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Potentiometric detection of carboxylic acids and inorganic anions in ion-exclusion chromatography using camphorsulphonic acid as eluent

Bronisław K. Głód☆, Paul R. Haddad* and Peter W. Alexander

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington N.S.W. 2033 (Australia)

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ABSTRACT

The use of potentiometric detection in ion-exclusion chromatography of carboxylic acids (oxalic, citric, tartaric, malic, lactic, succinic and acetic acid) is reported. A comparison of the performance characteristics of potentiometric detection with those obtained by UV absorbance is given. A treatment of the electrode response characteristics, based on ionic equilibria in the bulk solution, is presented in order to determine the mechanism of response at the indicator electrode. The results show that the response is Nernstian and arises as a result of the effect of solute species on the concentration of Cu(II) generated at the electrode surface. Experimental data for inorganic anions and aliphatic acids show close agreement with the theoretical response. The selectivity of the potentiometric detector is illustrated by reference to the analysis of white wine.

INTRODUCTION

Potentiometry has frequently been applied to selective detection in flow-injection analysis through the use of membrane electrodes. More recent investigations [1–3] have shown that metallic wire electrodes can also be successfully utilized as the indicator electrode for potentiometric detection in liquid chromatography. Metallic copper indicator electrodes have been particularly successful in this regard and can give sensitive and quite universal potentiometric response even when copper ions are not present in the mobile phase.

In previous papers we have utilized the metallic copper wire electrode as a potentiometric detector in various chromatographic systems and for the analysis of many different classes of compounds [1–3], including carboxylic acids. These reports have shown that detection of carboxylic acids is possible after separation using anion-exchange and ion-exclusion columns. The mobile phase components used in these studies (phthalate, phosphate or citrate buffers) are characterised by relatively high complexation with the copper ions. In some cases (*e.g.* ref. 1) this leads to the observation of indirect detection wherein the sensing electrode monitors the decrease in the concentration of the mobile phase buffer which accompanies the elution of a solute. Detection limits using phosphoric acid mobile phases were in the range 0.2 nmol (for oxalic acid by ion-exchange chromatography [1]) to 200 nmol (for acetic acid by ion-exclusion chromatography [3]).

The present study shows the advantages of separation and potentiometric detection of carboxylic acids in ion-exclusion chromatography using camphorsulphonic acid as the mobile phase buffer. Direct potentiometric response to some inorganic anions (*e.g.* chloride and phosphate) is also noted. A theoretical treatment of the electrode response characteristics based on ionic equilibria in the bulk solution is presented in order to determine the mechanism of response at the indicator electrode.

☆ Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

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The results show that the response is Nernstian and arises due to the effect of eluted solutes on the Cu(II) concentration generated spontaneously at the electrode surface.

THEORY

The potential of a metallic copper electrode is based on the Cu^{2+}/Cu^0 redox couple existing at the electrode surface. When such an electrode is equilibrated with a mobile phase containing a copper-complexing ligand, or when a copper-complexing solute contacts the electrode, the potential is dependent on the mass transport of the ligand or solute to the electrode surface and hence on flow-rate. However, the theoretical electrode response can be derived more easily in terms of the Nernst equation with the assumption that the electrode potential is determined by the bulk concentrations of complexing species and that mass transport effects need not be considered. Therefore, in the following theoretical treatment the approximation is made that at a constant flow-rate the electrode potential is dependent on Nernstian response to the bulk ligand concentrations. We begin by assuming 1:1 stoichiometry for the copper–ligand complex and by neglecting complexation of Cu^+ (carboxylic acids show weak complexation of Cu^+ in comparison to Cu^{2+}). Moreover, the detector cell design eliminates reactions with the silver/silver chloride reference electrode.

In the presence of a complexing agent, B^{n-}, in a buffered mobile phase and in a neutral medium, the potential of the metallic copper electrode may be described by the Nernst equation:

$$E_1 = E^0_{Cu^{2+}/Cu^0} + \frac{RT}{2F}\ln[Cu^{2+}]_B \quad (1)$$

where R is the universal gas constant, T is the temperature and F is the Faraday constant. The subscript B denotes that the indicated concentration exists in the presence of the mobile phase buffer. When a copper-complexing solute ligand, L^{m-}, passes the electrode, the electrode potential will alter, producing a peak. The potential at the peak maximum is given by:

$$E_2 = E^0_{Cu^{2+}/Cu^0} + \frac{RT}{2F}\ln[Cu^{2+}]_L \quad (2)$$

where the subscript L denotes that the indicated concentration exists in the presence of both the solute ligand and the buffer (that is, during elution of the ligand). The complexation reaction between B^{n-} and Cu^{2+}, and the associated formation constant, are given below:

$$Cu^{2+} + B^{n-} \leftrightharpoons CuB^{(2-n)+} \quad (3)$$

$$K_B = \frac{[CuB^{(2-n)+}]_B}{[Cu^{2+}]_B[B^{n-}]_B} \quad (4)$$

At the peak maximum, the following equilibrium exists:

$$Cu^{2+} + L^{m-} \leftrightharpoons CuL^{(2-m)+} \quad (5)$$

and the following two constants must be considered:

$$K_B = \frac{[CuB^{(2-n)+}]_L}{[Cu^{2+}]_L[B^{n-}]_L} \quad (6)$$

$$K_L = \frac{[CuL^{(2-m)+}]_L}{[Cu^{2+}]_L[L^{m-}]_L} \quad (7)$$

The mass balance equation for copper ions at the electrode surface can be written as:

$$[Cu^{2+}]_B + [CuB^{(2-n)+}]_B = [Cu^{2+}]_L + [CuB^{(2-n)+}]_L + [CuL^{(2-m)+}]_L \quad (8)$$

By writing mass balance equations for B and L and combining these with eqns. 1, 2, 4 and 6–8, we can obtain the following expression for the change in electrode potential (ΔE) occurring at the peak maximum:

$$\Delta E = E_2 - E_1 = \frac{RT}{2F}\ln\left[\frac{1 + K_B c_B}{1 + K_B c_B + K_L c_L}\right] \quad (9)$$

where c_B and c_L are the total (analytical) concentrations of B and L (both free and complexed), respectively. Eqn. 9 may be rewritten as:

$$\Delta E = -29\log\left[1 + \left(\frac{K_L c_L}{1 + K_B c_B}\right)\right] \quad (10)$$

Taking into account dilution effects occurring on the chromatographic column, eqn. 10 becomes:

$$\Delta E = -29\log\left[1 + \left(\frac{c_i V_i K_L N^{0.5}}{(2\pi)^{0.5} V_R (1 + K_B c_B)}\right)\right] \quad (11)$$

where c_i and V_i are the injected concentration and volume of solute, V_R is the retention volume and N is the number of theoretical plates for the column. Eqn. 11 shows that the peak height is inversely proportional to the buffer concentration and to its copper complexation constant. This indicates that a low detection limit can be expected for low buffer concentrations. On the other hand, use of dilute buffers is likely to cause some experimental difficulties, such as elevated noise level during potential measurement on a high resistance cell and unstable pH. For practical analyses, the optimum chromatographic conditions are therefore likely to sacrifice some sensitivity in return for stable chromatography.

EXPERIMENTAL

Instrumentation and reagents

A Waters (Milford, MA, USA) Model 510 HPLC pump, Model U6K universal injector and a Model 484 tunable absorbance detector (operated at a wavelength of 210 nm) were used. The electrochemical cell used for potentiometric detection has been described previously [4] and consisted of a metallic copper indicator electrode and a Ag/AgCl reference electrode housed in a Perspex flow-through cell. The reference electrode was prepared using the electrolytic method described elsewhere [5]. The potential difference between the electrodes was monitored with an Activon (Sydney, Australia) Model 101 pH/millivolt meter. Separations were performed on a Bio-Rad (Richmond, VA, USA) Aminex ion-exclusion HPX-87H organic acid analysis column (300 × 7.8 mm I.D., hydrogen form 8% cross-linked cation exchanger, 9 μm particle diameter). Chromatograms were recorded on an ABB Goerz Metrawatt (Vienna, Austria) SE 120 recorder. The flow-rate used in all experiments was 1 ml/min.

All reagents were of analytical reagent grade and were used without further purification. Camphorsulphonic acid was obtained from Sigma (St. Louis, MO, USA). The mobile phase was prepared from triply distilled water passed through a Millipore (Bedford, MA, USA) Milli-Q water purification system and was filtered through a Millipore 0.45-μm membrane filter and degassed in an ultrasonic bath prior to use.

