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Comparison of capillary electrochromatography with high-performance liquid chromatography for the analysis of pirimicarb and related compounds

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Abstract

The applicability of capillary electrochromatography (CEC) to the analysis of pirimicarb and structurally related pyrimidines has been investigated. Methods were developed to improve the separation of closely related compounds. Resolution was achieved both by the use of running buffers containing a mixture of two organic modifiers to increase selectivity and reduce retention times. Solvent composition step gradients were used to separate compounds of widely differing retention factors. A comparison has been made between HPLC and CEC using identical separation parameters and the same stationary phase, from which two important conclusions are drawn. First, it has been shown that values of k' for the compounds analyzed were the same in both techniques. Secondly, although it is evident that CEC produces higher efficiencies than HPLC when running buffers with high organic solvent content are used, as the aqueous content of the running buffer is increased the efficiencies achieved in CEC and HPLC converge until they become equivalent. This is contrary to the theoretical model which predicts efficiencies are inherently higher using electrically rather than pressure driven flow. Disadvantages of the limited control of flow-rate in CEC in comparison with HPLC, are shown.

Keywords: Electrochromatography; Selectivity; Retention factors; Pirimcarb; Pyrimidines

1. Introduction

Capillary electrochromatography (CEC) is a well reviewed technique both from a practical perspective [1–5] and from theoretical or physical chemical perspectives [6–12]. The advantages that CEC offers over HPLC that have been cited include superior efficiency as a consequence of lower band broadening [13–15], the possibility of using sub-micron particles in beds of lengths that would create too high back pressures in HPLC, and the unique selectivity brought about by the superimposition of chromatographic and electrophoretic effects.

The differences between CEC and HPLC with regards to the parameters that control resolution is therefore of crucial importance in understanding the relative merits of the two techniques. Resolution (R_s), between two peaks, is related to retention, separation and number of plates as follows:

$$R_s = (1/4)\,(\alpha - 1)(N)^{1/2}(k'/1 + k') \quad (1)$$

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where k' is the average capacity factor for the two peaks.

Claims have also been made that the capacity factors differ in CEC and HPLC [16,17]. The capacity factor may be regarded as the product of the concentration distribution (or partition) coefficient (D) and the ratio of the volume of the disperse phase to the volume of the dispersion medium (ϕ) [6]. Applying the Van't Hoff relationship:

$$\mathrm{d}\ln k'/\mathrm{d}T = \mathrm{d}\ln D/\mathrm{d}T = \Delta H/(RT^2)^{-1} \quad (2)$$

$$-\ln k'/T = \Delta G/T = \Delta H/T - \Delta S \quad (3)$$

It has been found that peak widths in CEC can be $\frac{1}{2}$ to $\frac{1}{3}$ of those achievable in HPLC under comparable conditions [13–15,18]. Yan et al. [19] reported a 75% increase in efficiencies for polyaromatic hydrocarbons analyzed by CEC on the same column as used for HPLC. Whilst this may be the case for neutral compounds, opposite effects have been observed with strong bases, such as poorer peak shapes or even failure to elute [20]. In RP-HPLC bases may be analysed using deactivated silica based end-capped ODS stationary phases, however these stationary phases are not favourable to CEC as the deactivation of silica and end-capping dramatically reduces the charge density on the particles leading to a reduction in electroosmotic flow (EOF). These considerations led Smith and Evans [20] to investigate ion-exchange for the separation of bases. Certain newer octadecylsilane (ODS) phases, for example Waters Symmetry Shield [20], have also been found to be applicable to analysis of bases in CEC although the advantages over HPLC, in terms of resolution, may be limited.

The technique commonly used in HPLC and CE to separate basic substances at a low pH (at which the analyte bases would be protonated) and using amine bases as additives, has found some success when applied to CEC [21,22]. The charged bases experience electrophoretic acceleration and may even elute before the t_0 marker. This facilitates the simultaneous analysis of acids, neutrals and bases.

In the investigations reported in this article, a series of compounds of varying basicity were used to assess of the nature and extent of the intrinsic performance advantages that CEC is claimed to have over HPLC, specifically with regard to the expected higher efficiencies and differing capacity factors, both of which would lead to superior resolving power.

2. Experimental

Pirimicarb and related compounds (Fig. 1) were prepared in the laboratory (Zeneca Agrochemicals, Bracknell, UK). Thiourea and Tris buffer were purchased from Sigma–Aldrich (Poole, UK). All organic solvents and water were HPLC grade (Romil, Cambridge, UK).

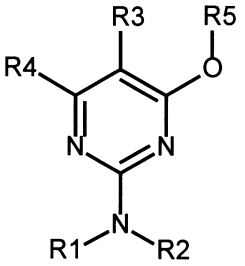
CEC was performed on a Hewlett-Packard HP 3D-CE instrument with diode array detection (Hewlett-Packard, Bracknell, UK). Pressurisation of both inlet and outlet vials was achieved using nitrogen at 10 to 12 bar. The capillary used for the study of capacity factors using individual injections was packed with CEC Hypersil C_{18}, 3 μm particle diameter, I.D. 50 μm, an O.D. of 375 μm and a total length of 33 cm (Hypersil, Runcorn, UK). The distance to the detector was 24.5 cm. The capillary, used to investigate separations by both isocratic and solvent composition step gradient techniques, was a Hewlett-Packard capillary (Hichrom, Reading, UK) packed with CEC Hypersil C_{18} stationary phase (3 μm particle diameter, I.D. 100 μm, O.D. 375 μm, total length 33 cm, distance to detector 24.5 cm).

