

## Short Communication

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### THE OPTIMUM COMPOSITION OF pH-SENSITIVE ACCEPTOR SOLUTIONS FOR MEMBRANE SEPARATION IN FLOW INJECTION ANALYSIS

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*Summary.* Gas diffusion membranes are frequently used to transfer volatile protolytes from a donor to an acceptor solution. This transfer is attended by a change in  $[H^+]$  or  $[OH^-]$  and an absorbance change of the acid-base indicator present. Conditions determining the linearity and the sensitivity of the calibration graphs are discussed.

The use of suitable membranes in continuous flow systems introduces the attractive possibility of selective transfer of the compound to be measured from a mostly ill-defined sample stream into a carrier stream of well-defined composition. This feature was first introduced into flow injection analysis (f.i.a.) for the determination of carbon dioxide in serum [1]. A similar approach was suggested for the determination of ammonia [2]. In both cases the compound which actually passes the membrane causes a protolytic reaction in the acceptor solution. The pH change thus obtained can be indicated photometrically if a suitable acid-base indicator is present in the solution.

With regard to selection of the optimum composition of such acceptor solutions, no general directives are available in the literature. In this contribution, such directives are developed starting from the principle that important criteria are the stability of the base-line, the sensitivity (i.e., slope of the calibration graph), and the linear range of the calibration graph. To meet the first criterion, it seems desirable to maintain a well-defined and stable pH value in the carrier stream when no sample is injected; this is achieved by using a buffer solution. It will be demonstrated that the last two criteria lead to mutually exclusive conditions for the buffer concentration. Larger buffer concentrations lead to larger linear ranges but to less sensitive response, whereas lower buffer concentrations provide higher sensitivity but narrower linear ranges.

In the case of membrane separation, the generation of a signal corresponding to the injection of a sample requires three steps: the transfer of the relevant species across the membrane, the influence of this compound on the pH of the acceptor solution by protolytic reactions, and an absorbance

change caused by this pH change. Although a combination of non-linear relations may result in a linear calibration graph in some particular case, it will be assumed in the following discussion that each consecutive step has a linear response: i.e., the (maximum) concentration in the acceptor stream of the compound to be detected is linearly dependent on the concentration injected in the donor stream; the concentration change in  $H^+$  or  $OH^-$  is linearly dependent on the concentration of the compound transferred across the membrane; and the absorbance measured photometrically is linearly dependent on  $[H^+]$  or  $[OH^-]$  in the solution.

The transfer process has been discussed [3]; it was shown that, in general, a linear dependence can be expected for this step. Hence, only the last two steps need closer consideration.

### Choice of indicator

For an acid-base indicator, I, with a protonation (stability) constant  $\beta_I$  and present in an analytical concentration  $C_I$ , the mass balance equation yields

$$[I] = C_I \{1 + \beta_I [H^+]\}^{-1}; \quad [HI] = \beta_I [H^+] C_I \{1 + \beta_I [H^+]\}^{-1} \quad (1)$$

(with charges omitted).

Thus, the absorbance can be expressed as

$$A = \epsilon_I b C_I \{1 + \beta_I [H^+]\}^{-1} + \epsilon_{HI} b \beta_I [H^+] C_I \{1 + \beta_I [H^+]\}^{-1} \quad (2)$$

Two extreme cases will be considered.

(i)  $\beta_I [H^+] \gg 1$  or  $\beta_I^{-1} K_w^{-1} [OH^-] \ll 1$ . This condition means that the indicator is predominantly present in the acidic form HI or  $HI^+$ . Equation 2 leads then to

$$A = \epsilon_I b C_I \beta_I^{-1} [H^+]^{-1} + \epsilon_{HI} b C_I \{1 - \beta_I^{-1} [H^+]^{-1}\} \quad (3)$$

which simplifies for  $\epsilon_I \rightarrow 0$  or  $\epsilon_{HI} \rightarrow 0$ , respectively to

$$\epsilon_I \rightarrow 0: \quad A = \epsilon_{HI} b C_I - \epsilon_{HI} b C_I \beta_I^{-1} K_w^{-1} [OH^-] \quad (3a)$$

$$\epsilon_{HI} \rightarrow 0: \quad A = \epsilon_I b C_I \beta_I^{-1} [H^+]^{-1} = \epsilon_I b C_I \beta_I^{-1} K_w^{-1} [OH^-] \quad (3b)$$

Clearly, the condition which leads to Eqns. 3a and 3b must be fulfilled to obtain an absorbance that changes linearly with  $[OH^-]$ . If such behaviour is required in, for example, the range  $8.0 < \text{pH} < 9.0$ , an indicator selected must have  $\log \beta_I > 9.0$ . However, an indicator with a much larger stability constant than is strictly necessary should be avoided because of the decrease in sensitivity that will occur.

