AD-A188 757 ELECTROSORPTIVE DETECTION OF SIMPLE ORGANIC COMPOUNDS IN LIQUID CHROMATOGRAPHY(U) PURDUE UNIV LAFAYETTE IN DEPT OF CHEMISTRY T RAMSTAD ET AL. 25 SEP 87 1/1

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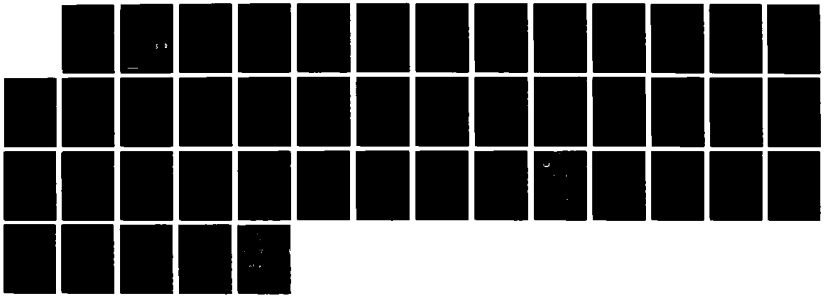

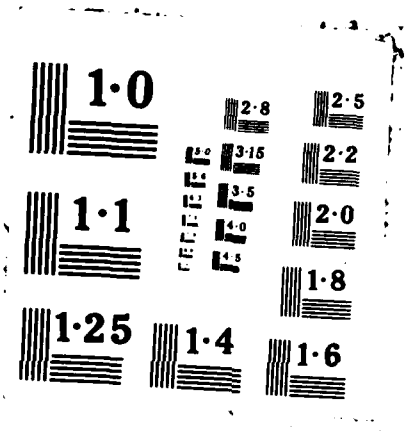
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Contract N00014-86-K-0556

Technical Report No. 73

Electrosorptive Detection of Simple Organic Compounds in Liquid Chromatography

by

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Prepared for Publication

in the

Journal of Chromatography

Purdue University

Department of Chemistry

West Lafayette, Indiana 47907

September 25, 1987

AD-A188 757

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 73	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Purdue University Department of Chemistry 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Division of Sponsored Programs Purdue Research Foundation
6c ADDRESS (City, State, and ZIP Code) Purdue University Department of Chemistry West Lafayette, Indiana 47907	7b ADDRESS (City, State, and ZIP Code) Purdue University West Lafayette, Indiana 47907
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-86-K-0556
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, Virginia 22217	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Electrosorptive Detection of Simple Organic Compounds in Liquid Chromatography

12 PERSONAL AUTHOR(S)
T. Ramstad and M. J. Weaver

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 10/1/86 TO 9/30/87	September 25, 1987	

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
analyte specific adsorption, large-volume wall-jet, Frumkin adsorption isotherm, potential-step coulometric method

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) / 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Electrosorptive Detection of Simple Organic Compounds in Liquid Chromatography

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Summary

The detection of a range of neutral organic compounds in liquid chromatography based on decreases in differential double-layer capacitance, ΔC_d, at a mercury-aqueous interface caused by analyte specific adsorption is described. The arrangement employs ac phase-selective measurements using a large-volume wall-jet configuration. The low-molecular-weight organic solutes examined include aliphatic alcohols, diols, mono- and dicarboxylic acids, amines, and alkanolamines. The differential capacitance measurements were conducted close to the potential of zero charge, where adsorption of such species is most extensive. Plots of ΔC_d versus analyte concentration were generally sigmoidal, in accordance with expectations from the Frumkin adsorption isotherm. A potential-step coulometric method, where variations in the nonfaradaic charge, $\Delta(\Delta q)$, are measured, was found to be a useful alternative detection scheme. Methods based on measuring transient capacitive currents associated with tensammetric adsorption-desorption behavior were also briefly investigated. A virtue of these double-layer capacitance (DLC) detection schemes is that the magnitude of the ΔC_d or $\Delta(\Delta q)$ response exhibits a clear sensitivity to the organic molecular structure, as anticipated in view of the known dependence of the adsorption thermodynamics upon solute hydrophobicity.

INTRODUCTION

Many batch electrochemical procedures based on *electrosorption* (ES), or *specific adsorption* at an electrode, have been published for the determination of surface-active (surfactant) organic compounds. These procedures have been developed almost exclusively for mercury as the electrode material, and fall under the general heading *tensammetry*. Early work in electrosorption analysis is reviewed in an ACS monograph (1) and in Jehring's comprehensive text (2). Most of the early methods were based on ac impedance involving the measurement of decreases in capacitive current induced by specific adsorption. These methods continue to be employed (3-12). Recent work has focussed on overcoming the limitation of such batch methods in distinguishing between components in mixtures. To this end, several recent studies have utilized instead various pulse techniques, taking advantage of the sharp capacitance-potential peaks associated with adsorption-desorption (so-called "tensammetric peaks") that are commonly found for organic adsorbates at the mercury-aqueous interface. These methods include galvanostatic pulses (13) as well as multiple potential-step perturbations analogous to normal (14-16) or differential pulse polarographic techniques (17-21).

Despite the gains made in discrimination through the application of pulse and other techniques, the resolving power for complex mixtures continues to be lacking. An obvious approach to dealing with this shortcoming is to couple electrosorption measurements to a chromatographic effluent. We shall label this general approach as LC-ES (liquid chromatography-electrosorptive detection). Kemula et al. applied an ac method based on changes in double-layer capacitance to LC detection (22,

23). Lankelma and Poppe investigated the use of electrosorptive detection for the determination of several nonionic as well as ionic surfactants in an LC couple (24). They measured the diminution in ac current at a fixed phase angle. DeJong et al. took a similar approach to the determination of a steroid hormone and several cardiac glycosides (25). Kemula and Kutner employed a variation on this technique, presenting the data as a reciprocal capacity (26, 27). The latter authors argued that this approach is better suited for measurements in solutions of low conductivity. Bond and co-workers developed microprocessor-based instrumentation with an assortment of excitation profiles from which to choose - alternating-current, square-wave, differential-pulse, and normal-pulse - for use in LC-ES (28, 29). After comparing these, they recommended the use of the normal pulse format with a complete series of potential steps applied to each mercury drop.

Batch electrosorptive analysis has undergone more study than has LC-ES, but the limitations of the former, particularly with regard to mixtures, are clear. Prior separation, as can be provided by LC, is essential in most practical situations. However, the few LC-ES studies noted above have not demonstrated great promise. A primary reason, in our opinion, has been the lack of suitable chromatography. All separations save one (24) were conducted by reversed-phase chromatography, and employed significant amounts of organic modifier in the mobile phase. This has the unfortunate consequence of diminishing the extent of analyte adsorption by competition with the organic modifier.

We have, therefore, sought in our work to demonstrate the potential of LC-ES by utilizing recent developments in column-packing technology that allow the use of strictly aqueous eluents in the separation of several

classes of low-molecular-weight, sparingly water-soluble organic compounds known to electrosorb (30). These include alcohols, diols, mono- and dicarboxylic acids, amines, and alkanolamines, all detected in the neutral form. Several of these compound classes are not readily detected by other means.

The primary means of detection utilized in this work is based on changes in the differential double-layer capacitance, ΔC_d, induced at a suitable potential by analyte specific adsorption. We have recently applied this approach to the determination of inorganic anions at both mercury (31) and silver (32) in ion chromatography. We also employ here the use of a related detection scheme based on potential-pulse coulometry (PPC) (33). Additionally, two techniques based on "tensammetric peak" detection were briefly investigated. The first involves the measurement of nonfaradaic current transients induced upon application of a potential step through the adsorption/desorption peak, while in the second the corresponding charge is measured. These techniques are complementary to DLC detection.

EXPERIMENTAL

Instrumentation/Measurement Techniques

Differential capacitance measurements were made utilizing ac impedance methodology, as detailed in ref. 31. The experimental arrangement is shown in Figure 1. In this scheme the time-dependent capacitance change, ΔC_d, resulting from analyte adsorption is obtained by means of phase-selective detection, and is calculated in real time by a computer using

$$C_d = (\omega E)^{-1}[(I_{out}^2 + I_{in}^2)/I_{out}] \quad (1)$$

In this expression, I_{in} is the in-phase and I_{out} the quadrature cell current from the lock-in analyzer, E is the magnitude of the superimposed sinusoid, and ω is its frequency in rad s^{-1}. Equation (1) will only be valid in the absence of reversible faradaic currents. We therefore included in the measurement scheme an amperometric monitor, which is the low-pass filter/amplifier shown in Figure 1. Ordinarily we operated at ac frequencies in the range 45-150 Hz. Capacitance measurements were made in the vicinity of the pzc, with the exact potential chosen to maximize the ΔC_d response.

In the PPC technique the double-layer charging current that flows in response to a potential step is integrated (33). We have applied PPC previously to the determination of inorganic ions at a silver electrode (33). The only change required to adapt the arrangement used there to mercury is the inclusion of a synchronized drop dislodgement pulse.

The primary means of tensammetric peak detection involved stepping or sweeping rapidly the potential in a negative direction through the adsorption/desorption peak and processing the resulting current by computer. The current transient that derives from the adsorption/desorption peak is identified as the largest value stored in memory, and is then output to the strip chart recorder. The excitation pulse or sweep used in tensammetric peak detection must account for the variation in the tensammetric peak potential with concentration (29). With each of these transient techniques the measurement was repeated about once a second, or as the chromatography dictated.

To support this work, several electronic modules were built in-house. These include a mercury drop knocker, a sample and hold amplifier, a low-pass filter/amplifier/(slave) sample and hold, a "computer interface" with a wideband amplifier, a synchronized analog coulometer, and a drop dislodgement detector. A detailed description of these modules and their incorporation into various electrosorptive detection schemes is given elsewhere (34). A PAR 5204 lock-in analyzer was also used along with a PAR 173 or 273 potentiostat and a DEC PDP-11/23 microcomputer.