Running buffers initially comprised of a series of acetonitrile–aqueous Tris (5 m*M*, pH 8.6) mixtures. Methanol was then added to the acetonitrile as organic modifier (4:1, v/v, and 1:1, v/v) to investigate the selectivity of the system.

HPLC analysis was performed on a Hewlett-Packard 1050 instrument. Detection was by UV at 214 nm. The HPLC columns (25 cm×2.1 mm, or 25 cm×3.2 mm) (Hypersil, Runcorn, UK), used for comparison with CEC, were packed with the same CEC Hypersil C_{18} stationary phase as the CEC capillaries. The mobile phase for HPLC used either Tris or ammonium acetate as indicated in the legends of the figures.

3. Results and discussion

The effect of methanol on the selectivity in CEC was investigated using three organic modifiers as



Compound	R1	R2	R3	R4	R5
Carbamates					
Compound 1	Me	Me	Me	Me	$CO.N(Me)_2$
Compound 2	CHO	Me	Me	Me	$CO.N(Me)_2$
Compound 3	H	Me	Me	Me	$CO.N(Me)_2$
Compound 4	Me	Me	Me	CH_2OH	$CO.N(Me)_2$
Compound 5	H	H	Me	Me	$CO.N(Me)_2$
Hydroxy pyrimidines					
Compound 6	H	Me	Me	Me	H
Compound 7	Me	CHO	Me	Me	H
Compound 8	Me	Me	Me	CH_2OH	H
Compound 9	H	H	Me	Me	H
Compound 10	H	Me	Me	CH_2OH	H
Compound 11	H	H	CH_2OH	Me	H

Fig. 1. Structures of pirimicarb and related compounds.

detailed in Table 1. These modifiers were also used in various proportions (30–80%) with aqueous Tris (5 m*M*, pH 8.6) to provide a range of running buffers (at varying overall ionic strength). Coinjections of compounds 1–5 and thiourea were made at each running buffer composition. It can be seen from the plots of ln k' vs. the percentage organic solvent (Fig. 2a – c) that the addition of methanol alters the selectivity, most notable in the resolution between compounds 3 and 4. Running buffer III (acetonitrile–methanol, 1:1, v/v, as the organic modifier) appears to give the best separation for all compounds across the running buffer composition range (Fig. 1c). However when the linear velocity of the mobile phase is examined (Fig. 3) it is clear there is also marked loss in EOF with increased methanol addition. When organic modifier III was used, the retention times of our analytes became inconvenient-

