CHROMSYMP. 2061

Measurement of limiting ionic equivalent conductance by single-column ion chromatography

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ABSTRACT

A new approach to the measurement of the limiting ionic equivalent conductance, λ, by single-column ion chromatography is proposed. When the eluent counter ion is replaced with an equivalent concentration of sample ion, a change in conductance, *i.e.*, a detector response, will be observed. By adjusting the pH of the eluent to change its degree of electrolytic dissociation, a pH might be found at which the response of sample ions is restrained. For a given eluent, λ is a function only of pH. The calibration graph of λ *versus* eluent pH to restrain the sample response can be obtained by eluting ions of known λ at different pH values and assessing the eluent pH where no detector response is given. From the calibration graph, λ values of other ions can be measured.

INTRODUCTION

An important aspect of non-analytical applications of chromatography, including gas and liquid chromatography, is in physico-chemical measurements [1,2]. The advantages of chromatography lie in its accuracy, convenience, specificity, versatility, speed and requirement for only small amounts of sample [2]. In this paper, a new approach for measuring limiting ionic equivalent conductance by single-column ion chromatography is proposed.

Ion chromatography (IC) can be subdivided into two types: that which uses a suppressor (dual-column IC) and that which does not (single-column IC) [3,4]. More commonly in single-column IC, the effluent from the ion-exchange column is sent to a conductivity detector, the response of which depends on the conductance of sample ions, counter ions and co-existing ions. Hence it is possible for single-column IC to be used for the measurement of limiting ionic equivalent conductance with some characteristics that the usual method does not possess.

THEORY

When the eluent anion is replaced with an equivalent concentration of a sample

anion in single-column IC, the resulting change in conductance, *i.e.*, the detector response, is given by

$$\Delta G = \frac{(\lambda_{E^+} + \lambda_{S^-})I_S - (\lambda_{E^+} + \lambda_{E^-})I_E I_S}{10^{-3}K} \cdot C_S \tag{1}$$

where ΔG is the detector response, K the cell constant, λ the limiting equivalent conductance of cation or anion, C the normality and I the degree of electrolytic dissociation, and E^+, E^-, E, S^- and S represent the eluent cation, eluent anion, eluent, sample anion, and sample, respectively [5]. A similar equation can be obtained for the cation-exchange process. If it is assumed that $\Delta G = 0$, then

$$(\lambda_{E^+} + \lambda_{S^-}) - (\lambda_{E^+} + \lambda_{E^-})I_E = 0$$

or

$$\lambda_{S^-} = (\lambda_{E^+} + \lambda_{E^-})I_E - \lambda_{E^+} \tag{2}$$

As λ_{E^+} and λ_{E^-} are constant for a given eluent and I_E depends on the ionization constant of the corresponding acid and the eluent pH, λ_{S^-} is a function only of the eluent pH at which the sample peak is restrained. The calibration graph of λ *versus* the eluent pH to restrain the sample peak can be obtained by eluting the ions with known λ at different pH values and assessing the eluent pH where no detector response is given. From the calibration graph, limiting equivalent conductances of other ions could be measured.

EXPERIMENTAL

Reagents and instrumentation
        The chemicals used were obtained from a variety of suppliers. Doubly distilled water was used for the preparations of aqueous solutions.
        Chromatographic experiments were performed on a Model HLC-601 ion chromatograph (Toyo Soda, Japan) equipped with a conductivity detector. The injection valve had a 100-μl loop. A TSK 3066 flat-bed pen recorder was connected to the 1-V output of the detector.

Chromatographic system
        An IC-Anion-SW anion-exchange column (Toyo Soda) was used. The mobile phase was 1 or 2 mM oxalic acid solution adjusted to the desired pH with 5% sodium hydroxide solution. All measurements were carried out at 25°C.

RESULTS AND DISCUSSION

Selection of counter ion
        The requirements which must be met by the counter ion in IC for the measurement of the limiting ionic equivalent conductance are the following. First, when an anion-exchange process is considered, the degree of electrolytic dissociation

of the acid corresponding to the counter ion should vary with a certain variable, such as the pH of the mobile phase, in order to establish the conditions satisfying eqn. 2 for different sample ions through changing the variable. Hence, it is necessary to select a weak acid as the electrolyte of the mobile phase. The dissociation constant, K_a, of the acid should be small enough to give a reasonable pH range in which I_E can be adjusted to meet $G = 0$, but not too small to achieve complete dissociation even in alkaline medium. Second, the limiting ionic equivalent conductance of the counter ion should be as large as possible. The measurement should be carried out only for sample ions with values of λ lower than that of the counter ion, otherwise, the contribution of sample ions to conductance can never be compensated for completely by that of the counter ions.