Cell/Electrode

A cell based on the large-volume wall-jet (LVWJ) concept (31,35,36) was used in most of the work reported here. The arrangement used with a DME is shown in Figure 2. The attributes of the LVWJ used in the present study have been enumerated previously (31). An important feature is that a high-concentration make-up stream can be conveniently added to maintain virtually any desired overall electrolyte concentration. DME capillaries used were 8 in. x 0.25 in. o.d. x either 0.004 or 0.005" i.d. (Wilmad Glass). For the most part, flat-bottom capillaries were used. A drop time of ca. one second was generally employed, either forced or natural. In the latter case, which was only used in DLC detection, a drop dislodgement detector served to synchronize the measurement to drop disengagement. A coiled platinum wire served as the auxiliary electrode, and an Ag/AgCl (3M NaCl) (Model RE-1, Bioanalytical Systems) as the reference electrode.

LC Methods

Several related chromatographies were employed in our studies. The

aqueous separations were accomplished using mixed interaction chromatography (MIC) (37), known variously as ion exclusion, ion-moderated partition, and Donnan exclusion chromatography (37). As MIC is commonly practiced, it makes use of cation exchange packings based on macroreticular resins composed of polymerized styrene-divinylbenzene derivatized with sulfonic acid groups. Generally the mobile phase consists only of dilute mineral acid. Sulfuric (and nitric) are acceptable choices from the standpoint of DLC detection since both are only weakly specifically adsorbing (38).

To separate alcohols, diols, mono- and dicarboxylic acids, we ordinarily used a Brownlee Polypore H cartridge (either 10 cm x 4.6 mm or 25 cm x 4.6 mm), generally at elevated temperature to improve column efficiency; either a Bio·rad Cation H^+ or Polypore H was used as the guard (3 cm x 4.6 mm cartridge). Elevated temperature capability was provided by an Alltech HPLC water jacket (Cat. No. 95024) in conjunction with a Haake (Type FJ) water bath. For ion exclusion separations of amines and alkanolamines, a Bio·rad Anion-OH guard was used alone with dilute, high-purity potassium hydroxide (Alfa) as eluent. Completing the LC system were a Waters 6000A pump and a Rheodyne 710 injector with either a 10 or 20 μL injection loop. To guard against background noise derived from dissolved O_2, the eluent was heated and deaerated and the cell contents blanketed with N_2 throughout an experiment. Most chemicals were purchased from Aldrich, although diols and glycols were obtained from Wilmad Glass (Cat. No. 213-12) and acetonitrile and methanol from Burdick & Jackson. The water was "Milli Q" purified water (Millipore Corp.).

BACKGROUND

The thermodynamic basis of DLC detection has been discussed earlier for inorganic anions (31). In that case the differential capacitance, C_d, at a given potential is increased progressively by specific adsorption to an extent determined by the anion surface concentration, Γ, and hence the bulk concentration, c_x. It was shown that the relationship between ΔC_d and c_x is approximately linear as long as Γ is proportional to c_x (i.e., Henry's Law applies).

In contrast to anions, adsorption of neutral organic species usually leads to marked decreases in C_d, a least in the vicinity of the pzc. This behavioral difference can be understood as follows. For anionic adsorbates, the extent of adsorption is typically strongly potential dependent, and yields substantial increases in the electrode charge at a given potential. These two coupled effects, which constitute the so-called "adsorption capacity" (39), necessarily yield large increases in C_d upon adsorption. For neutral organic molecules, on the other hand, the potential dependence of the adsorption in the vicinity of the pzc is commonly mild and nonmonotonic, so that the effect of the adsorption capacity is unimportant. However, in contrast to inorganic anions, the dielectric properties of the inner layer can be altered substantially upon organic adsorption; usually C_d will exhibit significant decreases since replacement of interfacial water by organic molecules will both decrease the polarity and increase the thickness of the inner-layer region.

The relationship between the capacitance at a given electrode potential and the fractional coverage of the organic adsorbate, θ, can be given approximately under these conditions as (39)

$$C_d = C_d^0(1-\theta) + C_d^1 \theta \qquad (2)$$

where C_d^0 is the capacitance in the absence of the adsorbate, and C_d^1 is the value for monolayer coverage (i.e., at saturation). From Eq. (2) it is simple to deduce that the decrease in capacitance, ΔC_d, brought about by adsorption will be proportional to the surface concentration, Γ, for $\theta \ll 1$. Additionally, if Henry's Law applies (i.e., $\Gamma \alpha c_x$), then ΔC_d will be proportional to the bulk concentration; such a simple linear ΔC_d-c_x relation is clearly desirable for analytical purposes.

For higher coverages, however, more complex ΔC_d-c_x relations are anticipated, dependening on the adsorption isotherm encountered. A convenient and much-used form for data analysis and interpretation is the Frumkin isotherm (40), which can be expressed as

$$Bc_x = [\theta/(1-\theta)] \exp(-2g\theta) \qquad (3)$$

where B is the adsorption coefficient, and g is a parameter describing the adsorbate-adsorbate interactions, having a positive or negative sign for systems displaying attractive or repulsive interactions, respectively. This relation is employed below.

RESULTS AND DISCUSSION

In this section we present our results for aqueous DLC detection applied to several classes of organic compounds - to alcohols, diols, mono- and dicarboxylic acids, amines, and alkanolamines. Sample chromatograms are shown for each class. The response-concentration behavior typifying these systems is discussed. While most application is to DLC detection, PPC and tensammetric peak detection are also briefly considered.

Alcohols

Alcohols were separated by mixed interaction chromatography utilizing dilute mineral acid as eluent; sulfuric and nitric acids gave roughly comparable performance. Capacitance-potential (C_d-E) curves under hydrodynamic flow were generated for nitrate and sulfate to establish an acceptable lower limit for the supporting electrolyte concentration. A concentration in excess of 0.05 M was found to be desirable. An optimization experiment that, in principle, should be performed at the start of each LC-DLC experiment is the determination of the potential at which the capacitance depression, ΔC_d, is a maximum for a representative substrate. While the surface excess, Γ, will be a maximum near the pzc, it does not necessarily follow that $|\Delta C_d|$ will be largest there. A potential in the range -0.50 to -0.525 V was found optimal for alcohols, diols, mono- and dicarboxylic acids. A slightly more positive potential was most effective for amines and alkanolamines.

Two illustrative separations of alcohols with double-layer capacitance detection at the DME are shown in Figure 3. Note that ΔC_d is negative. These separations were achieved on a (3 cm + 10 cm) Polypore H column

operated at 55°C The eluent consisted of 0.02 N H_2SO_4 delivered at 0.7 cm^3/min. Tenth molar $NaClO_4$ was initially placed in the large-volume wall-jet cell, with a 0.5 M $NaClO_4$ make-up added at 0.13 cm^3/min. The use of both nitric and sulfuric acids was investigated at concentrations ranging from 0.01 to 0.05 N. Considering chromatographic resolution, baseline noise, and the form of the ΔC_d-concn. response curves, 0.02 N H_2SO_4 was adjudged optimal.

It is well recognized that the extent of adsorption of an aliphatic organic compound at the mercury-aqueous interface depends on its alkyl content (2), i.e., on the degree of hydrophobicity. This effect is apparent in the chromatograms in Fig. 3. Thus 1-hexanol is more readily detected than is 1-butanol (Fig. 3a), as is 2-heptanol relative to *tert*-amyl alcohol [Fig. 3b; the latter is barely detectable even at 50 mM (10 μL loop)]. Alcohols containing fewer than four carbons are not readily detected by this technique.

A comprehensive comparison of relative capacitance depression at mercury was made for alcohols using flow injection analysis (FIA), i.e., in the absence of a preceding chromatographic column. The FIA stream consisted of 0.02 N H_2SO_4 + 0.07 M $NaClO_4$, which approximates the solution composition in the cell under chromatographic conditions (*vide supra*). Twenty microliter injections of 10 mM concentration were made for each alcohol tested, and the capacitance depression monitored at -0.50 V. The results, given in Table 1, are presented as dimensionless $\Delta C_d/C_d$ values (i.e., with respect to the baseline C_d value) and relative to the corresponding value (0.011) for 1-butanol, which is the shortest-chain alcohol that is readily detected by DLC. Equivalent measurements made in

the absence of sulfuric acid revealed slightly lower $\Delta C_d/C_d$ values for C_5 and higher alcohols, probably due to a "salting-out" effect. For more hydrophilic alcohols (C_3 and C_4), slightly lower $\Delta C_d/C_d$ values were observed with added acid.

The listed values clearly show the correlation between the magnitude of $\Delta C_d/C_d$ and hydrophobicity, i.e., the number of alkyl carbons. It is noteworthy that in the chromatographic experiments, adsorbability for the higher members was also observed to increase as the acid concentration was raised. However, acid concentrations could not be made higher than about 0.05 N, since the chromatography was then degraded somewhat.

Plots of ΔC_d versus bulk adsorbate concentration were generated for 1-pentanol and 3-hexanol under varying conditions of acid and electrolyte concentration. While not every curve was subjected to rigorous analysis, each was suggestive of underlying obeyance to the Frumkin adsorption isotherm. The $\Delta C_d/C_d$-concentration curve for 3-hexanol, shown in Figure 4, is representative. This curve was analyzed in terms of Eq. (3), with θ being obtained from the ΔC_d values using Eq. (2). This analysis yielded g = 1.40 ± 0.02 for $\theta \leq 0.7$, and B = 29.8 ± 2.0 M^{-1}. These values are consistent with literature values for similar alcohols obtained under conventional conditions, i.e., in stationary electrolytes (41, 42). More significantly, the sigmoidal shape of the ΔC_d-concentration curve, as exemplified in Fig. 4, can readily be accounted for by the form of the Frumkin isotherm [Eq. (3)]. The nonlinearity, although not severe below the plateau, can be attributed to the site occupancy, $(1-\theta)$, and interaction parameter terms, $g\theta$, in Eq. (3). In particular, the approach to a plateau denotes the onset of monolayer formation; above this point no

further change in $\Delta C_d/C_d$ will occur with increasing concentration, signaling the upper limit of the dynamic range for the system under consideration.