Table 1
Organic modifiers

Organic modifier	Acetonitrile (%)	Methanol (%)
I	100	0
II	80	20
III	50	50

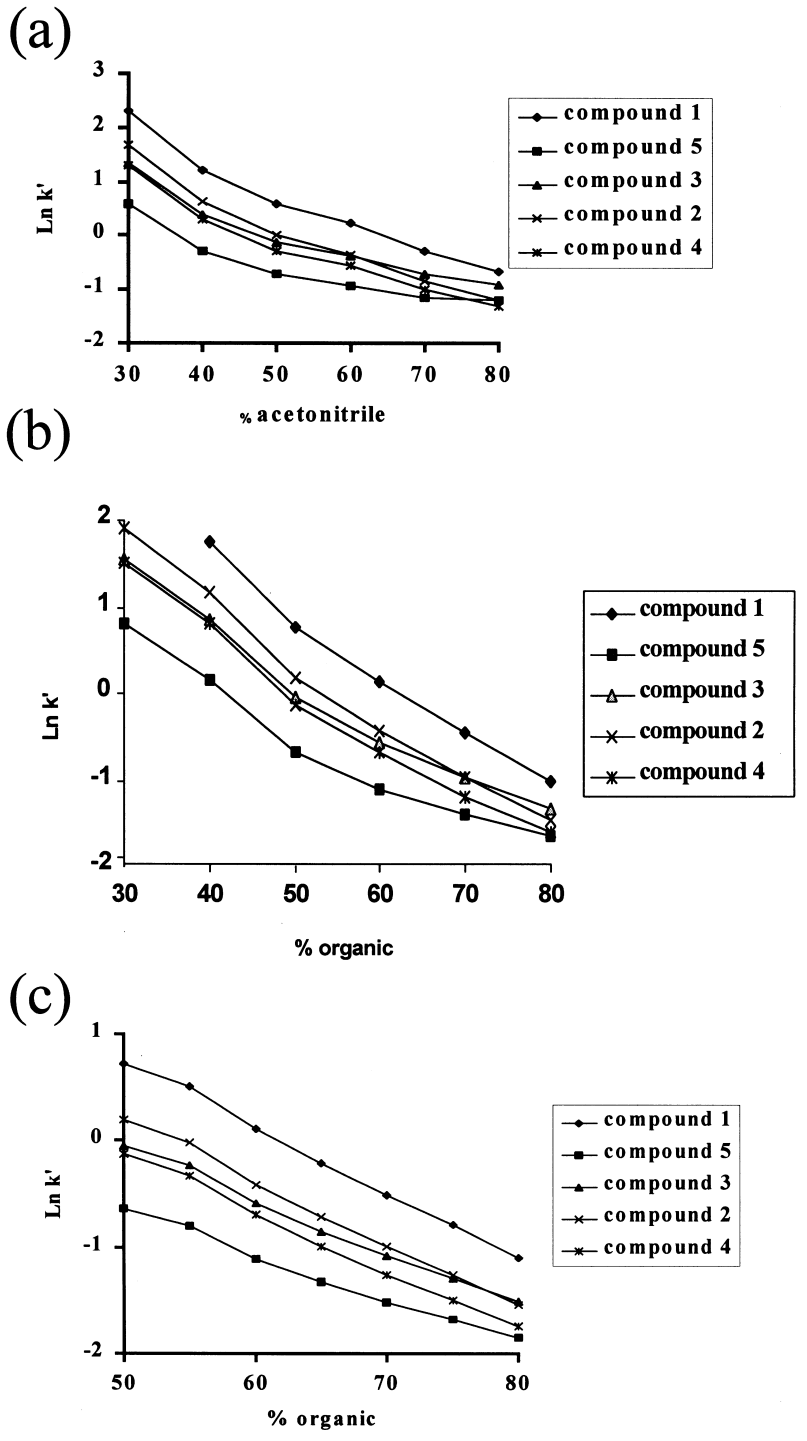


Fig. 2. Plots of ln k' vs. (a)% organic modifier I, (b)% organic modifier II and (c)% organic modifier III, for compounds 1–5

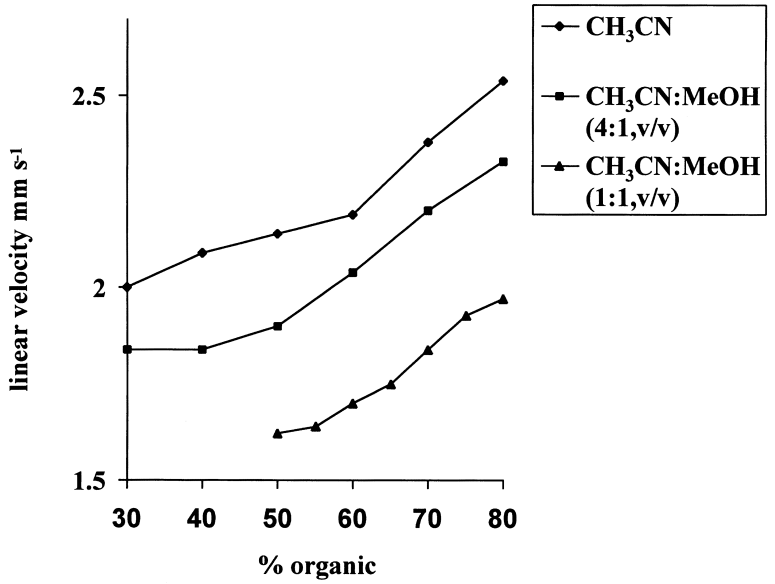


Fig. 3. Linear velocity vs. % organic for variations in composition within the running buffer.

ly long below the 50% organic content level. The same procedure was repeated using compounds 6–11 (Fig. 4), but only organic modifiers I and III were used. Again the methanol addition appears to give better resolution of the compounds and at 30% organic content the methanol–acetonitrile offers a significant selectivity improvement over pure acetonitrile. However, the same practical considerations regarding the reduction of EOF are still critical (Fig. 3). The addition of methanol was therefore discarded as a practical aid in this particular case. Acetonitrile alone was used as the organic modifier in all subsequent experiments.

When using CEC as a routine analytical tool in the laboratory it is often more convenient to coinject samples from individual vials rather than making injections of sample mixtures. In order to test the validity of the coinjection method, compounds 1–5 were analysed as a mixture (Fig. 5a) and as a coinjection of individual solutions (Fig. 5b). From the electrochromatograms it is clear that introduction of sample of the analytes by coinjection or as a mixture produce extremely similar plate numbers and retention times. It is therefore suggested that it is acceptable, in practice, to use the more convenient injection program technique for method development. Using the Ln k' vs. the percentage acetonitrile plots obtained in Figs. 2 and 4, optimised conditions were predicted to be 42% acetonitrile for the separation of compounds 1–5 and 12% acetonitrile for the separation of compounds 6–11. The electrochromatograms obtained using these conditions are shown in Figs. 5b and 6, respectively.