In this work, oxalic acid, which is a dibasic acid with $pK_1 = 1.27$ and $pK_2 = 4.27$, was selected. The fractions of oxalic acid present in solution in various forms are a function of pH. Oxalic acid in the form $H_2C_2O_4$ is gradually converted into $HC_2O_4^-$ and finally $C_2O_4^{2-}$ as the pH increases from 0 to about 6. The limiting ionic equivalent conductance of $C_2O_4^{2-}$, 74.2 S cm^2 equiv.$^{-1}$ (25°C), is larger than those of most inorganic anion and many organic anions. On the other hand, the reducing property of oxalic acid limits its application to the measurement of oxidizing anions.

Restraint of conductance

Using 1 mM oxalic acid at different pH values as the mobile phase, samples containing SCN$^-$ were injected and the variation of peak height with pH was observed; the results are shown in Figs. 1 and 2. At low pH, the ionization of oxalic acid is restrained and the contribution of SCN$^-$ to the conductance is larger than that of the replaced oxalate anion, so that a positive peak will be obtained. At high pH, because oxalic acid is ionized almost completely and the SCN$^-$ anion has a smaller equivalent conductance than the oxalate anion, a negative peak is obtained. There will be a pH between the two extreme situations where the ion-exchange process is not accompanied by the corresponding conductance response. The key step in the measurement of limiting ionic equivalent conductance by IC is to seek the pH that restrains the conductance. Sometimes the peak of the sample ion does not disappear completely, but has the shape of a sine curve near the pH where conductance is restrained. If so, fitting can be used to obtain the pH at which $\Delta G = 0$.

The degree of electrolytic dissociation of a given weak acid depends on the hydrogen ion concentration, not on its analytical concentration, when the effect of activity coefficient is ignored. Therefore, the pH at which $\Delta G = 0$ is not influenced significantly by the oxalic acid concentration. For example, with 1 and 2 mM oxalic acid solutions as mobile phases, the pH values evaluated by the approach described previously are 4.63 and 4.42, respectively. The slight difference between the two might result from ignoring the effect of activity coefficient.

Effect of sample ion concentration on measurement

The sample ion concentration is not involved in eqn. 2 and so does not influence the measurement of the pH at which $G = 0$. However, the detector response, ΔG, is proportional to the concentration of sample ion, C_S, when $\Delta G \neq 0$. The plots of peak height *versus* pH of the mobile phase for samples with different concentrations are shown in Fig. 2 and indicate that the restraining points coincide with each other, although the peak height increases with increasing sample ion concentration.
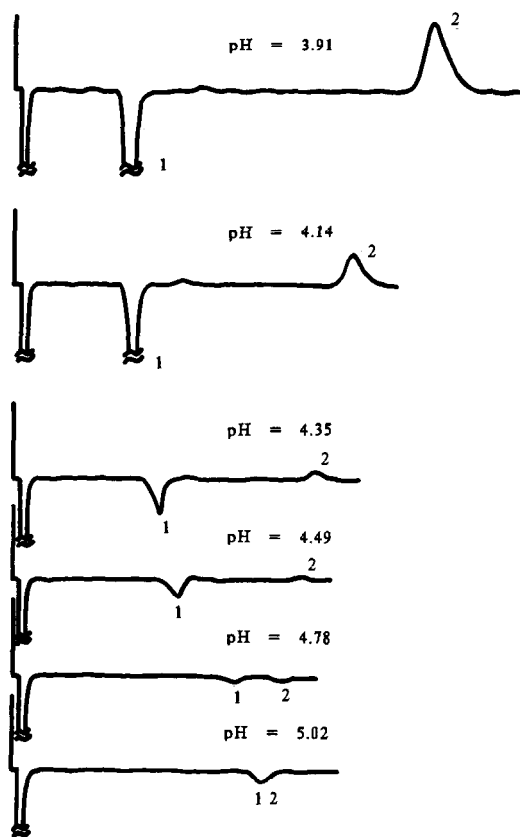
Fig. 1. Chromatograms of 40 ppm of SCN⁻ at different pH values. 1 = System peak; 2 = SCN⁻.
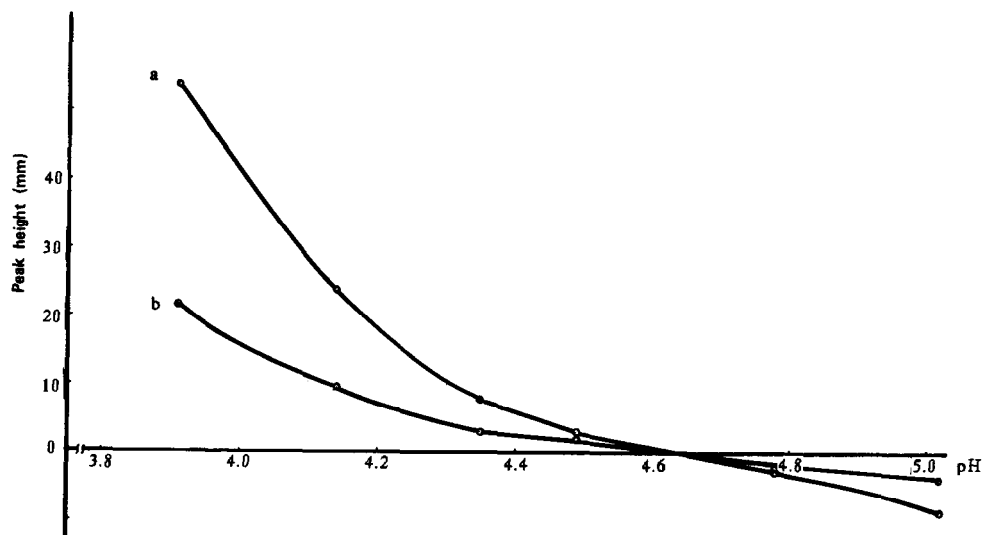
Fig. 2. Peak height *versus* pH. Concentration of SCN⁻ in sample: (a) 100 ppm; (b) 40 ppm.