Procedures

Chromatograms were recorded using 1 m*M* camphorsulphonic acid as mobile phase. The column was equilibrated for at least 30 min prior to use and was operated at ambient temperature. Stock solutions of solute acids were prepared as 10 m*M* solutions in Milli-Q water and diluted to the required concentrations before use. Solute solutions (20 μl) were injected into the chromatographic system with a 100-μl syringe (Hamilton, Reno, NV, USA) and the potentiometric and UV signals were

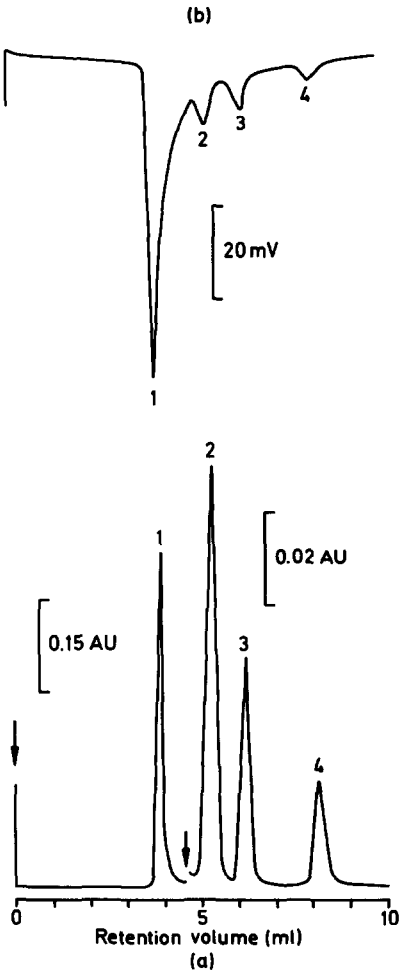

Fig. 1. Ion-exclusion chromatograms obtained with (a) UV and (b) potentiometric detectors. Sample: 10^{-7} mol of: 1 = oxalic, 2 = tartaric, 3 = malic and 4 = succinic cids. Column: Bio-Rad Aminex HPX 87-H 300 × 7.8 mm I.D. Mobile phase: 1 m*M* camphorsulphonic acid.

monitored continuously on the chart recorder. The wine sample was filtered and injected without further treatment.

RESULTS AND DISCUSSION

Conditions of ion-exclusion separation

This study aimed to identify the optimal chromatographic conditions from the potentiometric detection viewpoint as well as that of the chromatographic separation itself. From eqn. 11, maximum sensitivity is expected when a low concentration of a weakly copper-complexing buffer is used. Such dilute buffers are suited to ion-exclusion chromatography, in which even pure water can be used as a mobile phase [6,7]. However, it is conventional to use a dilute acid (*e.g.* 0.1–1 m*M*) as eluent in order to ensure that the peak shape is symmetrical and that the retention time is independent of solute concentration. In our experiments, phosphoric acid, phthalic acid, benzoic acid, naphthalenesulphonic acid and camphorsulphonic acid were employed as eluent buffers. Best results were obtained with camphorsulphonic acid, which is characterised by very weak complexation of copper ions and by a high dissociation constant, thereby giving a solution of high conductance. Ion-exclusion chromatograms obtained using 1 m*M* camphorsulphonic acid with potentiometric and UV detection are shown in Figs. 1 and 2 for a range of carboxylic acids (citric, tartaric, acetic, malic, lactic, oxalic and succinic) and inorganic anions (chloride and phosphate).

Detection limits

Detection limits obtained with the potentiometric detector are presented in Table I, together with those for UV detection. It is interesting to note that for oxalic acid and chloride, a better detection limit was obtained using the potentiometric detector than was achievable by UV detection. Furthermore, the potentiomeric detection limit for oxalic acid was 10 times lower than that reported previously [1–3] when alternative eluents were employed. For other species, the UV detector was the more sensitive.

Calibration plots

Calibration curves for the potentiometric detector are presented in Fig. 3. The largest potentiometric response is observed for oxalic acid and occurs

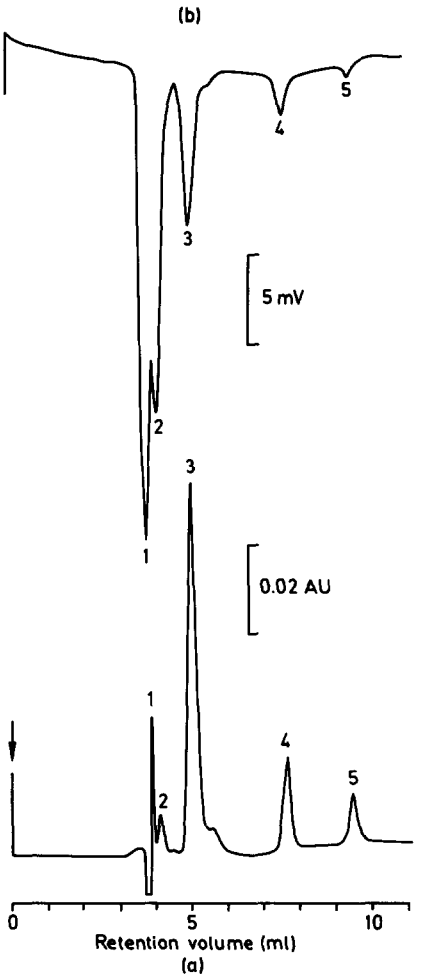

Fig. 2. Ion-exclusion chromatograms obtained with (a) UV and (b) potentiometric detectors. Sample: 10^{-7} mol of: 1 = chloride, 2 = phosphate, 3 = citric acid, 4 = lactic acid and 5 = acetic acid. Other conditions as for Fig. 1.