The significantly different polarities of the two groups of compounds (as reflected by the difference in organic content required for optimum separation) makes it impossible to separate all 11 compounds satisfactorily in one isocratic analysis. A solvent composition step gradient was therefore designed, initially using a polar running buffer to elute compounds 6–11 followed by a less polar running buffer to elute compounds 1–5 (Fig. 7). Under these conditions, significant band broadening was observed for the co-eluting of compounds 6 and 7, which is apparently a consequence of the introduction of the discontinuity in the running buffer and the delay in the run of about 1 min during the changing of the buffer vials. A system peak can also be observed at ~12 min, which is caused by the changeover of running buffers. These experiments highlight the fact that the lack of a gradient facility on most CEC instruments seriously restricts method optimization, especially when dealing with a range of compounds of differing polarities. The ability in HPLC to run

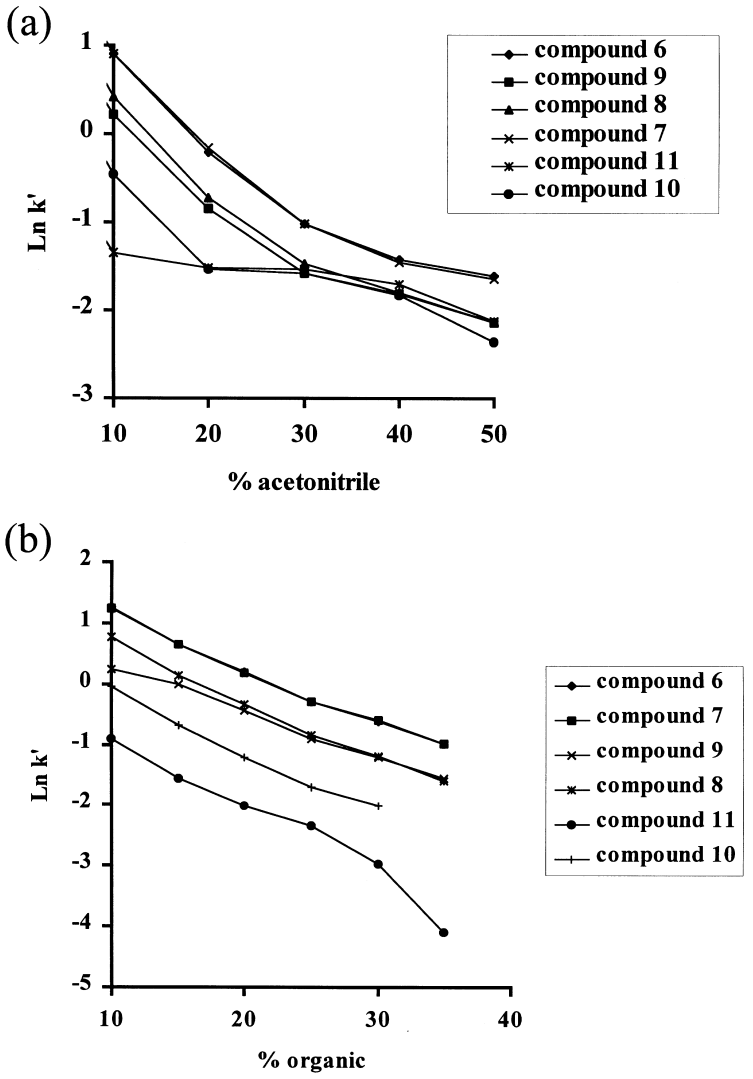


Fig. 4. ln k' vs. (a) % organic modifier I and (b) organic modifier II, for compounds 6–11.

solvent gradients offers a more versatile approach to method development.

Comparison was made between CEC and HPLC using the same stationary phase with the same linear velocity of the mobile phase. Initial experiments in HPLC using Tris buffer at pH 8.6 led to deterioration of the LC column within 1–2 h of use. Typical silica based ODS phases are prone to dissolution of the base silica at higher pH [23]. This instability at higher pH in LC is increased by the higher mechanical stress of hydrodynamic conditions. The ability of the stationary phase to withstand the high pH under electrically driven conditions is a minor advantage of CEC that might be useful in particular instances. In this case, substitution of ammonium acetate for HPLC had no measurable effect upon the chromatographic performance but did preserve the life of the LC column, hence ammonium acetate was used for some of the analyses (as indicated in the legends). For compounds 1–5, a similar resolution profile is observed (Fig. 8), with CEC giving baseline resolution in just over half the time taken by

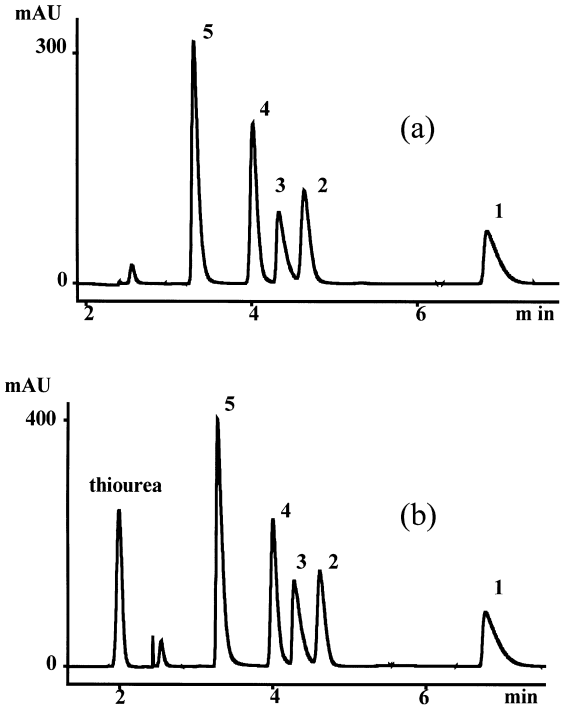


Fig. 5. Separation of compounds 1–5. Voltage 30 kV. Three-micrometer CEC Hypersil C_{18}, 100 μm I.D., packed length 24.5 cm, total length 33 cm. Buffer: acetonitrile–5 m*M* aqueous Tris pH 8.6 (42:58, v/v). (a) Injection of mixed components for 20 s at 10 kV and (b) individual injections of 5 s at 5 kV for each component.