TABLE I

LIMITING IONIC EQUIVALENT CONDUCTANCES AND pH VALUES AT WHICH $\Delta G = 0$ FOR DIFFERENT ANIONS

Anion	λ_{S^-} at 25°C (S cm^2 equiv.$^{-1}$)^a	pH ($\Delta G = 0$)
CH_3COO^-	40.9	3.86
$HCOO^-$	54.6	4.05
ClO_3^-	64.6	4.24
SCN^-	66.0	4.42
ClO_4^-	67.9	4.65
$C_2O_4^{2-}$	74.2	

^{a} Data taken from ref. 6.

Effect of co-existing ions

The common practice in measuring limiting ionic equivalent conductance is to subtract the limiting equivalent conductance of co-existing ions from that of the electrolyte. In IC, the sample ion is carried along the column, independently of the others, toward the outlet. Hence the measurement by the proposed method is characterized as "absolute".

Strength of acids corresponding to sample ions

As in the discussion of the effect of sample ion concentration, the strength of the acids corresponding to sample anions influences the detector response, as I_S is involved in eqn. 1. However, I_S does not appear in eqn. 2 when $\Delta G = 0$, so the proposed method is suitable for the measurement of both strong and weak acid anions. This differs from the common practice of measuring limiting equivalent conductance.

Calibration graph

The pH values when $\Delta G = 0$ and the limiting ionic equivalent conductances for some anions are listed in Table I. The existence of a correlation between them indicates
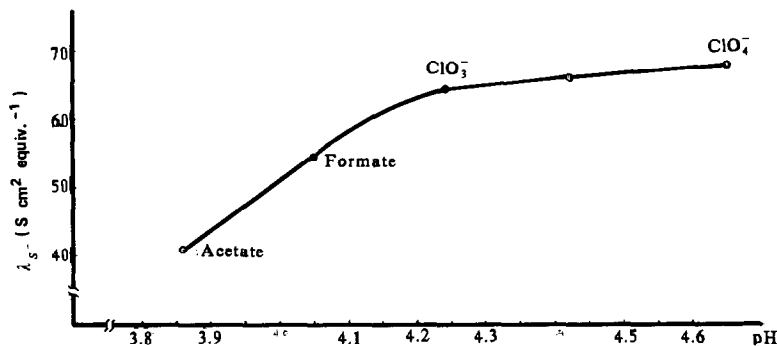
Fig. 3. Calibration graph of λ_{S^-} versus the pH value to restrain the detector response.

that measurement by IC is feasible. A calibration graph of λ_S- *versus* pH is given in Fig. 3 from the data in Table I. The shape of the plot depends on the nature of the counter ion. With oxalic acid, a 2-mM solution has a pH of 2.75 and the degree of electrolytic dissociation changes with pH up to about pH 6. The slope of the graph decreases with increasing pH.

CONCLUSION

The principle of measuring limiting ionic equivalent conductance by IC has been introduced. In addition to oxalic acid, other counter ions might be selected for setting up systems for the measurement of anions. Based on the same principle, a system for cationic measurement might be established. For instance, ethylenediamine as the counter ion for cation exchange might be used for this purpose. The proposed method has the advantages that it is suitable for both strong and weak electrolytes, co-existing ions are not involved in the measurement and the concentration of the sample ions does not influence the measurement.

ACKNOWLEDGEMENT

REFERENCES

1 M. A. Kaiser, in R. L. Grob (Editor), *Modern Practice of Gas Chromatography*, Wiley, New York, 1977, Ch. 11, p. 553.
2 Cs. Horváth, in C. F. Simpson (Editor), *Techniques in Liquid Chromatography*, Wiley, New York, 1982, Ch. 10, p. 229.
3 J. S. Fritz, D. T. Gjerde and C. Pohlandt, *Ion Chromatography*, Hüthig, New York, 1982, p. 84.
4 D. T. Gjerde, J. S. Fritz and G. Schmuchler, *J. Chromatogr.*, 186 (1979) 509.
5 D. T. Gjerde and J. S. Fritz, *Anal. Chem.*, 53 (1981) 2324.
6 J. A. Dean (Editor), *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 11th ed., 1973.