

DETERMINATION OF CARBONATE ALKALINITY AND APPARENT DISSOCIATION CONSTANTS IN A MULTIPROTOLYTIC SYSTEM

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(Received 22 August 1984. Revised 10 June 1985. Accepted 2 August 1985)

Summary—A method for analysing the carbonate system in a multicomponent solution is presented, which does not need knowledge of the total composition of the system. It is based on two titrations with acid, starting at the same pH, one of the original solution and the other after removal of carbonate species as carbon dioxide and restoration of the pH to the value for the original solution by addition of carbonate-free base. The differential titration curve, obtained by subtracting one titration curve from the other, is associated with the carbonate system. A procedure is proposed for calculating from the differential titration curve the apparent first and second dissociation constants of carbonic acid, total CO_2 and the carbonate alkalinity at the original pH of the solution.

It is well recognized that the carbonate system plays a major role in natural waters and biological fluids as well as in many industrial processes. Consequently, there is often a need to characterize it in various solutions of complex ionic composition. Since the apparent dissociation constants¹ of carbonic acid, which are usually applied in such cases, are dependent on the ionic strength and composition of the medium,² there is the additional problem of determining the constants in the test solution. This problem can be approached by a general purpose strategy in which an attempt is made to determine all the components of protolytic species by an acid-base titration,³⁻⁵ but difficulties can arise because of the large number of unknowns to be determined and possible overlap of reaction equilibria. Although statistical analyses have been suggested to improve matters,^{6,7} this approach is futile when the solution contains other species which exhibit protolytic behaviour over the same pH range as the carbonate system. For example, a high phosphate concentration would severely interfere in any attempt to determine the components of the carbonate system from an acid-base titration.

In the present investigation we explored the possibility of analysing the carbonate system, in a multiprotolytic system, by separating the titration response of the carbonate system from that of other protolytes present. This was accomplished by means of the difference between acid-base titration curves obtained with and without the carbonate system present. The titration curve for the carbonate-free

solution was obtained by driving off carbon dioxide from the original solution at low pH and titrating the modified sample. It can be shown that the differential titration curve is a function of only the carbonate system and hence can be used to determine the components and apparent constants of this system. The suggested approach was applied to study of the carbonate system and total alkalinity in the urine of healthy adults, to improve characterization of the mechanism of hydrogen-ion secretion by the kidney and the sources of high pCO_2 differentials between the blood and urine.

THEORETICAL CONSIDERATIONS

The total charge held by the ions in a complex solution can be divided into two parts: the ionic charge of the protolytic species (QP), and the charge of the non-protolytic species (QN).⁸ The term "protolytic species" means those components that can interact with H^+ (or OH^-) over the pH-range of interest. This definition is akin to the definition of "alkalinity" suggested recently,⁹ except that it is more loosely defined.

The charge held by the protolytic species (which is assumed here to be negative to conform with the concept of "alkalinity") at any stage during an acid titration, $(\text{QP})_t$, can be related to the initial value $(\text{QP})_0$ by:

$$\begin{aligned}(\text{QP})_t &= (\text{QP})_0 - V_t N_a \\ &= \sum_i (\text{TC})_i V_0 B_i (\text{pH}_t, K'_1, K'_2, \dots, K'_i) \\ &\quad + ([\text{OH}^-] - [\text{H}^+])(V_0 + V_t)\end{aligned}\quad (1)$$

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where (TC)_{*i*} is the total concentration of the *i*th component, *V*₀ the initial volume of solution, *N*_{*a*} the normality of the titrant acid, *V*_{*t*} the volume of acid added by stage *t* in the titration, pH_{*t*} the pH at stage *t*, *K*'_{*j*} the *j*th apparent dissociation constant of component *i*, and *B*_{*i*} relates the total charge of component *i* to (TC)_{*i*}. For the carbonate system:¹

$$(\text{TC})_{\text{CO}_2} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (2)$$

where

$$[\text{H}_2\text{CO}_3^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] \quad (3)$$

