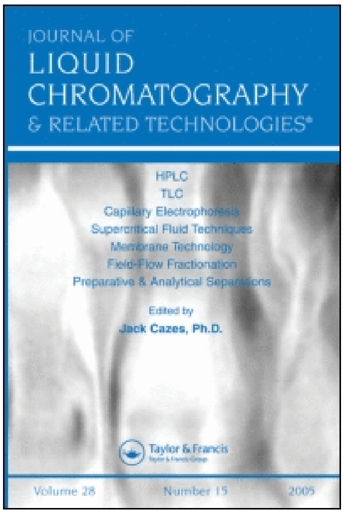

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Ge, Hailin and Wallace, G. G.(1990) 'Electrochemically Controlled Liquid Chromatography on Conducting Polymer Stationary Phases', Journal of Liquid Chromatography & Related Technologies, 13: 16, 3245 — 3260
To link to this Article: DOI: 10.1080/01483919008049099
URL: http://dx.doi.org/10.1080/01483919008049099

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(16), 3245-3260 (1990)

ELECTROCHEMICALLY CONTROLLED LIQUID CHROMATOGRAPHY ON CONDUCTING POLYMER STATIONARY PHASES

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Abstract

Electrochemically controlled high performance liquid chromatography (EC/HPLC) using a conducting polymer stationary phase, has been investigated in the present paper. Polypyrrole coated reticulated vitreous carbon (RVC) particles have been employed as the stationary phase. Chromatographic characterization has been carried out using various molecular probes. The results indicate that chromatographic retention can be altered by the imposition of small electrical potentials on the stationary phase and that such effects can be used to improve the separation of certain compounds.

INTRODUCTION

In attempts to introduce an extra dimension to chromatographic separations, electrochemically controlled high performance liquid chromatography (EC/HPLC) has been investigated by various workers (1-4). The application of an external potential to a chromatographic stationary phase can be used to affect the equilibrium between mobile and stationary phases by:

(i) inducing a reversible electrochemical process which changes the chemical form and physical properties of the analyte e.g. metal deposition

$$M^{n+} + ne^{-} \rightleftharpoons M^{0} \qquad (1)$$

(ii) inducing chemical and/or physical changes in the stationary phase e.g. oxide layer formation

$$Pt \xrightleftharpoons{2[O]} PtO_2 \qquad (2)$$

(iii) inducing changes in the mobile phase e.g. hydroxide formation by reduction of oxygen in the eluent.

$$O_2 + 4e^{-} + 2H^{+} \rightleftharpoons 2OH^{-} \qquad (3)$$

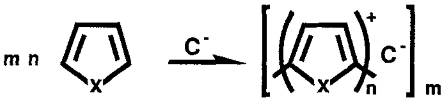
The first mechanism above has been employed predominantly to separate metal ions(1) while the second approach has been used to affect selectivity in the separation of organic species(8); to date mechanism (iii) has not been widely employed.

In order to effect EC controlled separations various stationary phases have been employed. These include silver granules (5), graphite particles (6), mercury-nickel amalgam particles (7) and platinum wire. In more recent work others have attempted to extend the range of materials available for electrochromatography by employing polymer coated particles (8). The availability of materials with suitable electrochemical and physical properties remains the limiting factor in the development and use of EC/HPLC. Given that the materials must be conductive yet have the physical properties of a material such as silica to effect highly efficient chromatography the criteria which must be met are demanding.

In these laboratories (9) and others (10) inherently conducting polymers have been the subject of interesting investigations. These materials are readily synthesized and they display several interesting properties.

In this work particles coated with inherently conductive polymers have been investigated for use as chromatographic stationary phases.

Conducting polymers are readily synthesized according to:



(4)

m= the number of charged polymer complexes

n= the number of monomer units which share one charge

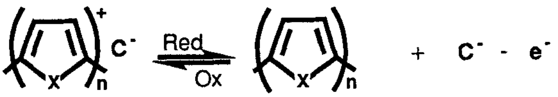
x= N, S or O

C^-= counterion

where the monomer is either electrochemically or chemically polymerized.

This procedure can be used to produce a range of chromatographic stationary phases by appropriate choice of either the monomer and/or the counterion.