To note the effect, if any, of varying the concentration of mineral acid on the shape of the ΔC_d-concn. response curves, 1,7-heptanediol was chromatographed on Polypore H with 0.002 N H_2SO_4 as eluent (10 times lower than the usual concentration, *vide supra*). To achieve a sufficient ionic strength for DLC detection, a make-up stream was teed-in post-column. Several effects were apparent: for the moderately hydrophobic 1,7-heptanediol, the detection limit was lowered for smaller acid concentrations. Also, the ΔC_d-concn. curve was observed to be only slightly nonlinear. Hence, depending on the molecular system and on experimental conditions, the shape of the ΔC_d-concn. response curve may vary somewhat.

Diols

Short-chain diols are also separable by mixed interaction chromatography using dilute sulfuric acid in the eluent, as for low-molecular-weight alcohols. An example with DLC detection is shown in Figure 5. Again, as for the alcohols, the dependence of the ΔC_d response on hydrophobicity is apparent: the detection limits are lower the longer the chain. An example of this dependence is provided by the response for 1,5-pentanediol relative to that for 2,4-pentanediol. The three contiguous methylene groups in the former as opposed to isolated groups in the latter lend greater detectability to 1,5-pentanediol. This enhancing effect of contiguous carbons is also evident from a comparison of the ΔC_d responses

for 1,5-pentane- and 2,5-hexanediol. It is of interest to note that the strongly hydrophilic triol glycerol was not detectable under the conditions used here, at least at a concentration of 25 mM.

While the C_d depression is greater for 1,8-octanediol than for 1,7-heptanediol, an even larger effect is observed in going from 1,8-octanediol to 1,9-nonanediol (not shown). However, the attraction to the column packing is also greater for this more hydrophobic compound, resulting in a significantly longer retention time; therefore the peak is broad. To counter this, some organic modifier could be added, but of course this would diminish the electrosorption.

It is apparent that there are conflicting requirements to successful application of electrosorptive detection for such hydrophobic organic species. On the one hand we desire a highly surface-active substance. However, such a species will usually also exhibit a high preference for a column packing, thereby necessitating the addition of organic modifier to achieve reasonable k' (capacity factor) values. Hence, in general, it may not be possible in LC-ES to achieve the same low detection limits for surface-active compounds as are possible in batch electrochemical experiments.

Relative capacitance response data such as those in Table 1 were not generated for the diols. Nevertheless, comparison of Figures 3 and 5 allows an assessment of the relative sensitivities of the DLC technique to alcohols and diols. Clearly, for both classes of compounds, the response is largely determined by the number and arrangement of $-CH_n$ groups. A welcome feature of analytical consequence for diols relative to alcohols is that the greater water solubility lent the former through the additional

alcoholic group expands the number of compounds determinable by DLC.

Carboxylic Acids

The relative $\Delta C_d/C_d$ responses of aliphatic carboxylic acids were also determined by FIA; the resulting data are shown in Table 2. These were obtained at E = -0.50 V with 0.02 N H_2SO_4/0.075 M $NaClO_4$ as the FIA stream, which approximates closely the composition of the mobile phase used in the present LC-ES experiments. The acidic stream assured that the carboxylates were in the protonated form. As in Table 1, the values are listed relative to the normalized response for the n-C_4 member of the group (butyric acid, for which $\Delta C_d/C_d$ = 0.018). Again, it is apparent that detectability improves significantly with increased chain length and hydrophobicity. Comparison of the values in Table 2 with those in Table 1 reveals that somewhat smaller capacitance depressions are obtained for carboxylic acids than for the corresponding alcohols. This probably stems from the lower water solubility of the latter.

A separation of five aliphatic acids with DLC detection is shown in Figure 6. Consistent with the data given in Table 2 and with the results obtained for both alcohols and diols, the detectability clearly increases as we progress from butyric acid, which is miscible with water, through heptanoic acid, which is only sparingly soluble. Octanoic acid (not shown) is strongly retained on the column, with a fwhm of 1.4 min. Some organic modifier would be necessary to yield even moderate column efficiency for this strongly retained acid.

Calibration (ΔC_d-concn.) curves for the acids were not subjected to rigorous analysis. However, their shape is suggestive of Frumkin behavior

with strong, attractive interadsorbate interactions. Thus for some acids there was a very sharp rise in the ΔC_d-concn. curve, reflecting rapid increases in coverage with increasing analyte concentration. A few also exhibited an apparent "threshold effect", in that no change in capacitance is apparent until a certain bulk concentration is reached, whereupon easily measurable ΔC_d values were obtained. This behavior also stems from the presence of large attractive interadsorbate interactions (27).

Dicarboxylic Acids

Relative responses for several dicarboxylic acids were determined by measuring the areas under peaks obtained using a 10-cm Polypore H column with 0.02 N H_2SO_4 as eluent. The results are compiled in Table 3. . In this case the capacitance changes are listed relative to glutaric acid, which contains five carbons. This was done because succinic acid is only marginally determinable by DLC due to its high water solubility. Improved detectability with increasing molecular hydrophobicity is as previously noted for alcohols, diols and monocarboxylic acids.

A separation of six dicarboxylic acids with DLC detection is shown in Figure 7. In order to achieve baseline resolution of early-eluting compounds, a 25-cm Polypore H column was used in place of the earlier-used 10-cm cartridge. Note that there is some "noise" in the azelaic acid peak. Similar noise was also noted for other highly hydrophobic/surface-active compounds.

Amines

Aliphatic amines may be separated by ion-moderated partition

chromatography using dilute hydroxide as the eluent (43). Although a preferred column is the Bio·rad HPX-72-0, we used the less expensive, recommended guard alone, the Bio·rad Anion-OH. Values of $\Delta C_d/C_d$ were measured for the aliphatic amines, again by FIA, at -0.50 V in a stream consisting of 0.02 N NaOH + 0.075 M $NaClO_4$. As the hydroxyl ion is very weakly adsorbing (44), it interferes only minimally with solute specific adsorption. The $\Delta C_d/C_d$ responses obtained for the amines normalized to that for butylamine (0.020) are listed in Table 4. Comparison with Tables 1 and 2 reveals that the capacitance depression of amines increases to a slightly greater extent with chain length than for alcohols and decidedly more than for acids. Also, the absolute $\Delta C_d/C_d$ values are greater for amines than for either alcohols or acids. This is made apparent in Table 5, which compares absolute $\Delta C_d/C_d$ values for these three classes of compounds. Table 5 consists of data selected from those used to generate the relative values given in Tables 1, 2, and 4.

A separation of four amines on the Anion-OH guard (3 cm x 4.6 mm) with DLC detection is shown in Figure 8. Maximal response for the amines was found in the region -0.425 V to -0.45 V. The dynamic range for the higher amines using the guard column proved quite limited, symptomatic of strong, attractive interadsorbate interactions. A "threshold effect", previously mentioned with respect to acids, was also observed for some higher amines. The clipped peaks for hexyl- and heptylamine seen in Figure 8 are due to saturation capacitance depression, associated with the onset of monolayer formation.

Baseline noise tended to be higher with the alkaline eluent (high-purity KOH used), when monitoring near the pzc, compared to an acidic

eluent of equal concentration. As a final note, the amines are not only detectable as neutrals in basic solution, but also as the protonated, cationic partner of an ion-pair. The DLC detection of this and other charged organic species will be discussed elsewhere.

Alkanolamines

Alkanolamines were also separated on the Anion-OH guard and detected as neutrals by DLC although this short column did not yield much resolution under the conditions investigated. A two-component separation with DLC detection is shown in Figure 9. As for the amines in alkaline solution, baseline noise tended to be high.

Comparison of DLC to Conventional Means of Detection

There is no obvious conventional method of choice for determining several of the classes of compounds examined here. Hence, the application of DLC detection to these compounds is of more than passing interest.

Refractive index (RI) has traditionally been used to detect alcohols and diols (45, 46), although other methods, including indirect photometric detection (47) and post-column derivatization followed by UV-Vis measurement (48), have been employed. Refractive index may also be used to detect carboxylic acids (49). A more selective method for aliphatic acids utilizes conductivity (50, 51), but this is not a sensitive measure for weak acids. Yet another, UV detection, is a more restricted approach, largely confined to conjugated acids (52).

We compared the present DLC approach with refractive index detection, for the determination of several acids and diols. The comparisons, shown

in Figure 10, were made using a Polypore H column with 0.02 N H_2SO_4 as the eluent. It can be seen that these two techniques are comparable for moderately surface-active compounds, RI is superior for weakly surface-active materials, and DLC superior for the more strongly surface-active substances. The more selective nature of DLC detection is apparent.

Potential-Pulse Coulometric Detection

An alternate means of electrosorptive detection, closely related to DLC, is provided by potential-pulse coulometry (PPC) (33). Rather then evaluating the differential capacitance at a given potential by ac impedance, the PPC method as configured for the present systems involves measuring the change in electrode charge, Δq, produced by a small (ca 0.1 V) negative potential step in the vicinity of the pzc. Since the capacitance is usually approximately independent of potential in this region, Δq is essentially proportional to C_d ($\Delta q \approx C_d \Delta E$, where ΔE is the amplitude of the potential step). The measurement in the PPC method is typically complete within 0.2-0.3 ms.

Analogously to conventional DLC, detection by PPC involves measurement of $\Delta(\Delta q)$ [or $\Delta(\Delta q)/\Delta q$] as the chromatographic elution proceeds. The signal-to-noise evident in the resultant chromatograms was typically about one-half that obtained by DLC detection for all compound types investigated here. As expected, calibration curves obtained by small-potential-step coulometry exhibit the same shape as those obtained by DLC.