HPLC. With compounds 6–11 however the separations are equivalent both in terms of time and resolution (Fig. 9). A more detailed comparison of

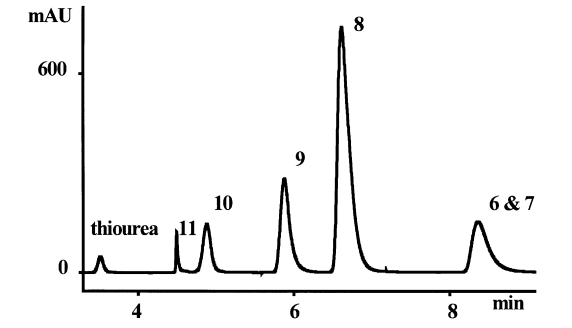


Fig. 6. Separation of compounds 6–11. Injection 5 s/5 kV per compound. Voltage 30 kV. Three-micrometer CEC Hypersil C_{18}, 100 μm I.D., packed length 24.5 cm, total length 33 cm. Buffer: acetonitrile–5 m*M* aqueous Tris pH 8.6 (12:88, v/v).

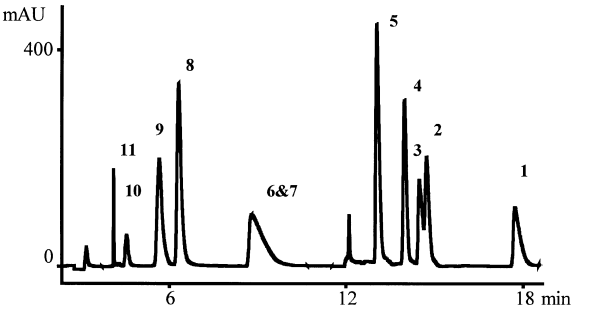


Fig. 7. Separation of compounds 1–11 using a solvent composition step gradient. Injection 20 s/10 kV for compounds 1–5, and 5 s/5 kV per compound for compounds 6–11. Voltage 30 kV. Three-micrometer CEC Hypersil C_{18}, 100 μm I.D., packed length 24.5 cm, total length 33 cm. Buffer: acetonitrile/5 m*M* aqueous Tris pH 8.6 (12:88, v/v) for 7 min followed by acetonitrile–5 m*M* aqueous Tris pH 8.6 (50:50, v/v) for 15 min.

the two separation methods was made by constructing plots of ln k' against percentage acetonitrile for compounds 2, 3, and 4 (Fig. 10). With the exception of one outlying data point, the CEC and HPLC

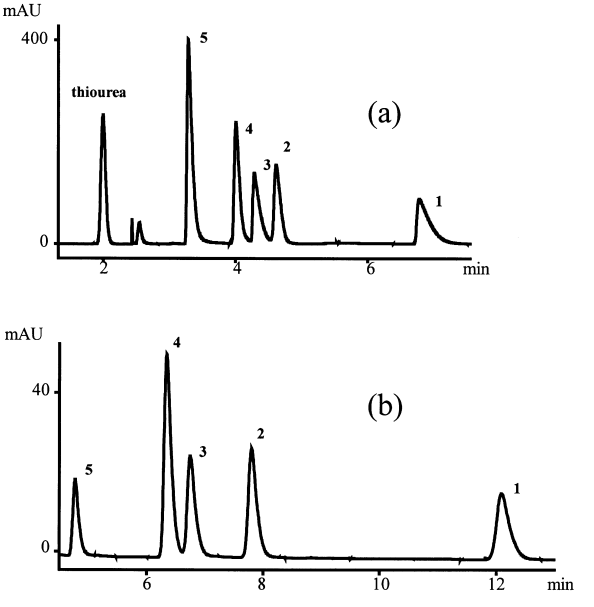


Fig. 8. CEC and HPLC separations of compounds 1–5 (a) Individual Injections of 5 s/5 kV for each component. Voltage 30 kV. Three-micrometer CEC Hypersil C_{18}, 100 μm I.D., packed length 24.5 cm, total length 33 cm. Buffer: acetonitrile–5 m*M* aqueous Tris pH 8.6 (42:58, v/v). (b) Column: 3 μm CEC Hypersil C_{18}, 250 mm×2.1 mm. Mobile phase acetonitrile–5 m*M* aqueous Tris pH 8.6 (42:58, v/v). Flow rate 0.2 ml min^{-1}.