Another interesting feature of these materials is the ability to release the counterion under electrochemical control according to:



(5)

This process dramatically affects the chemical and physical properties of the polymer (9,10). It is likely that less dramatic changes occur over smaller potential ranges and it is these changes and their influence on chromatographic properties which is the subject of this work.

Another area addressed in this work is the ability to achieve efficient potential control while maintaining highly efficient chromatography. Potentiostatic control using a three electrode system is not so readily achieved with columns designed for HPLC.

A new column design based on the use of a Waters Radial Compression Module (RCM) has been developed. This new design allows efficient potentiostatic control of the chromatographic stationary phases.

EXPERIMENTAL SECTION

Instrumentation

All HPLC experiments were carried out with a Kortec K350 HPLC Pump (ICI), an ERC-7210 spectrophotometric detector at 254 nm (ERMA Optical Works) and a Rheodyne 7512 Injector with a 20 μl sample loop. A home-made potentiostat was used as the electrochemical controller.

Reagent

HPLC grade acetonitrile and distilled, deionized (Milli Q Water System) water were used in this experiment throughout. Ammonia acetate (AR, Ajax) was used as the electrolyte in the mobile phase as required. Pyrrole (Sigma) was distilled before use and diluted as a monomer solution in a 50% H_2O and 50% CH_3CN solvent with 0.1M NaCl or 0.1M sodium dodecyl sulfate (SDS) . Test samples are described in Table 1.

Table 1 Test samples*

compound	Concentration (ppm)	Interaction
Benzene	170	Basic unit and Hydrophobicity
Toluene	230	Hydrophobicity
Dimethyl-phthalate	10	Polarity
Diethyl-phthalate	10	Polarity
Phenol	30	Proton donor
Benzoic acid	20	Anion exchange
Aniline	40	Electron donor
N,N-Dimethyl aniline	20	Absorption

*All samples were analytical grade, stored in 1% methanol and diluted in mobile phase as required

Eluent: a. 20% CH_3CN and 80% H_2O
b. 0.1M NH_4Ac in 20% CH_3CN and 80% H_2O

Flow rate: 0.5ml/min

Preparation of Packings

Vitreous carbon packings 4~40 μm were obtained from crushing Reticulated Vitreous Carbon (RVC) into particles, sieving and further classifying by means of deposition in a water and ethanol mixture. These packings were soaked in chromic-sulfuric acid overnight and then rinsed with water and acetonitrile in a vacuum filter system. Polypyrrole

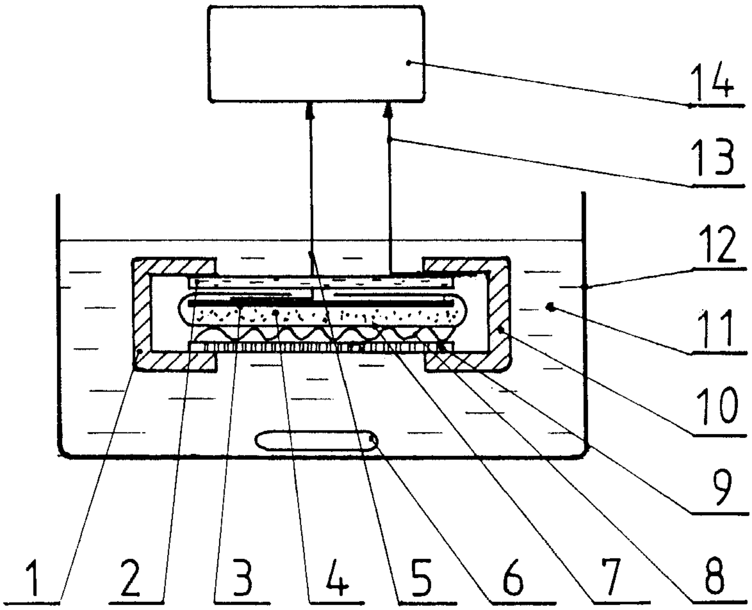


FIGURE 1 Parallel plate cell for electrodeposition of conducting polymers

1. Stainless steel clamp; 2. Glass plate;

3. Tantalum foil; 4. Packings; 5. Tantlum wire;

6. Magnetic stirrer; 7. Filter paper; 8. Porous membrane;

9. Stainless steel sieve; 10. Stainless steel clamp;

11. Monomer solution; 12. Container; 13. Tantalum wire;

and 14. Galvanostat.

chloride (PP/Cl) and polypyrrole dodecyl sulfate (PP/DS) were coated galvanostatically on RVC particles using a parallel plate cell as described in Figure 1.