Tensammetric (Adsorption/Desorption) Peak Detection

As noted above, an inevitable limitation on the quantitative utility

of conventional DLC detection methods is that ΔC_d will respond to varying analyte concentration only within the region where the adsorbate coverage is below a monolayer. This can provide a significant limitation for the determination of the more strongly surface-active compounds. However, even under these conditions the position and amplitude of the "tensammetric" C_d-E peaks, signaling where adsorption-desorption occurs on either side of the pzc, are still dependent on the analyte concentration. This suggests the suitability of detection methods that sense these properties, rather than C_d close to the pzc.

We have employed a scheme utilizing either a negative-going pulse or rapid potential sweep applied near the end of drop lifetime, arranged so to span one of the adsorption-desorption regions. The resulting transient capacitive current, i_c, is sampled at the computer's maximum sampling rate ($\sim 2.5 \times 10^4\ s^{-1}$) and stored. The stored values are then scanned and the maximum value, $(i_c)_{max}$, output to a recorder. This $(i_c)_{max}$ value will reflect the amplitude of the C_d-E adsorption-desorption peak, which is dependent upon the analyte concentration. At lower concentrations $(i_c)_{max}$ is usually observed to vary roughly linearly with concentration, while at higher values a change in proportion to the logarithm of concentration is ordinarily observed (53). Although this scheme has less general value than conventional DLC detection, it is in a sense complementary in view of its utility at higher analyte concentrations and/or adsorbabilities.

A cursory examination was also made of the utility of applying a potential step through the tensammetric peak and integrating the current. However, this is complicated by the difference in sign of the capacitive current in the depression and adsorption/desorption regions; the result can

be a transient partial cancelation of charge. This approach should be more useful when restricted to capacitive current of only one sign, i.e., to only the current associated with the adsorption/desorption peak.

CONCLUSION

We have demonstrated the applicability of electrosorptive detection in liquid chromatography utilizing aqueous eluents to the determination of several classes of low-molecular-weight, neutral organic compounds, specifically alcohols, diols, mono- and dicarboxylic acids, amines, and alkanolamines. The primary and most useful means of detection is differential double-layer capacitance depression, monitored at a potential in the vicinity of the pzc, although small potential-step coulometry provides an alternate, closely related approach. The magnitude of the response, either ΔC_d or $\Delta(\Delta q)$ for these two techniques, shows a clear dependence on carbon number and structure - i.e., on the extent of hydrophobicity. The ΔC_d-concn. behavior evident in the response curves may be accounted for in terms of underlying Frumkin behavior. Detection based on tensammetric peak height may also be employed, but was found to be only marginally useful for the weakly-to-moderately-adsorbing molecular systems investigated in this work.

As stated, compounds examined in this work may be classified as weakly-to-moderately specifically adsorbing. Hence, these compounds do not serve to fully realize the potential of LC-ES. To this end, noniogenic surfactants, water-soluble polymers, and, possibly, larger biomolecules may be logical candidates. With regard to surfactants, complications may arise from the need to incorporate high concentrations of organic modifier in the

mobile phase. Interestingly, this appears not to be the case for ionic surfactants, since these compounds may be detected at potentials far removed from the pzc (54). The sorptive properties of many water-soluble polymers have been characterized (55); for these large molecules, changes in double-layer capacitance may be substantial. As to the last of these molecule types, proteins and other biomolecules often contain significant hydrophobic portions, which are highly surface active (56). Hydrophobic interaction chromatography, which capitalizes on this property, and which has experienced explosive growth in recent years (57), may well be suitable for coupling to electrosorptive detection, since DLC exhibits considerable tolerance to concentration gradients (31).

Acknowledgments

David Milner made valuable contributions in instrumentation development and computer programming. This work was supported in part by the Office of Naval Research.

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Table 1

Relative Capacitance Depression of

Alcohols by DLC[1], Normalized to 1-Butanol

Compound	Relative $\Delta C_d/C_d$[2]
2-Propanol	--
1-Propanol	--
Isobutyl Alcohol	0.62
sec-Butyl Alcohol	0.62
tert-Butyl Alcohol	--
1-Butanol	1.00
tert-Amyl Alcohol	1.19
3-Methyl-1-butanol	2.19
2-Methyl-1-butanol	2.43
3-Pentanol	2.52
2-Pentanol	2.67
1-Pentanol	4.14
3-Hexanol	22.4
2-Hexanol	27.0
1-Hexanol	45.3
(±)-2-Heptanol[3]	115
1-Heptanol[3]	220

[1]For 20-μL injections of 10 mM concentration, E = -0.50 V.

[2]Relative to 1-butanol.

[3]Lower concentrations run and the values extrapolated upward to 10 mM (not rigorously correct because of the nonlinear Frumkin isotherm that applies).

Table 2

Relative Capacitance Depression of Carboxylic Acids by DLC[1], Normalized to Butyric Acid

Compound	Relative $\Delta C_d/C_d$[2]
Acetic Acid	--
Propionic Acid	--
Butyric Acid	1.00
(±)-2-Methylbutyric Acid	1.67
Isovaleric Acid	1.58
Valeric Acid	3.74
Hexanoic Acid	14.4
Heptanoic Acid[3]	77
Octanoic Acid[3]	330

[1]For 20-μL injections of 10 mM concentration, E = -0.50 V.

[2]Relative to butyric acid.

[3]Two millimolar and one millimolar concentrations used for heptanoic and octanoic acids, respectively, and the responses extrapolated upward.

Table 3

Relative Capacitance Depression of Dicarboxylic Acids by DLC[1], Normalized to Glutaric Acid

Compound	Relative $\Delta C_d/C_d$[2]
Succinic (C_4)[3]	0.26
Glutaric (C_5)	1
Adipic (C_6)	2.91
Pimelic (C_7)	5.44
Suberic (C_8)	11.6
Azelaic (C_9)[3]	37
Sebacic (C_{10})[3]	97

[1]For 20-μL injections of 10 mM concentration, E = -0.525 V.

[2]Relative to glutaric acid.

[3]Higher (succinic) and lower (azelaic, sebacic) concentrations, respectively, run and the values extrapolated to 10 mM.

Table 4

Relative Capacitance Depression of

Amines by DLC[1], Normalized to Butylamine

Compound	Relative $\Delta C_d/C_d$[2]
Isopropylamine	--
Propylamine	--
sec-Butylamine	0.70
Butylamine	1.00
tert-Amylamine	1.20
Isoamylamine	4.35
Amylamine	9.0
Hexylamine[3]	48
Heptylamine[3]	230
Octylamine[3]	720

[1]For 20-μL injections of 10 mM concentration, E = -0.50 V.

[2]Relative to butylamine.

[3]Lower concentrations injected, and the responses extrapolated to 10 mM.

Table 5

Capacitance Depression of Alcohols, Acids, and Amines by DLC[1]

Compound	$\Delta C_d/C_d$[2]
1-Butanol	0.011
Butylamine	0.020
Butyric Acid	0.018
3-Methyl-1-butanol	0.026
Isoamylamine	0.087
Isovaleric Acid	0.028
tert-Amyl Alcohol	0.014
tert-Amylamine	0.024
1-Pentanol	0.048
Amylamine	0.180
Valeric Acid	0.067
1-Hexanol*	0.527
Hexylamine*	0.97
Hexanoic Acid*	0.260
1-Heptanol*	2.54
Heptylamine*	4.58
Heptanoic Acid*	1.38
Octylamine*	14.4
Octanoic Acid*	6.01

[1] For 20-μL injections of 10 mM concentration, except where noted by asterisk, utilizing the conditions of Tables 1, 2, and 4. For the C_6's, 5 mM concentrations were used, for the C_7's, 2 mM, and for the C_8's, 1 mM; the values obtained were then extrapolated to 10 mM.

[2] The $\Delta C_d/C_d$ values are the *actual* relative change in capacitance measured.

Figure Captions

Figure 1. Block diagram of the instrumental arrangement for double-layer capacitance detection at the DME with simultaneous faradaic electrochemical detection.

Figure 2. Large-volume wall-jet cell/electrode assembly with drop knocker for the DME.

Figure 3. Two separations of alcohols with DLC detection. Conditions: column, (3 cm + 10 cm) Polypore H operated @ 55° C; eluent, 0.02 N H_2SO_4 pumped at 0.7 cm^3/min; initially in large-volume wall-jet cell, 0.1 M $NaClO_4$; make-up, 0.53 M $NaClO_4$; sample loop size, 10 μL; DME, 0.004" i.d.; forced drop time, 1s; f = 145 Hz; E = -0.525 V.

Figure 4. ΔC_d-concn. response curve obtained at Hg for 3-hexanol using the conditions of Fig. 3 except for a 20 μL loop size and E = -0.55 V.

Figure 5. Separation of six diols with DLC detection; conditions as in Fig. 3.

