiooni-  
konstandi ( $pK_2$  ja  $pK_3$ ) arvutamiseks lähtudes NTA ja naatriumkarbo-  
naadi segu vesilahuse pH väärtustest. Seejuures on arvesse võetud nii  
NTA dissotsiatsiooni kui ka NTA ja  $Na^+$ -ioonide vahelist kompleksimoo-  
dustamise tasakaalu ( $\log K_{MX}=1,22$ ). Leitud on  $pK_2$  ja  $pK_3$  väärtused  
 $2,87 \pm 0,03$  ning  $10,06 \pm 0,01$ .

## МЕТОД ВЫЧИСЛЕНИЯ КОНСТАНТ ДИССОЦИАЦИИ НИТРИЛОТРИУКСУСНОЙ КИСЛОТЫ

Юло ХАЛДНА, Ирина ЯКОВЛЕВА

Предложен метод вычисления двух констант ( $pK_2$  и  $pK_3$ ) диссоциа-  
ции нитрилотриуксусной кислоты (НТ). За исходные данные приняты  
значения pH водных растворов, содержащих НТ и карбонат натрия.  
Учтены трехступенчатая диссоциация НТ и комплексообразование НТ  
с натрий-ионами ( $\log K_{MX}=1,22$ ). Найдено, что константы  $pK_2$  и  $pK_3$   
имеют значения  $2,87 \pm 0,03$  и  $10,06 \pm 0,01$  соответственно.