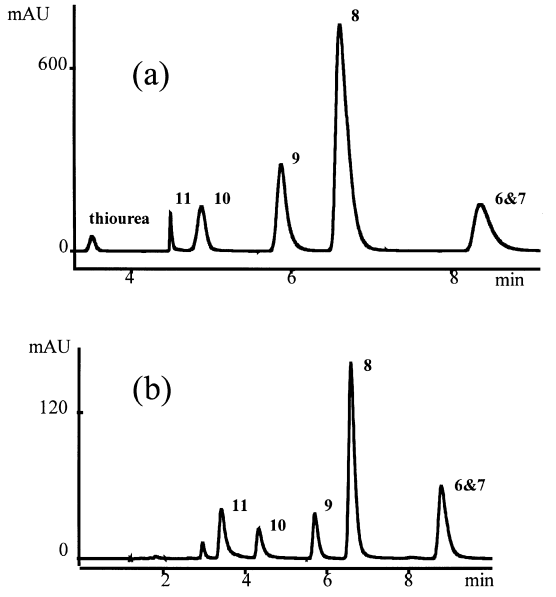


Fig. 9. CEC and HPLC separations of compounds 6–11 (a) Injection 5 s/5 kV per compound. Voltage 30 kV. Three-micrometer CEC Hypersil C_{18}, 100 μm I.D., packed length 24.5 cm, total length 33 cm. Buffer: acetonitrile–5 m*M* aqueous Tris pH 8.6 (12:88, v/v). (b) Column: 3 μm Hypersil CEC, 250 mm×2.1 mm I.D. Mobile phase acetonitrile–5 m*M* aqueous Tris pH 8.6 (12:88, v/v). Flow rate 0.2 ml min^{-1}.

profiles are identical in each of the three plots, indicating that the behaviour in CEC can be compared directly with that in HPLC. The sole anomaly (Fig. 10) arises from the behaviour of compound 3 in HPLC for which the ln k' against percentage acetonitrile deviates from linearity. The anomaly was observed for the mobile phase containing 50% organic when ammonium acetate was used (Fig. 10), and at 42% organic when Tris was used (Fig. 8). It is not obvious why this deviation has occurred but the behaviour of compound 3 in CEC clearly follows the usual linear relationship (Fig. 10). This therefore shows that, in general, any advantages of CEC over HPLC, for the analysis of neutral compounds, do not arise from a difference in k'. In other words CEC offers no distinct advantage over HPLC in terms of k'.

The finding that the retention factor is virtually identical in the two techniques is in agreement with the recently reported results of Zhang et al. [24–26] but in contrast to other reports claiming that the capacity factor is different in CEC and HPLC [16,17]. Van't Hoff plots have been used to determine the enthalpies and entropies associated with the distribution between mobile and stationary phases by Vissers et al. [16] who concluded that the retention factors in CEC were about 20% higher than those calculated from HPLC data. Whilst the authors reported using the same column for HPLC and CEC, it was necessary to correct for the effect of Joule heating, particularly since the capillaries had a relatively large internal diameter (320 μm). The possibility that the electric field could alter the nature of the stationary phase in such a way that the partition coefficient could be different in CEC was mentioned. Djordjevic et al. [17] concluded that the entropy of solute transfer, from the mobile to the stationary phase, was more negative in CEC than in HPLC. Enthalpies were similar (within experimental error) and therefore Gibbs free energies were less negative in CEC. The authors conclude that column temperature could be used to control selectivity in CEC but appeared to be uncertain as to whether the observations were due to differences between the set temperature and the true CEC column temperature, however the trend towards lower k' in CEC is consistent with extra Joule heating effects. In findings where previously impossible separations (by HPLC) or those requiring gradients and long analysis times could be performed rapidly by CEC, there is perhaps also an implication of variance in k' [27,28]. However, some of these improvements may simply be due to differences in the stationary phases, most notably the particle diameter, where 5 μm is most commonly used in HPLC and 3 μm is the favoured size in CEC. It has at least been shown that selectivity is not necessarily different in practice between HPLC and CEC. Real modification to selectivity would have to arise from the superimposition of chromatographic and electrophoretic effects, which have been described mathematically by Horvath [29].

The comparison of efficiencies produced by CEC and HPLC highlighted an interesting and unpredicted phenomenon (Fig. 11). At running buffer compositions containing high organic content CEC out-performs HPLC significantly, to a similar degree as reported previously [13–15,30]. However as the running buffer becomes more aqueous the differ-