The function *B* for the carbonate system can be written explicitly in the form:

$$B_{\text{CO}_2} = \frac{\{\text{H}^+\}K'_1 + 2K'_1K'_2}{\{\text{H}^+\}^2 + \{\text{H}^+\}K'_1 + K'_1K'_2} \quad (4)$$

where {H⁺} is the activity of H⁺ as measured by a glass electrode, and *K*₁ and *K*₂ are the apparent first and second dissociation constants of carbonic acid. In this case, the carbonate alkalinity,¹ (CA), at a given pH is related to (TC)_{CO₂} by

$$(\text{CA}) = (\text{TC})_{\text{CO}_2} B_{\text{CO}_2} \quad (5)$$

If the titration with acid is continued to a pH at which carbonic acid is virtually completely undissociated, *e.g.*, pH < p*K*'₁ - 2, and carbon dioxide is then stripped off and the pH restored to that of the solution *before* the titration, by addition of base of normality *N*_{*b*}, the (QP) of the restored solution, (QP)_{*R*}, will be

$$(\text{QP})_{\text{R}} = (\text{QP})_0 - V_a N_a + V_b N_b \quad (6)$$

where *V*_{*a*} and *V*_{*b*} are the total volumes of added acid and base, respectively. Hence, (QP) during acid titration of the carbonate-free solution, (QP)_{*t*}, will be:

$$(\text{QP})_t = (\text{QP})_0 - V_a N_a + N_b V_b - V'_t N_a \quad (7)$$

where *V*'_{*t*} is the volume of acid added by stage *t* in the second titration. By subtracting (QP)_{*t*} from (QP)_{*t*} at points of equal pH along the titration curves we obtain

$$\begin{aligned} (\text{QP})_t - (\text{QP})'_t &= N_a V_a - N_b V_b - N_a (V_t - V'_t) \\ &= (\text{TC})_{\text{CO}_2} V_0 B_{\text{CO}_2} + ([\text{OH}^-] - [\text{H}^+]) \\ &\quad \times (V_t - V_a - B_b - V'_t) \end{aligned} \quad (8)$$

The last term in equation (8) is negligibly small since the two factors are small, the first because titrations are usually done within the range in which [H⁺] and [OH⁻] are small compared to (QP), and the second because *N*_{*a*} and *N*_{*b*} can be made high enough for the volume difference to be only a small fraction of the total volume. The equation can thus be rewritten in the form:

$$\begin{aligned} \frac{N_a V_a - N_b V_b - N_a (V_t - V'_t)}{V_0} \\ = (\text{TC})_{\text{CO}_2} \frac{\{\text{H}^+\}K'_1 + 2K'_1K'_2}{\{\text{H}^+\}^2 + \{\text{H}^+\}K'_1 + K'_1K'_2} = z \end{aligned} \quad (9)$$

Following an approach suggested earlier,¹⁰ this equation can be rewritten in a linear form:

$$y = m + kx \quad (10)$$

where

$$x = z(K'_2 + \{\text{H}^+\}) / (2K'_2 + \{\text{H}^+\})$$

$$y = z(K_2 + \{\text{H}^+\}) / (2K_2 + \{\text{H}^+\})$$

$$m = (\text{TC})_{\text{CO}_2} K'_1$$

$$k = -K'_1$$

The equation can be solved for *m* and *k* by an iterative least-squares fitting procedure in which *K*'₂ is incremented by trial and error until a best fit is obtained.^{10,11} The *K*'₂ that gives the best fit, together with the (TC)_{CO₂} calculated from the resulting *m* and *k*, will constitute a complete characterization of the carbonate system in the original complex solution.

It should be emphasised that the analytical and computational procedure given above for the determination of *K*'₁, *K*'₂ and (TC)_{CO₂} implicitly assumes that the apparent constants of all the protolytic species stay constant during the whole procedure. The error introduced by this assumption should be negligible if the dilution during titration is small (*i.e.*, if *V*_{*a*} ≪ *V*₀ and *V*_{*b*} ≪ *V*₀ and if there is no appreciable change in the ionic strength due to the addition of acid and base and the elimination of CO₂ from the solution.

The foregoing analysis also assumes that (TC)_{CO₂} during any given titration is kept constant, *i.e.*, that there is no appreciable exchange of CO₂ between the solution and the overlying gas phase. This could prove to be a problem if (TC)_{CO₂} is large enough to cause a high *p*_{CO₂} build-up at low pH. In such cases the approach given by Edmond¹² might be adopted, in which the titration is done in a completely sealed flask with a bellows or other means of allowing addition of acid during the titration. We have found, however, that if the stirring is slow the rate of CO₂ exchange does not constitute a problem.