EC/HPLC Column

A specially designed column which can be employed with the Waters RCM-100 or RCM 8 x 10 radical compression cartridge holders was developed. This was similar to the column used in previous work (11).

EC/HPLC

All samples were injected in triplicate and an average retention time was taken. The dead volume was measured by injecting water and recording the first dip. In EC/HPLC experiments, injections were not made until the baseline became stable after application of a potential.

RESULTS AND DISCUSSION

In previous work in these laboratories RVC particles were coated either by passing a monomer solution through a packed column and applying a potential or by using an electrochemical cell wherein a rotating electrode coated particles in a slurry solution.

In this work an alternative means of particle coating has been developed. A parallel plate cell (Figure 1) has been employed. Using galvanostatic polymer growth much higher current densities can be employed with this cell compared to those described previously, since the larger contact area between particles and the tantalum foil, and the thinner particle layer are given in this cell which reduces the cell resistance significantly. This enables shorter coating times to be employed. Current up to 20 mA was employed.

Chromatography

Both polypyrrole chloride and polypyrrole dodecylsulfate coated particles were employed in these studies. The polymers were coated onto RVC particles. Chromatographic behavior on RVC as well as polymer coated RVC with and without applied potential was investigated. It is well known that at moderately negative potentials counterions may be released from these polymers (12) and at positive potentials irreversible oxidation of the polymer may occur (13). Consequently the potential range considered in this work was restricted to prevent irreversible changes in the polymer coating.

Molecular probes previously used by other workers to characterize stationary phases (14-16) are employed in this work. Test samples chosen gave information about different chromatographic interactions, e.g. hydrophobicity, polarity and ion exchange. The test compounds used are summarized in Table 1. Interaction indices were given by the relative retention of the test samples vs. benzene.

Chromatography on RVC particles

The RVC was crushed and sized before packing into a suitable column as described in the experimental section and then the test compounds were injected. Results obtained using two selected eluents are summarized in Table 2. It was found that, compared with other samples, both toluene and dimethylaniline were strongly retained and that the eluted peaks tailed markedly. Retention was not affected by the addition of salt. Such behavior is indicative of irreversible adsorption.

Application of an external potential to the column had a effect on the hydrophobicity of the RVC particles as is evidenced by the data shown in Figure 2a. Since there are low other interactions, no dramatic influences of potentials on retention are expected. The application of a potential also had a slight effect on the polarity (Figure 2b) and proton donor (Figure 2c) properties respectively. Application of an external potential had little influence on the retention of benzoic acid indicating that the ion exchange properties could be affected only slightly on bare RVC particles. Only a narrow range of potentials was used to investigate the effect of potential on electron donor properties since the test compound aniline was oxidized on the packing when the applied potential was greater than +0.20V and on

Table II - Retention on different columns

SAMPLE	PACKING MATERIAL	MOBILE PHASE			
		20% CH_3CN + 80% H_2O		0.1M NH_4Ac in 20% CH_3CN + 80% H_2O	
		CAPACITY FACTORS			
			k'/k' benzene		k'/k' benzene
Benzene	RVC	0.52	1.00	0.58	1.00
	PP/Cl/RVC	0.75	1.00	0.78	1.00
	PP/DS/RVC	1.39	1.00	1.20	1.00
Toluene	RVC	1.69	3.25	1.69	2.91
	PP/Cl/RVC	1.66	2.21	1.69	2.17
	PP/DS/RVC	2.62	1.88	3.28	2.73
Dimethyl -phthalate	RVC	0.27	0.52	0.57	0.98
	PPCl/RVC	1.03	1.37	1.17	1.50
	PP/DS/RVC	2.36	1.70	2.84	2.37
Phenol	RVC	0.35	0.67	0.40	0.69
	PP/Cl/RVC	0.66	0.88	0.65	0.83
	PP/DS/RVC	0.96	0.69	1.11	0.93
Benzoic Acid	RVC	0.35	0.67	0.17	0.29
	PP/Cl/RVC	∞	∞	0.65	0.83
	PP/DS/RVC	∞	∞	4.04	3.37
Aniline	RVC	0.31	0.60	0.32	0.55
	PP/Cl/RVC	1.06	1.41	0.59	0.76
	PP/DS/RVC	∞	∞	1.02	0.85
N,N- -Dimethyl aniline	RVC	2.24	4.31	3.56	6.14
	PP/Cl/RVC	4.50	6.00	2.69	3.45
	PP/DS/RVC	∞	∞	5.89	4.91