because the stereochemistry of this species is favourable for copper complexation. Calibration plots are non-linear over the concentration range studied, in comparison to the UV calibration plots (not shown) which exhibited linearity over a small range of low concentrations.

Eqn. 11 can be rearranged to permit calculation of K_L, the complexation constant between the solute and Cu(II). Values of K_L (expressed as the average obtained for a series of solute injections up to $5 \cdot 10^{-8}$ mol) are presented in Table I. A clear inverse correlation exists between the detection limit and the

TABLE I

RETENTION VOLUMES (V_R), DETECTION LIMITS FOR UV (D_L^{UV}) AND POTENTIOMETRIC DETECTORS (D_L^{Pot}), AND COMPLEXATION CONSTANTS (K_L) CALCULATED FROM EQN. 11.

Solute (acid)	V_R (ml)	D_L^{UV} (nmol)	D_L^{Pot} (nmol)	K_L
Oxalic acid	3.85	0.05	0.02	$1.2 \cdot 10^5$
KCl	3.90	0.50	0.2	$9.3 \cdot 10^3$
Na_3PO_4	4.05	0.17	20	$1.7 \cdot 10^2$
Citric acid	4.95	0.03	0.2	$1.6 \cdot 10^4$
Tartaric acid	5.50	0.03	0.3	$1.5 \cdot 10^4$
Malic acid	6.05	0.06	0.4	$1.4 \cdot 10^4$
Lactic acid	7.70	0.09	10	$3.9 \cdot 10^2$
Succinic acid	8.15	0.14	10	$3.4 \cdot 10^2$
Acetic acid	9.45	0.27	50	$7.6 \cdot 10^1$

magnitude of the complexation constant. Fig. 4 shows the theoretical calibration curves for the potentiomeric detector, calculated from eqn. 11 using the complexation constants presented in Table I. Experimental calibration data are also shown and it can be seen that good agreement between theoretical and experimental data exists. Whilst it is recognised that the complexation constants used for this calculation are not from independent measurements, it is noteworthy that it was possible to correctly predict the shapes of the calibration curves.

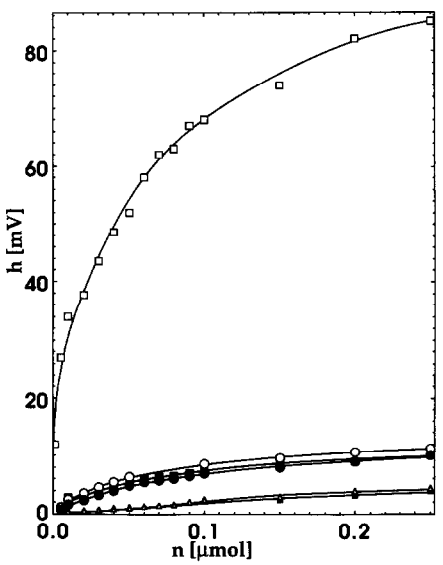

Fig. 3. Calibration curves obtained for potentiometric detection. Solutes: □ = oxalic acid; ○ = tartaric acid; ■ = malic acid; ● = succinic acid; △ = citric acid; ▲ = lactic acid. Other conditions as in Fig. 1. h = Peak height, n = amount of injected sample.