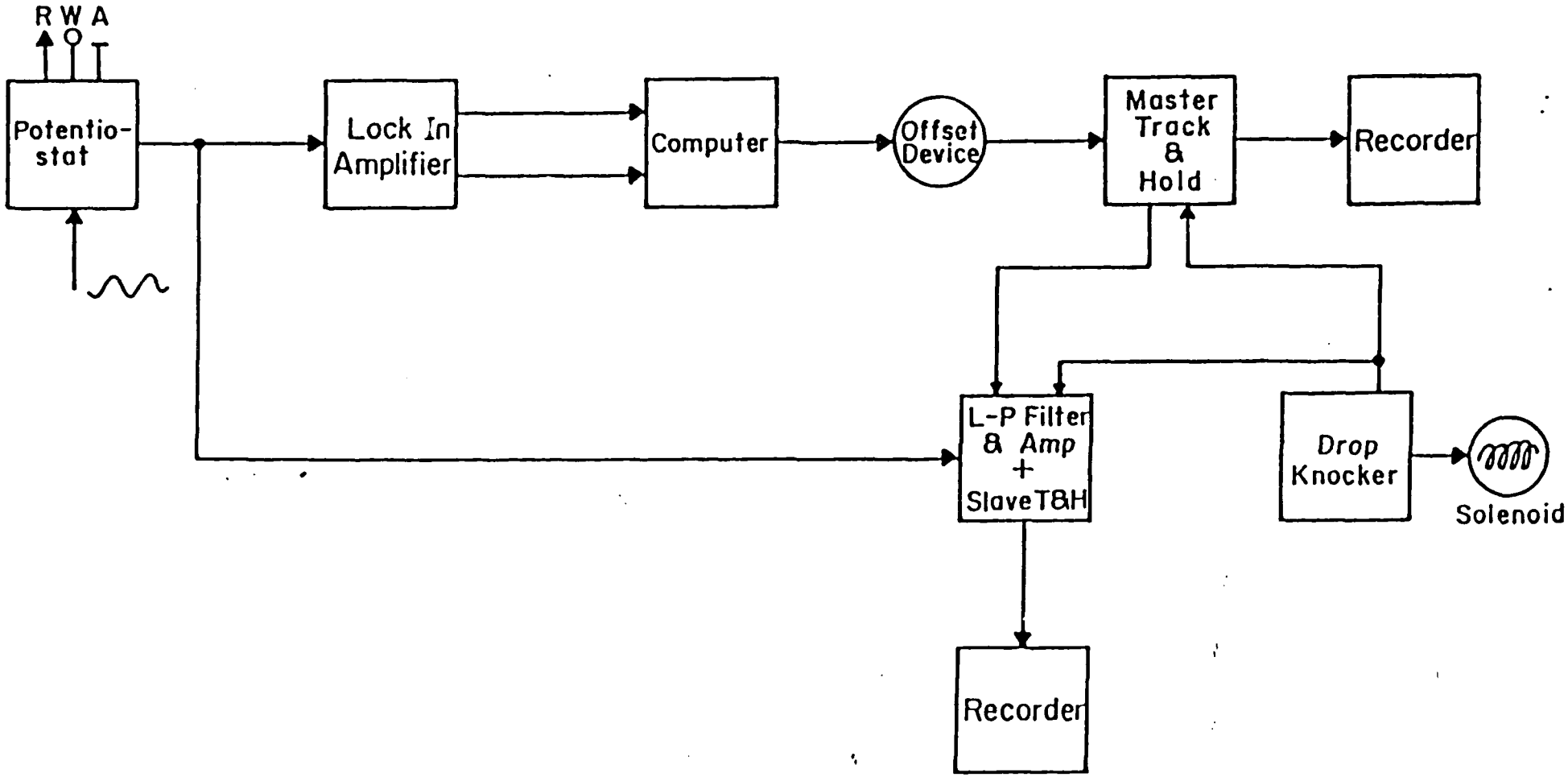
Figure 6. Separation of five carboxylic acids with DLC detection; conditions as in Fig. 3 except that $t_{col} \simeq 60°$ C.

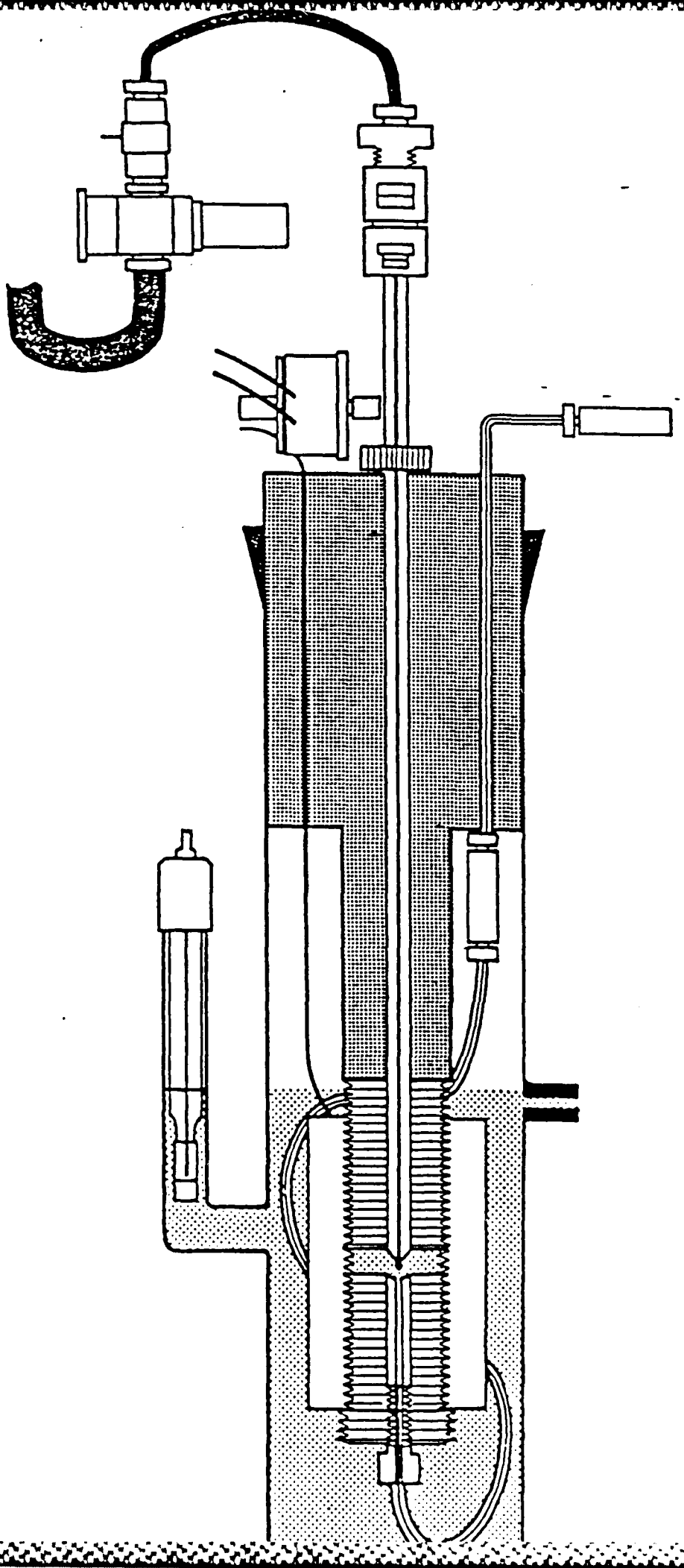
Figure 7. Separation of six dicarboxylic acids with DLC detection; conditions as in Fig. 3 except that $t_{col} \simeq 65°C$ and the Polypore H column was 25 cm rather than 10 cm long.

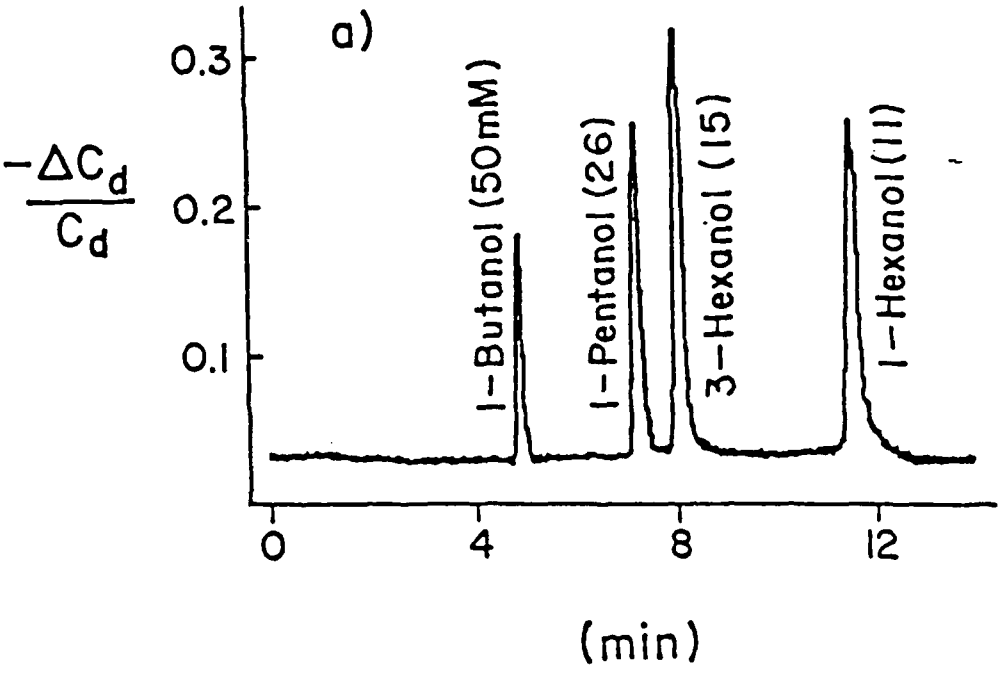
Figure 8. A separation of four aliphatic amines with DLC detection at E = -0.45 V. Conditions: column, Bio·rad Anion-OH guard, 3 cm x 4.6 mm; eluent, 0.015 N KOH (high-purity, Alfa).