(ii)  $\beta_I [H^+] \ll 1$ . In this case the indicator is predominantly present in the alkaline form I or  $I^-$ . Equation 2 then leads to

$$A = \epsilon_I b C_I \{1 - \beta_I [H^+]\} + \epsilon_{HI} b C_I \beta_I [H^+] \quad (4)$$

or

$$\text{for } \epsilon_I \rightarrow 0: \quad A = \epsilon_{HI} b C_I \beta_I [H^+] \quad (4a)$$

$$\text{for } \epsilon_{\text{HI}} \rightarrow 0: \quad A = \epsilon_1 b C_I - \epsilon_1 b C_I \beta_I [\text{H}^+] \quad (4b)$$

This condition leads to a linear dependence of the absorbance on  $[\text{H}^+]$  and should, therefore, be used for  $\text{H}^+$ -generating compounds like carbon dioxide and acetic acid.

From the photometric point of view, it is preferable to have situations leading to Eqn. 3b or Eqn. 4a because in these cases the signal corresponds to an increase in the absorbance starting from a relatively low absorbance level, whereas for the situations found in Eqns. 3a and 4b a decrease in absorbance from a relatively high background is observed.

### *Choice of buffer system*

When the compound that passes the membrane is absorbed in an acceptor solution containing several different protolytes, rather complicated expressions are obtained between its concentration and  $[\text{H}^+]$  or  $[\text{OH}^-]$ . A simpler case, first discussed here, occurs when the buffer solution consists of the same protolyte as the one that passes the membrane.

The buffer solution contains  $C_a$  M of the weak acid HA and  $C_b$  M of the base  $\text{A}^-$  (e.g. NaA). If the stability constant of this protolyte is denoted by  $\beta_A$  then

$$[\text{A}^-] = (C_a + C_b) \{1 + \beta_A [\text{H}^+]\}^{-1} \quad (5)$$

The charge balance leads to  $[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{A}^-]$ , which for the case  $[\text{H}^+] \gg [\text{OH}^-]$  (pH < 6.5) yields

$$[\text{H}^+] + C_b = (C_a + C_b) \{1 + \beta_A [\text{H}^+]\}^{-1} \quad (6)$$

or

$$[\text{H}^+] = \{-(1 + \beta_A C_b) + \{(1 + \beta_A C_b)^2 + 4\beta_A C_a\}^{1/2}\} (2\beta_A)^{-1} \quad (7)$$

This equation leads to

$$d[\text{H}^+]/dC_a = \{(1 + \beta_A C_b)^2 + 4\beta_A C_a\}^{-1/2} \quad (8)$$

From Eqn. 8 it is readily seen that  $[\text{H}^+]$  is linearly dependent on  $C_a$  if  $4\beta_A C_a \ll (1 + \beta_A C_b)^2$ . For a more quantitative condition, Eqn. 8 can better be rewritten as

$$d[\text{H}^+]/dC_a = (1 + \beta_A C_b)^{-1} [1 + 4\beta_A C_a (1 + \beta_A C_b)^{-2}]^{-1/2} \quad (8a)$$

Deviation of linearity is less than 2% as long as  $4\beta_A C_a (1 + \beta_A C_b)^{-2} \leq 0.04$ , or

$$C_a \leq 0.01 (1 + \beta_A C_b)^2 \beta_A^{-1} \quad (9)$$

In this case

$$[\text{H}^+] = C_a (1 + \beta_A C_b)^{-1} \quad (10)$$

The same result can be obtained directly from the charge balance (Eqn. 6), provided that  $\beta_A [\text{H}^+] \ll 1$ . Combination of Eqns. 9 and 10 leads to the constraint  $[\text{H}^+]_{\text{lim}} = 0.01 (1 + \beta_A C_b) \beta_A^{-1}$ , or

$$[H^+]_{lim} = 0.01 \{ \beta_A^{-1} + C_b \} \quad (11)$$

From Eqn. 10, it can be taken that the maximum sensitivity is found for  $\beta_A C_b \ll 1$ . In that case,  $\Delta[H^+] = \Delta C_A$ , i.e., each molecule passing the membrane generates one  $H^+$  ion.

Figure 1 shows a graphical representation of Eqn. 10 as well as the constraint expressed by Eqn. 11 for the case of acetic acid ( $\log \beta_A = 4.7$ ). It can be seen that a larger sensitivity is coupled with a narrower linear range.

For an alkaline buffer consisting of  $C_b$  M of base B and  $C_a$  M of the corresponding acid  $BH^+$  (e.g.,  $BHCl$ ) and assuming  $pH > 7.5$  a similar argument as given above leads to a set of equations comparable to Eqns. 9 and 10

$$C_b \leq 0.01(1 + C_a K_w^{-1} \beta_A^{-1})^2 K_w \beta_A \quad (12)$$

$$[OH^-] = C_b(1 + C_a K_w^{-1} \beta_A^{-1})^{-1} \quad (13)$$

Comparison with the corresponding Eqns. 9 and 10 shows that  $C_a$  and  $C_b$  are mutually changed, while  $\beta_A$  is replaced by  $(K_w \beta_A)^{-1}$ . Thus Fig. 1 also applies for ammonia with a  $\log \beta_A$  value of 9.3 if the coordinates  $C_a$  and  $C_b$  are interchanged and the  $[H^+]$  axis is replaced by  $[OH^-]$ .