The second titration, after CO₂ has been stripped off, can be done by back-titration with sodium hydroxide or by the method selected by us, *viz.* restoring the pH by addition of alkali, followed by titration with acid. The latter method was chosen for two practical reasons: one is that it does not require a second motor-driven burette and the other is that a burette used for dispensing alkali requires a guard tube to eliminate contamination with atmospheric carbon dioxide. However, the method introduces an additional source of uncertainty. Another point that should be made is the practical problem which might arise when attempting to subtract (QP)_{*t*} from (QP)_{*t*} to obtain the differential titration curve. Since the titrations are usually done by adding equal increments of acid, a pH-value on the second titration curve that is identical with that at a particular titration point on the first curve will not coincide with a titration point, so direct subtraction of *V*'_{*t*} from *V*_{*t*} is impossible. The

problem can be overcome either by performing a titration in fixed pH increments, *i.e.*, with variable increments of acid, or by fitting a polynomial to the titration curve and recalculating the volume increments for the equi-pH points. The latter approach was applied here since the titration system¹³ delivers equal increments of titration acid.

EXPERIMENTAL

Instrumentation

The microcomputer-based titration system was similar to the assembly described earlier.¹³

Solutions

The test solution was artificial urine¹⁴ of ionic strength 0.165M and total phosphate concentration 0.015M. The salts were dissolved in 0.1M hydrochloric acid to prevent precipitation of calcium sulphate. The pH was then raised to about 7 by neutralization with sodium hydroxide while air was bubbled through the solution to equilibrate it with atmospheric carbon dioxide.

Titration and computation

The first titration was done with 1M hydrochloric acid to pH 2.5, the CO₂ was stripped by passage of nitrogen, the pH was restored to not less than the original value (but not more than 0.2 pH units higher) by addition of 5M sodium hydroxide, and the second titration was also done with 1M hydrochloric acid to about pH 2.5. The titration curves were fitted to a high-order polynomial of the form

$$V_1 = \sum_{j=0}^P A_j (\text{pH}_1)^j \quad (11)$$

where P is the order of the polynomial. Usually a 7th order polynomial was found to fit the complete titration curve well. By use of these experimental polynomials, the differential titration curve was calculated by evaluating $(V_1 - V_1')$ for equally spaced pH values. The differential titration curve was then used in the iterative least-squares fitting procedure^{11,13} to derive $K_1'K_2'$ and $(\text{TC})_{\text{CO}_2}$ for the original solution. All calculations were done by computer

programs written in BASIC and run on a microcomputer system which comprised a Commodore CBM 3032, a printer, a dual disc-driver model 3040, a cassette deck, and a Textronic model 4662 x - y plotter. The system is compatible with the magnetic recording formats of the microcomputer-based titrator.¹³ It should be emphasized that the mention of specific hardware models is only for information and does not constitute an endorsement or recommendation of specific brands.

RESULTS AND DISCUSSION

A typical set of results, including the titration curves for the original solution and the CO₂-free solution, and the differential titration curve, is exemplified in Fig. 1. The solid lines connecting the points of the first and second titration curves are for the 7th degree polynomial used. Fitting the polynomial to the complete titration curve, as in Fig. 1, is not really necessary, since the points below pH 5 add little to the regression line [(equation 10)] from which K_1' and K_2' are derived. Hence, it would suffice to perform the fitting over a limited range from the original pH (pH_0) to about pH 5. This considerably eases the task of choosing the polynomial since this portion of the titration curve does not include a sharp inflection and hence a lower-degree polynomial will suffice.

The shape of the differential titration curve (Fig. 1, DIF) is sigmoid and independent of pH below a certain critical value (~ 5), as a direct consequence of the fact that the two titration curves, for the original and CO₂-free solution, are identical in the pH range where the carbon dioxide is virtually all present as undissociated H₂CO₃ and dissolved CO₂ [CO₂ (aq)]. In this pH range, the buffering is controlled by the other protolytic species and not by the carbonate

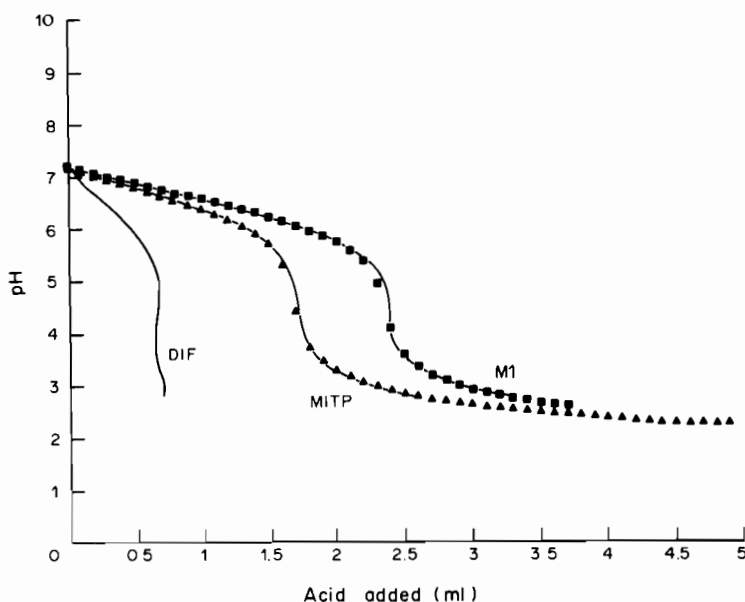


Fig. 1. Acid titration curves for original artificial urine before (M1) and after (MITP) driving off CO₂, and the difference between the two curves (DIF).