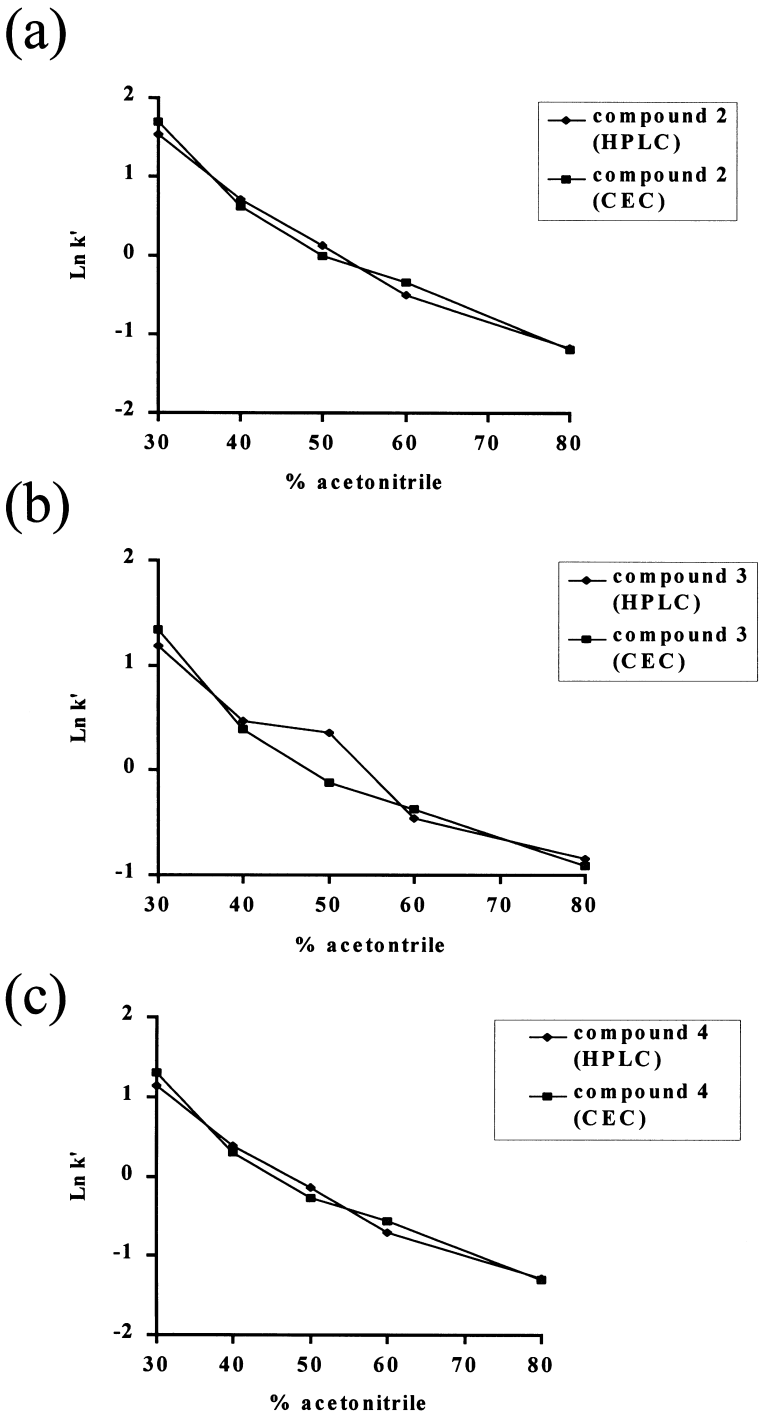


Fig. 10. Comparison of CEC and HPLC for ln k' vs. % acetonitrile for (a) compound 2, (b) compound 3 and (c) compound 4.. Note: ammonium acetate (50 m*M*) was used as the mobile phase additive for HPLC.