If it is not the compound HA that passes the membrane into an acceptor solution containing the buffer  $HA/A^-$ , but another protolyte, HP, the charge balance is given by

$$[H^+] + [Na^+] = [A^-] + [OH^-] + [P^-] \quad (14)$$

or when  $[H^+] \gg [OH^-]$

$$[H^+] + C_b = (C_a + C_b) \{ 1 + \beta_A [H^+] \}^{-1} + \Delta C \{ 1 + \beta_P [H^+] \}^{-1} \quad (15)$$

where  $\Delta C$  is the analytical concentration of the protolyte HP and  $\beta_P$  is its stability constant. Equation 15 is a cubic equation in  $[H^+]$  and so no explicit expression of  $[H^+]$  in dependence on  $\Delta C$  can be found unless some assumptions are made. It will be assumed that again  $\beta_A [H^+] \ll 1$  but also that  $\beta_P [H^+] \ll 1$ . If this latter condition is not fulfilled, hardly any influence of

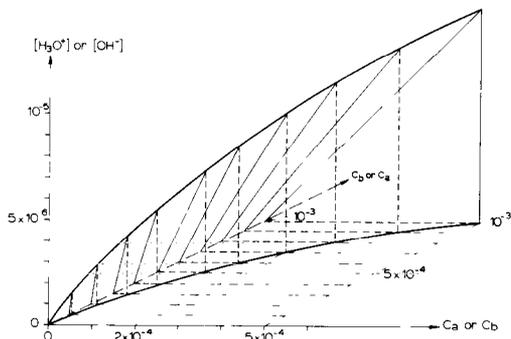


Fig. 1. Dependence of  $[H^+]$  response on  $C_a$  at different values of  $C_b$  calculated for  $\log \beta_A = 4.7$ . The curved line corresponds to the constraint expressed by Eqn. 11. Also the dependence of the  $[OH^-]$  response on  $C_b$  at different values of  $C_a$  for base with  $\log \beta_A = 9.3$ .

the transferred protolyte can be expected. With these assumptions, Eqn. 15 can be simplified to

$$[H^+] + C_b = (C_a + C_b)\{1 - \beta_A[H^+]\} + \Delta C\{1 - \beta_P[H^+]\}$$

or

$$[H^+] = (C_a + \Delta C)\{1 + (C_a + C_b)\beta_A + \Delta C\beta_P\}^{-1} \quad (16)$$

The slope of the calibration graph is then obtained from

$$d[H^+]/d\Delta C = \{1 + (C_a + C_b)\beta_A - C_a\beta_P\}\{1 + (C_a + C_b)\beta_A + \Delta C\beta_P\}^{-2} \quad (17)$$

This slope is independent of  $\Delta C$  if

$$\Delta C\beta_P \ll \{1 + (C_a + C_b)\beta_A\} \quad (18)$$

Generally,  $(C_a + C_b)\beta_A > 1$  as well as  $C_a\beta_P > 1$  holds true so that Eqns. 17 and 18 can be simplified to

$$d[H^+]/d\Delta C = \{(C_a + C_b)\beta_A\}^{-1} - C_a\beta_P\{(C_a + C_b)\beta_A\}^{-2} \quad (19)$$

and  $\Delta C\beta_P \ll (C_a + C_b)\beta_A$ . In most cases  $\Delta C < (C_a + C_b)$ , thus Eqn. 20 implies that  $\beta_P \ll \beta_A$ , i.e., the protolyte HA should not be a stronger protolyte than HP. From Eqn. 20 it can be seen that greater sensitivity is obtained with a lower total buffer concentration. When the buffer concentration is decreased, the buffer action is ultimately taken over by the indicator.

To conclude this general, theoretical treatment, the use of the derived equations will be illustrated. In a previous paper [3], ammonia was determined by using an ammonia/ammonium chloride buffer as the acceptor solution. If the concentration to be determined in the donor stream is in the range  $10^{-2}$ – $10^{-4}$  M, and if under the prevailing circumstances about 10% of the ammonia is transferred across the membrane, then the maximum change in concentration in the acceptor stream is about  $10^{-3}$  M. To have a linear range up to  $C_b \approx 10^{-3}$  M, Eqn. 12 leads to  $C_a \geq 10^{-2.85}$  M when the value  $\log \beta_A = 9.3$  is used for ammonia. By combination of Eqns. 12 and 13, the limiting hydroxide ion concentration is obtained

$$[OH^-]_{lim} = 10^{-2}(10^{-4.7} + 10^{-1.85}) \approx 10^{-3.85}$$

or  $pH_{lim} = 10.15$ . In the earlier paper, a pH of 9.0 was adopted. Hence, for the indicator  $\log \beta_I > 9.0$  which means that phenolphthalein is a reasonable choice.

#### REFERENCES

- 1 H. Baadenhuijsen and H. E. H. Seuren-Jacobs, *Clin. Chem.*, 25 (1979) 443.
- 2 J. Růžička and E. H. Hansen, *Flow Injection Analysis*, Wiley, New York, 1981.
- 3 W. E. van der Linden, *Anal. Chim. Acta*, 151 (1983) 359.