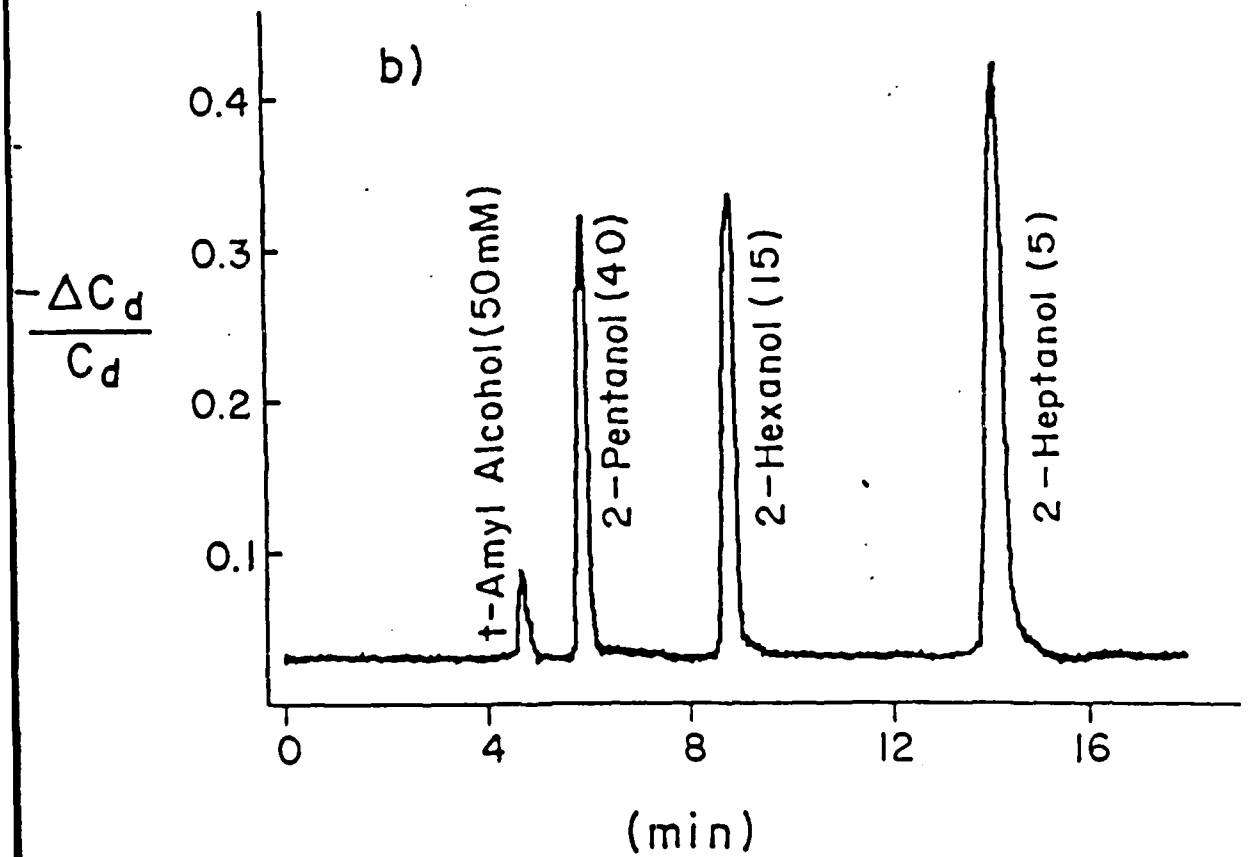
Figure 9. Separation of two alkanolamines with DLC detection; conditions as in Fig. 8.

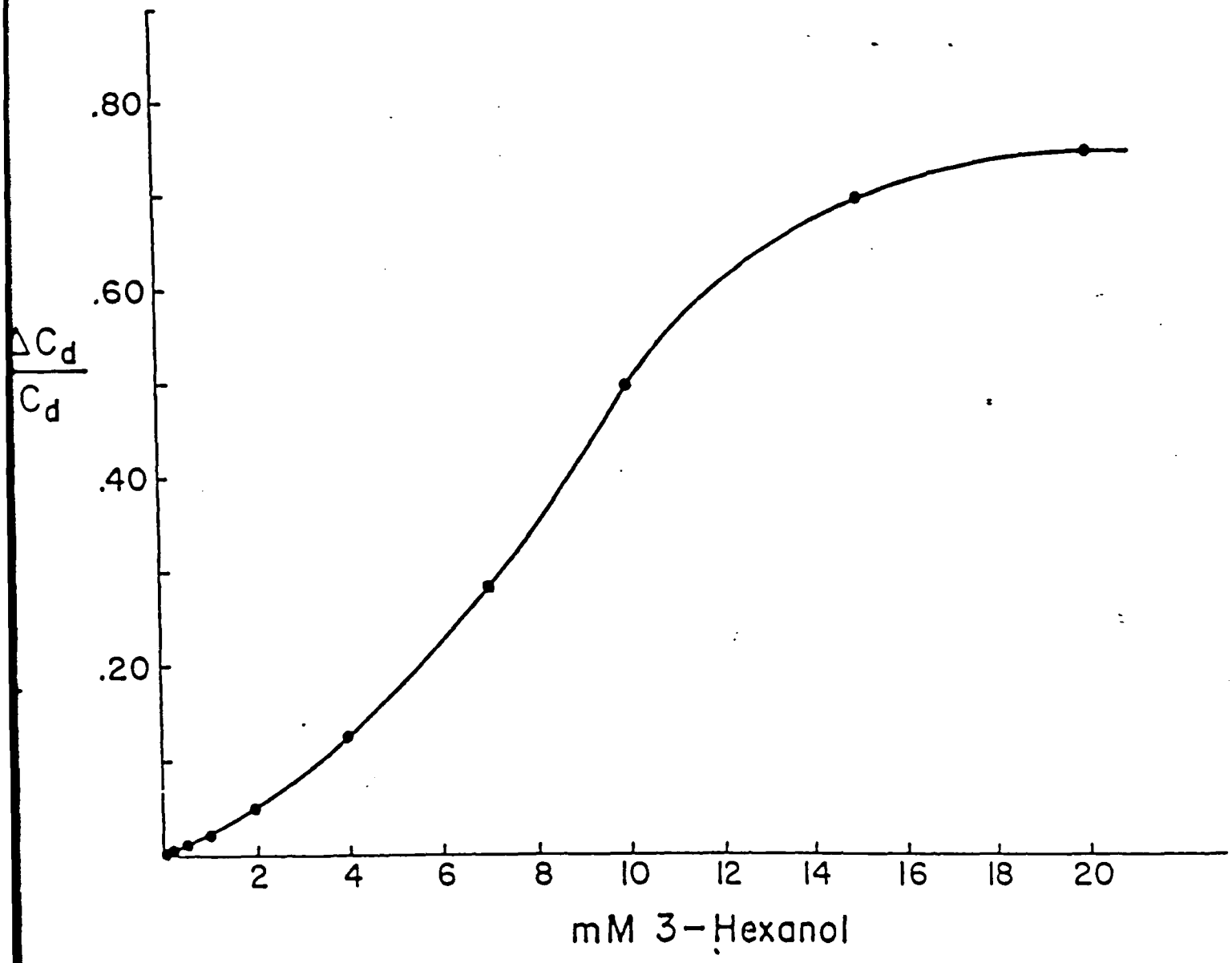
Figure 10. Comparison of DLC and RI detection for a) acids, and b) diols; conditions are as in Figs. 6 and 5, respectively.

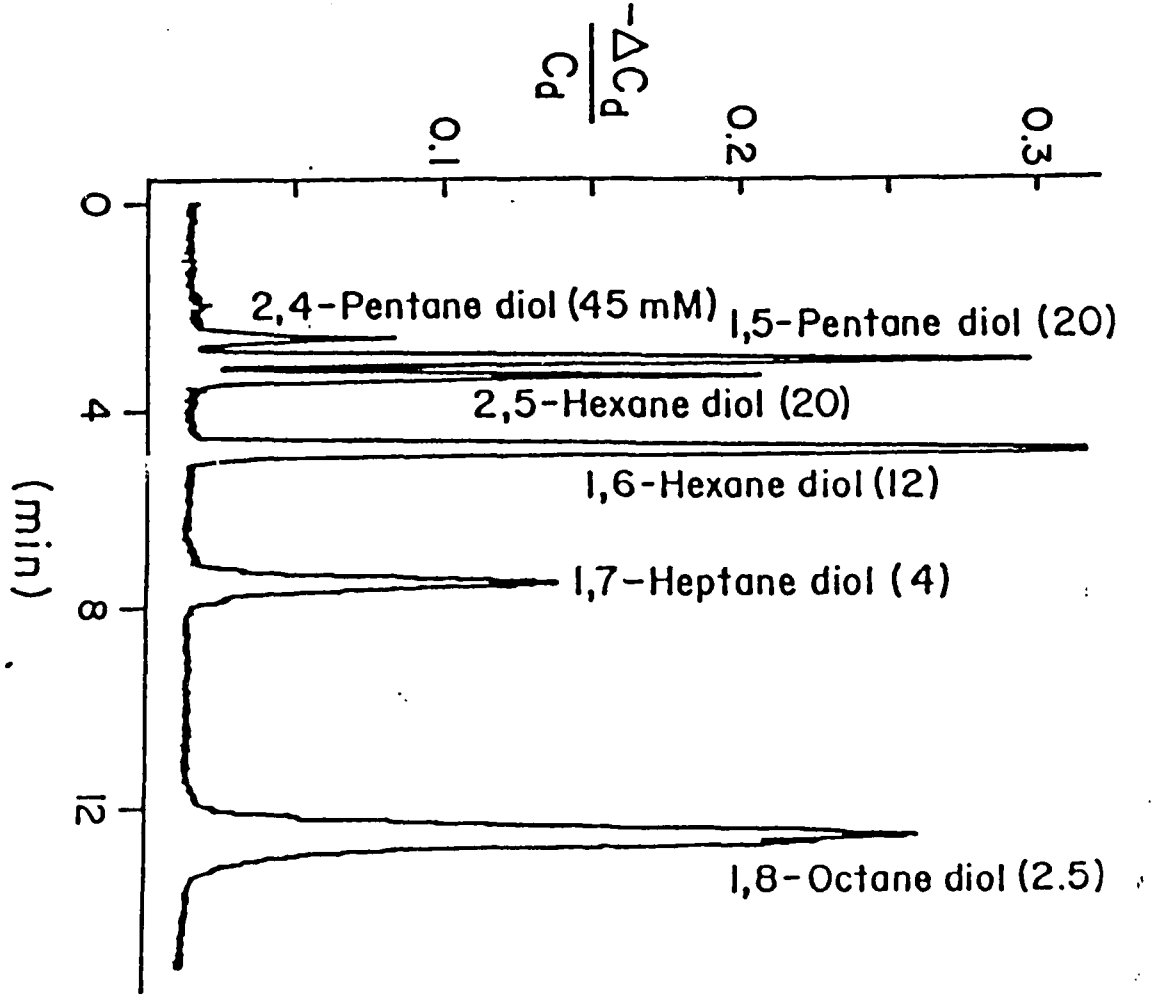

R W A
Potentio-stat
Lock In Amplifier
Computer
Offset Device
Master Track & Hold
Recorder
L-P Filter & Amp + SlaveT&H
Drop Knocker
Solenoid
Recorder