Table 1. Titration results for artificial urine sample

pH ₀ *	Ionic strength, M	pH,†	Carbonate alkalinity, meq/l.	(TC) _{CO₂} , mM	pK' ₁	pK' ₂	R ² ‡
7.65	0.165	7.75	16.4	16.5	6.25	9.59	0.99992

*Initial pH of sample.

†Initial pH of sample in second titration.

‡Correlation coefficient of least-squares fitting.

system, in either titration. This conclusion can be arrived at mathematically by noticing that for $\text{pH} < \text{p}K'_1 - 2$, *i.e.*, when $B_{\text{CO}_2} \rightarrow 0$, equation (5), the differential titration curve, equation (8), is reduced to

$$N_a V_a - N_b V_b - N_a (V_1 - V'_1) = 0 \quad (12)$$

By application of the iterative procedure for the best fit of the data to the straight line of equation (10), K'_2 was guessed and $(\text{TC})_{\text{CO}_2}$ calculated from the slope and intercept of the line (Table 1). The criterion chosen for the goodness of fit was the correlation coefficient, which exhibits a maximum for the best K'_2 , as discussed by Sass and Ben-Yaakov.¹⁰

It should be emphasised that a precondition for accurate K'_1 and/or K'_2 determination is that the titration curves used in the curve fitting include points with pH values which are numerically close (say within one unit) to the $\text{p}K'$ of interest. Points with pH values too far from the pertinent $\text{p}K'$ are insensitive to that dissociation constant and hence cannot be used to obtain a valid value for it. Consequently, the K'_2 values obtained here may have an appreciable uncertainty. However, since the value of pH_0 was at least 2 units smaller than $\text{p}K'_2$ the effect of K'_2 on the analysis was small and hence high accuracy was not essential in its determination in this case.

The carbonate alkalinity of the original solution can be calculated from pH_0 and the derived values of $(\text{TC})_{\text{CO}_2}$, $\text{p}K'_1$ and $\text{p}K'_2$,¹ or by an acid-base balance [which is based on the fact that $(V_1 - V'_1)$ at pH below, say, 4 is directly related to the carbonate alkalinity in the original solution, *i.e.*, the contribution of the carbonate system to (QP) at pH_0]. Carbonate alkalinity in the original sample can be directly calculated from equation (12) for pH values below pH 4.5, if the solution pH is restored to pH_0 by the base. If the restored pH differs from pH_0 , the volume of base V_b required to reach the original pH_0 of the solution can be calculated from the polynomial fitting [equation (11)] to the second titration. It should be emphasised that the methods suggested here for calculating the carbonate alkalinity in the original solution constitute, in fact, a hitherto novel approach to measuring a parameter (carbonate alkalinity) which could not have been estimated for a multiprotolytic system by published methods. Carbonate alkalinity estimation by the Gran or modified Gran methods^{9,10,12,15} or by end-point titration^{16,17} cannot be used for a multiprotolytic system, es-

pecially if the ionic composition of the solution is unknown. Similarly, no other published method is available for the determination of $\text{p}K'_1$ and $\text{p}K'_2$ of one species in a multiprotolytic system such as the one studied here.

The proposed method for estimating carbonate alkalinity and the apparent dissociation constants of carbonic acid in solutions of unknown ionic composition is limited, of course, to cases in which carbon dioxide is the sole protolytic gas present when the pH is lowered to below pH 4.5. This is not a severe limitation, however, especially in studying biological solutions, as ammonia is completely protonated at low pH. The method can be applied, for example, to urine, for better understanding of the relationships between $(\text{TC})_{\text{CO}_2}$ and p_{CO_2} and to help resolve pending questions concerning the significance of high p_{CO_2} differentials between blood and urine.¹⁸

Acknowledgement—I should like to thank Dr. R. A. Chalmers for his critical review of the manuscript, which helped to sort out some confusing inconsistencies.

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