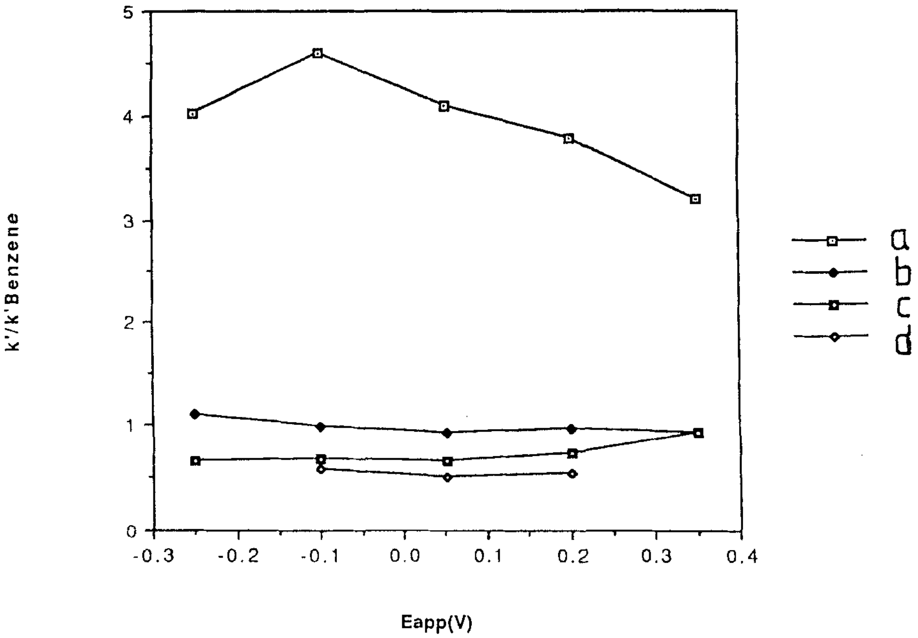


FIGURE 2 Effect of application of potential on chromatographic interactions on RVC packings

a. hydrophobicity index;
b. polarity index;
c. proton donor index;
d. electron donor index.

the counter electrode when Eapp was less than -0.25V. However, even in this limited potential range slight effects were observed on the application of potential (Figure 2d).

Chromatography on polymer coated RVC

RVC particles coated with either PP/Cl or PP/DS were investigated. The capacity factors obtained on these packing for selected test compounds with and without the addition of salt to the eluent, are summarized in Table II.

A comparison of the capacity factor ratios of toluene to benzene which has been used previously (14) as a hydrophobicity index indicates that with no salt present hydrophobicity of the packing increased according to:

PP/DS < PP/Cl < RVC

Low hydrophobicity of PP/DS probably is due to an unwashed, strongly absorbed layer of SDS with a polar end facing to the solution which reduces hydrophobic interaction between the sample and the polymer. Such absorption of SDS was found in many packing materials (17).

In the presence of salt this order was altered to:

PP/Cl < PP/DS < RVC

Increasing of the hydrophobicity of the PP/DS is probably due to removal of the absorbed SDS by the salt solution and exposure of the non polar part of the DS molecule in the polymer.

A comparison of the capacity factor ratio of diethylphthalate and benzene which has been used previously as a polarity index (15) indicated that the stationary phase polarity increased according to:

RVC < PP/DS < PP/Cl

This order did not alter with or without the presence of salt.

The relative retention data of phenol to benzene was low on both RVC and polymer coated phases indicating that proton accepting sites were not available.

However, the high retention values obtained for aniline and N,N-dimethylaniline on polymer coated phases indicated that the stationary phase had high electron acceptor capabilities. Addition of electrolyte decreased the retention of the aniline based compounds presumably due to solvation of the electron accepting sites (18).