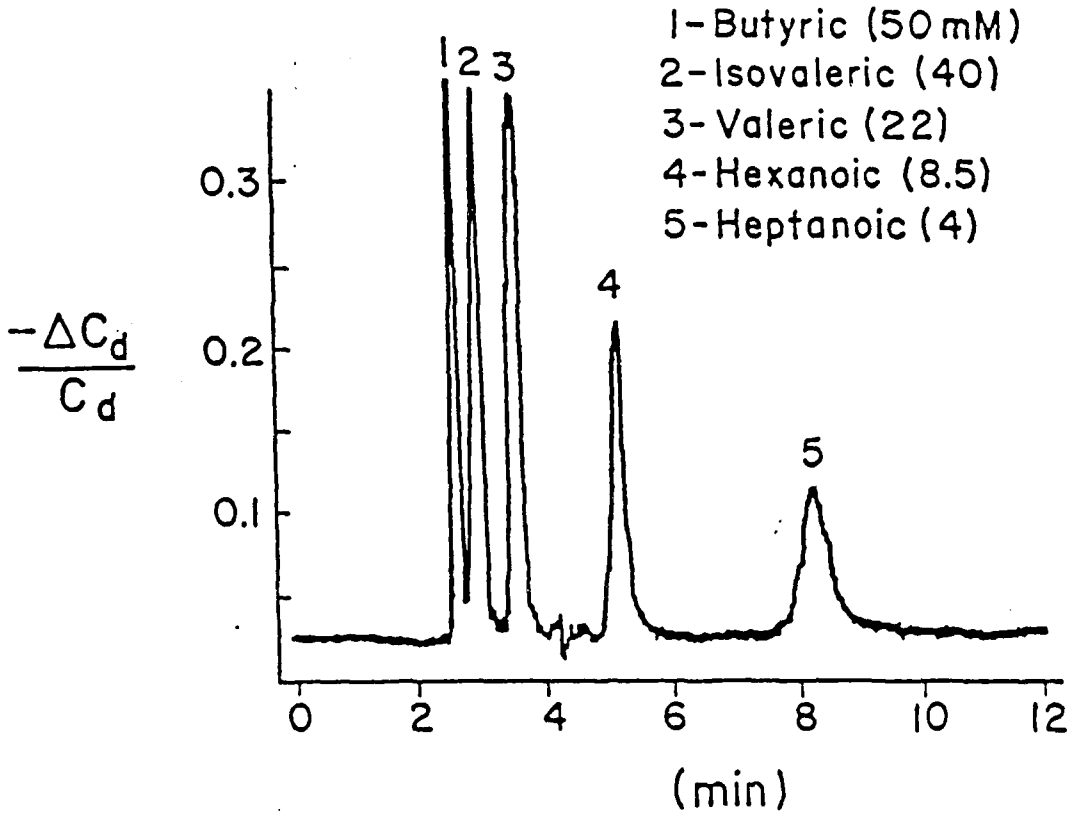


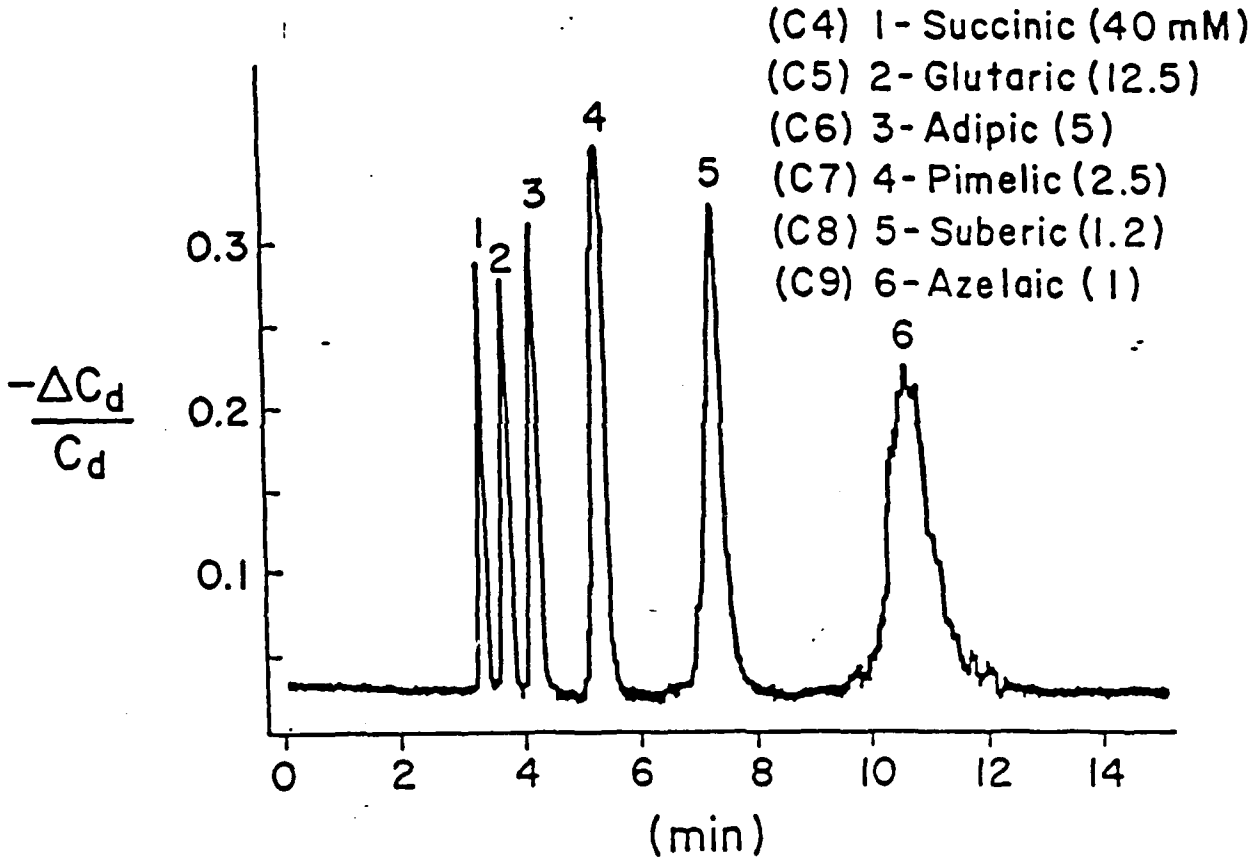

a)
$-\frac{\Delta C_d}{C_d}$
0.3
0.2
0.1
1-Butanol (50mM)
1-Pentanol (26)
3-Hexanol (15)
1-Hexanol (11)
0
4
8
12
(min)

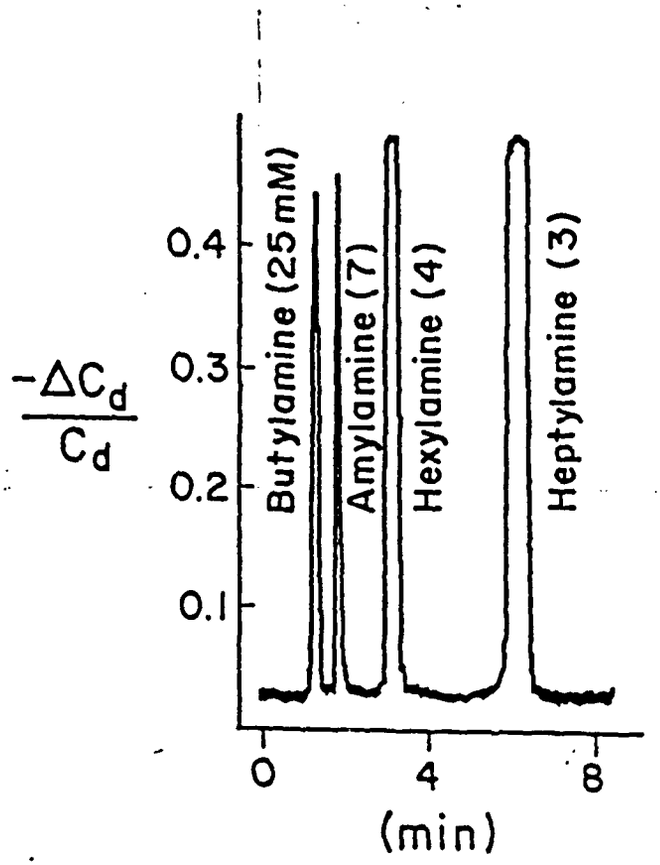

b)
$-\frac{\Delta C_d}{C_d}$
0.4
0.3
0.2
0.1
t-Amyl Alcohol (50mM)
2-Pentanol (40)
2-Hexanol (15)
2-Heptanol (5)
0
4
8
12
16
(min)