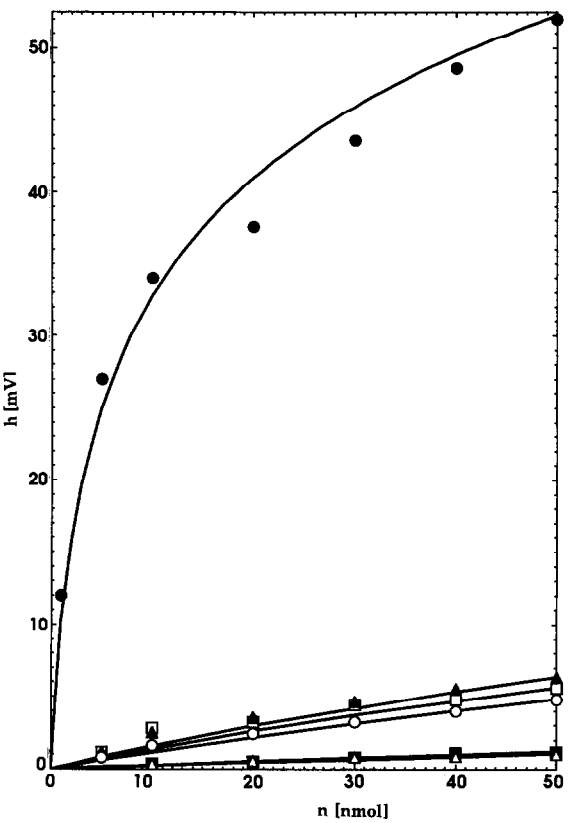

Fig. 4. Theoretical (solid lines) calibration curves for potentiometric detection, calculated from eqn. 11. Experimental values (taken from Fig. 3) are shown as points. Solutes: ● = oxalic acid; ▲ = tartaric acid; □ = malic acid; ○ = succinic acid; ■ = citric acid; △ = lactic acid.

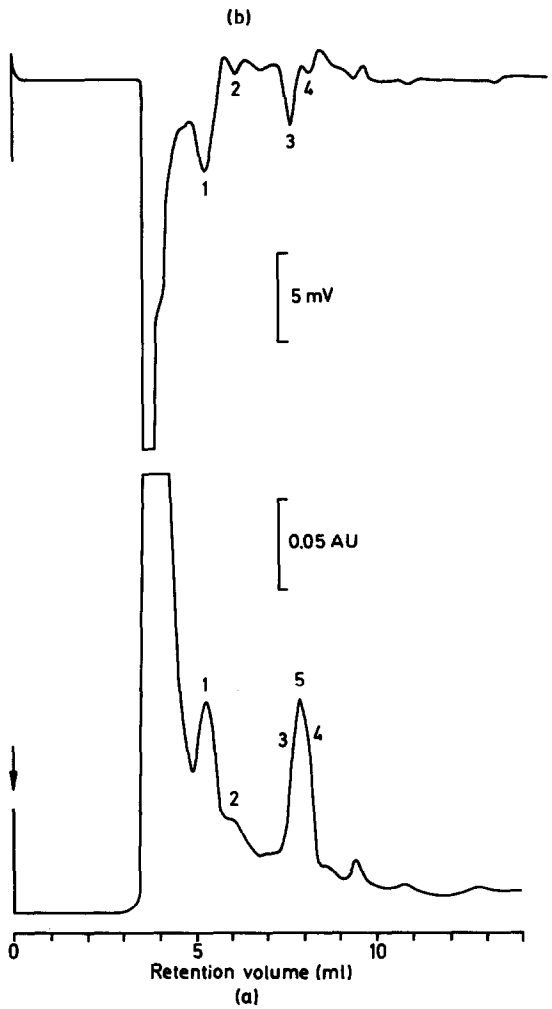

Fig. 5. Ion-exclusion chromatogram of white wine. Injection volume: 10 μl. Peak: 1 = tartaric acid, 2 = malic acid and fructose, 3 = lactic acid, 4 = succinic acid and 5 = unknown. Other conditions as in Fig. 1.

Agreement between theory and experiment decreased when larger amounts of solute were injected, suggesting that the simple theoretical model used is valid only for small solute concentrations.

Selectivity

Potentiometric detectors generally show high selectivity which favours their use in flow-injection analysis rather than as chromatographic detectors. However, the metallic copper electrode shows response to a wide range of solutes including amines, amino acids, oxidants, reductants, *etc.*, as well as to the carboxylic acids and inorganic anions studied here. The selectivity of this detector therefore falls between the extremes of conventional potentiometric devices (high selectivity) and universal (low selectivity) detectors, such as UV. This intermediate selectivity means that the copper electrode detector can be employed for general purpose use, but may also exhibit advantageous selectivity in certain applications.

One example of this is the analysis of wine using the chromatographic conditions described in this paper, as shown in Fig. 5. With UV detection (Fig. 5a), peaks for lactic acid and succinic acid are obscured by an unidentifieed component, and malic acid is co-eluted with fructose. In contrast, the insensitivity of the potentiometric detector to both fructose and the unidentified interferent permits the determination of each of these carboxylic acids (Fig. 5b).

CONCLUSIONS

The results show that improved detection limits for the potentiometric detector can be achieved by correct choice of the mobile phase buffer, giving a sensitivity rivalling the UV detector and detection selectivity which differs from that attainable with UV detection. The theoretical description of detector response enabled us to predict the direction of the response and the shape of the calibration curves.

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