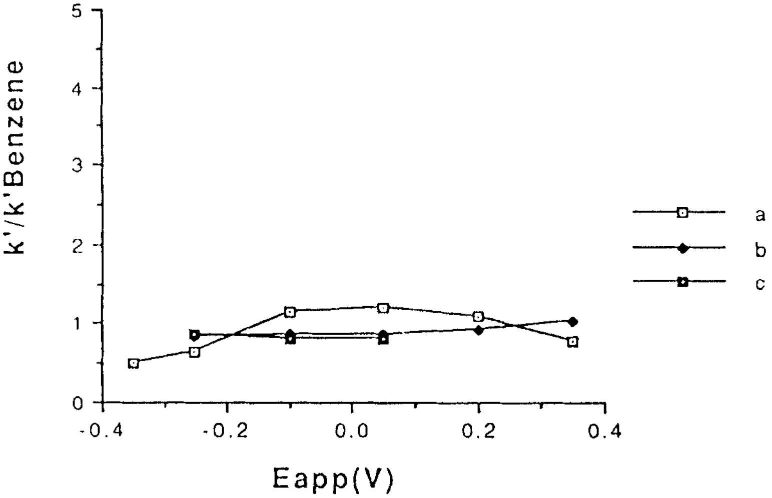


FIGURE 3 Effect of application of potential on chromatographic interactions on the PP/Cl/RVC stationary phase,

a. ion exchange index;
b. proton donor index
c. electron donor index.

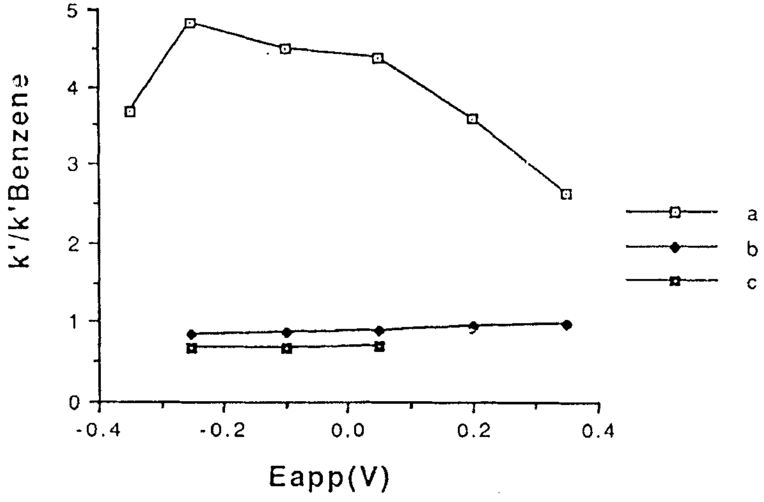


FIGURE 4 Effect of application of potential on chromatographic interactions on conducting polymer stationary phases.

a. ion exchange index;
b. proton donor index;
c. electron donor index on PP/DS

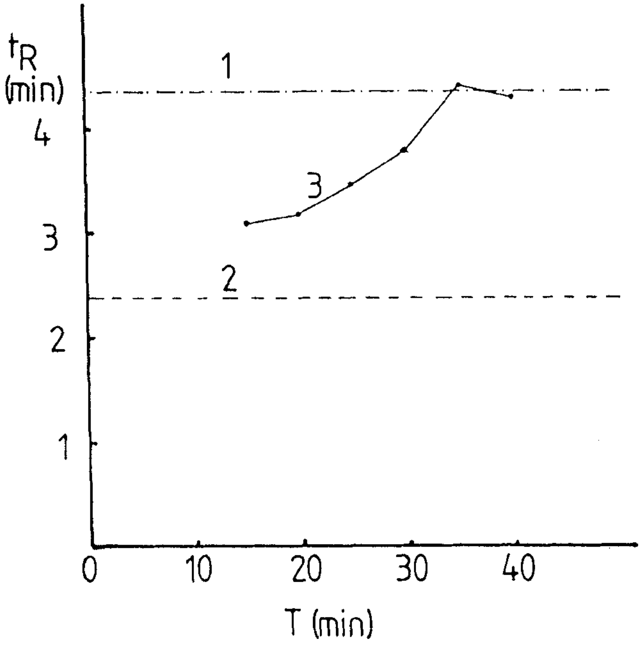


FIGURE 5 Reversibility of application of a potential on a conducting polymer stationary phase.