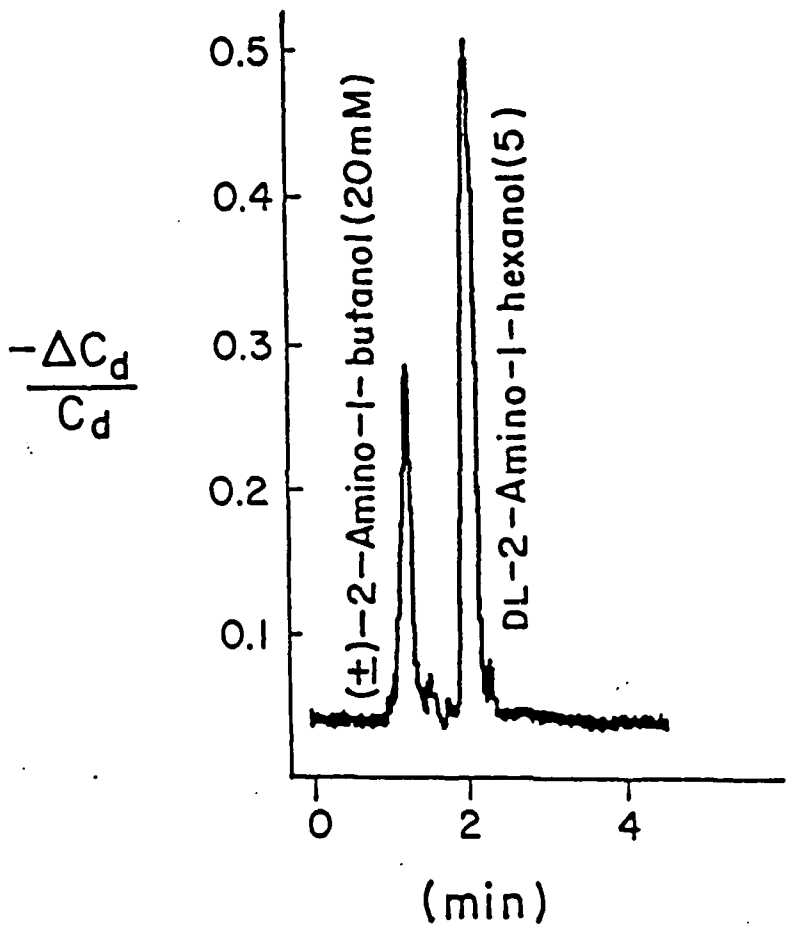

.80
.60
.40
.20
$\frac{\Delta C_d}{C_d}$
2
4
6
8
10
12
14
16
18
20
mM 3-Hexanol


$-\frac{\Delta C_d}{C_d}$
0.1
0.2
0.3
0
4
8
12
(min)
2,4-Pentane diol (45 mM)
1,5-Pentane diol (20)
2,5-Hexane diol (20)
1,6-Hexane diol (12)
1,7-Heptane diol (4)
1,8-Octane diol (2.5)

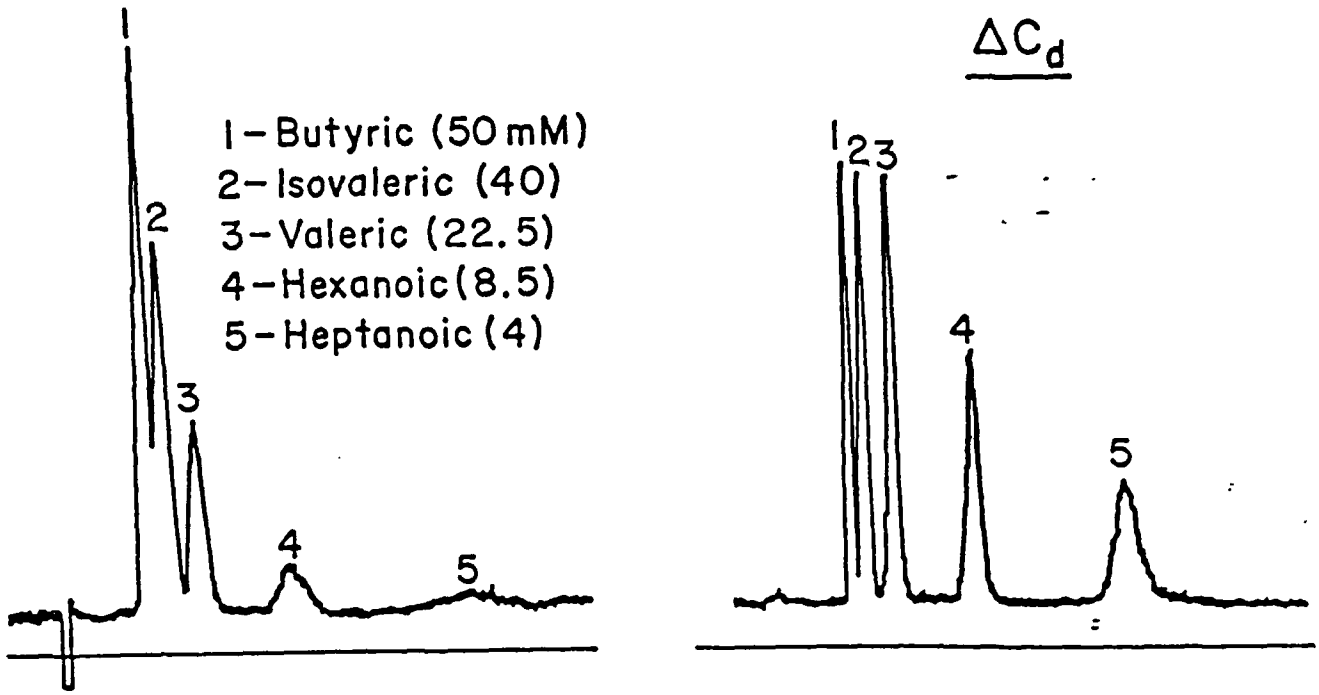

1-Butyric (50 mM)
2-Isovaleric (40)
3-Valeric (22)
4-Hexanoic (8.5)
5-Heptanoic (4)
1 2 3
4
5
$\frac{-\Delta C_d}{C_d}$
0.3
0.2
0.1
0
2
4
6
8
10
12
(min)


(C4) 1 - Succinic (40 mM)
(C5) 2 - Glutaric (12.5)
(C6) 3 - Adipic (5)
(C7) 4 - Pimelic (2.5)
(C8) 5 - Suberic (1.2)
(C9) 6 - Azelaic (1)
1
2
3
4
5
6
0.3
0.2
0.1
$-\frac{\Delta C_d}{C_d}$
0
2
4
6
8
10
12
14
(min)

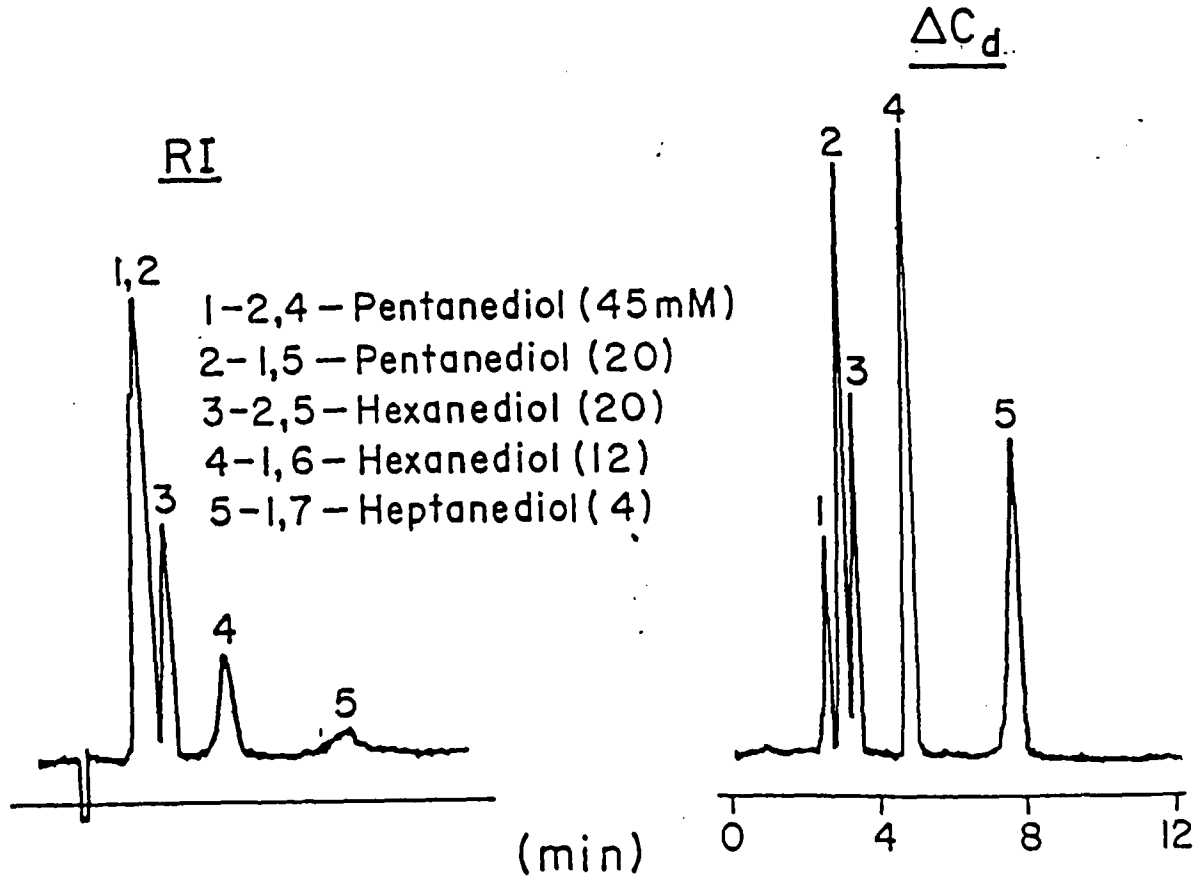

$\frac{-\Delta C_d}{C_d}$
0.4
0.3
0.2
0.1
Butylamine (25 mM)
Amylamine (7)
Hexylamine (4)
Heptylamine (3)
0
4
8
(min)


$\frac{-\Delta C_d}{|C_d|}$
0.5
0.4
0.3
0.2
0.1
(±)-2-Amino-1-butanol (20mM)
DL-2-Amino-1-hexanol(5)
0
2
4
(min)

a) Acids



b) Diols



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MARCH, 1988

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