Column: PP/DS/RVC; Eluent: 50:50/CH_3CN: 0.5M acetate butter pH = 4.5; Sample: 30 ppm benzoic acid; curves due to:

1. retention without a potential
2. retention with Eapp = -0.24V vs Ag/AgCl
3. retention after release of Eapp.

On both polymer coated stationary phases high retention of benzoic acid due to ion exchange interactions was observed. Addition of salt decreased these interactions as would be expected (10).

The application of potential had significant effects on some aspects of the chromatographic behavior of both PP/Cl and PP/DS coated particles.

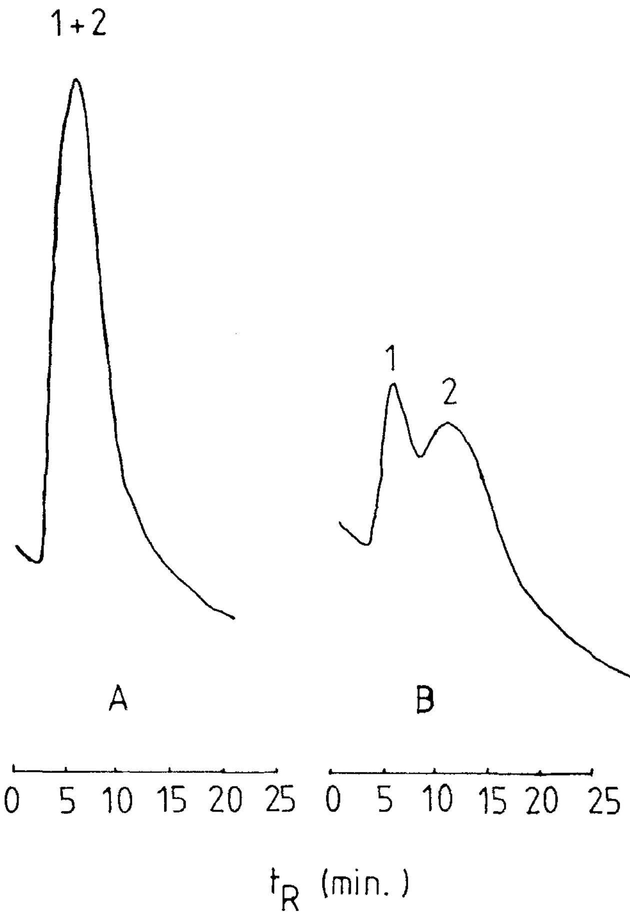


FIGURE 6 The effect of a potential on HPLC separation
Column: PP/DS/RVC; Eluent: 8:92/CH_3CN: 0.02M acetate buffer pH = 4.5; Sample: 1 = 50 ppm theophylline, 2 = 50 ppm caffeine; A = without Eapp; B = Eapp = -0.35V vs Ag/AgCl.

Little variation in the hydrophobicity of these packings with applied potential was observed in the potential range investigated. Since the polymer would not undergo a transition change from the oxidized to reduced form in this potential region as shown by many workers using cyclic voltammetry (10) this was to be expected. The polarity index was slightly decreased by application of more negative potentials on either polymer coated phase. The proton donor capabilities (Figures 3b and 4b) were affected by the application of potentials. In this case it may have been due to the effect of the RVC substrate. The electron donor capabilities were little affected (Figures 3C and 4C).

Ion exchange properties were dramatically affected by applied potential (Figures 3a and 4a). The way in which these properties vary with potential depends on the counterion employed.

Within the potential range investigated the reversibility of electrochemical effects on the stationary phase was investigated. Using benzoic acid retention as a test case it was found that the retention time decreased from level 1 to level 2 due to application of a -0.24V vs. Ag/AgCl potential (Figure 5) and that the retention time went back to original one gradually in 30 minutes after release of the potential. This indicates that the polymer can return to its original state after EC/HPLC.

A Practical Example

The separation of caffeine and theophylline with and without applied potential was considered. Despite the low column efficiency obtained it was found (Figure 5) that the application of an anodic potential can affect a separation using solvent conditions under which that separation is not normally achieved.

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