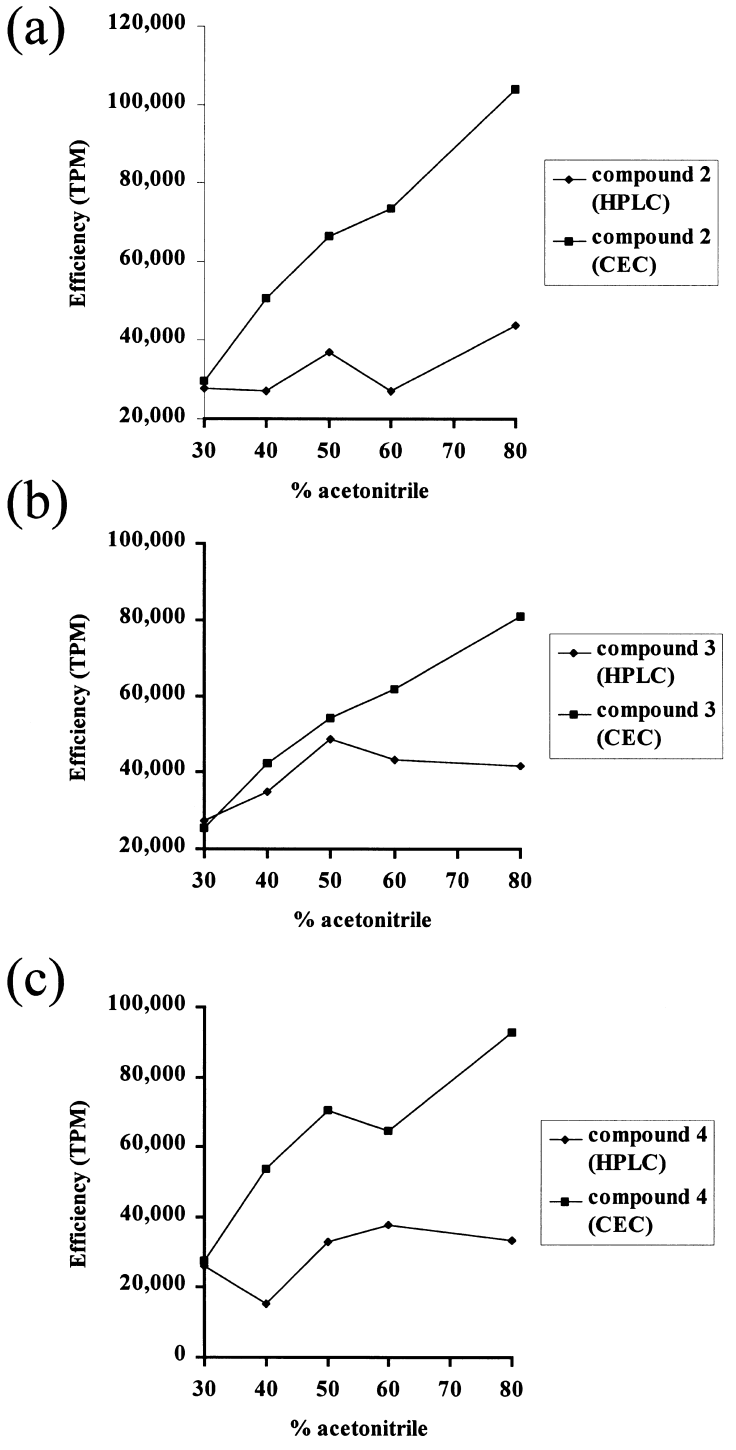


Fig. 11. Comparison of efficiency vs. % organic modifier for CEC and HPLC using (a) compound 2, (b) compound 3 and (c) compound 4. Note: ammonium acetate (50 m*M*) was used as the mobile phase additive for HPLC.

ences become less marked until a point is reached where the efficiency plots converge and the two techniques perform to the same level. To some extent this could be influenced by differences in the flow-rates of the two techniques. In HPLC the flow-rate is directly controlled and steady, whereas in CEC it varies as the running buffer composition alters. Hence at high organic composition the faster flow-rate contributes to a diminution in plate height. As the aqueous content increases, k' increases, and the linear velocity of the liquid phase decreases from 2.54 mm s^{-1} to 2.00 mm s^{-1}. However examination of published data [30,31] for the similar (3 μm diameter porous silica based Hypersil ODS) phases shows that at these flow-rates correspond to the flat part of the van Deemter plot in CEC, i.e. peak dispersion is constant. Thus the difference in flow-rates makes an insignificant contribution to the convergence in efficiency.

It is implicit that if the flow-rate could be controlled in CEC, the advantages offered by the technique would be significantly enhanced. The advantage of being able to select and control the flow-rate is reflected in Fig. 12, where an increased linear velocity in LC of 7 mm s^{-1} can be used to achieve an adequate and faster separation than by CEC.

Of the factors contributing to peak dispersion in capillaries under pressure and electrically driven conditions, the resistance to mass transfer in the mobile phase has been described in a detailed theoretical paper by Martin and Guiochon [32]. It was predicted that the ratio of the resistance to mass transfer in the mobile phase, for electrically driven (plug) flow in comparison with pressure driven (parabolic) flow, is highest at low k'. The greatest advantages of electrically driven flow are found at $k' < 1$, and as k' increases beyond 1 the ratio decreases and converges to a value of about 1.8. Therefore, there is still a theoretical advantage in using electrically driven flow, even when k' is large. It also is widely held that electrochromatography is more efficient than pressure driven chromatography [33]. Convergence in efficiency is only to be excepted at very high or very low flow-rates [7] or if the electrically driven system is subject to double layer overlap [34]. In this instance, the ionic strength of the running buffer increases from 1 to nearly 4 m*M* at higher aqueous content which would lead to a decrease in the thickness of the electrical double layer, but for 3-μm particles double layer overlap (in the interstices) would not occur at these buffer concentrations [35]. The experimental observations reported herein delineate conditions in which peak dispersion in CEC and HPLC are identical. The convergence in efficiency occurs at running buffers with high aqueous content (70%) where $\ln k' > 1$. This is contrary to the widely accepted view that electrically driven plug flow confers intrinsic superiority in chromatographic separations and appears outside of current theoretical understanding.

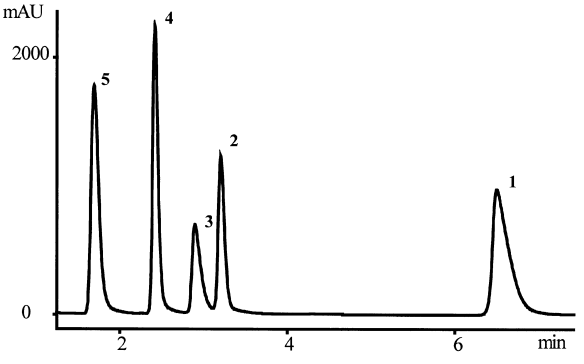


Fig. 12. Separation of compounds 1–5 by HPLC. Column: 3 μm CEC Hypersil C_{18}, 150 mm ×3.2 mm I.D. Mobile phase acetonitrile–5 m*M* aqueous Tris pH 8.6 (27:73, v/v). Flow rate 1 ml min^{-1}.

4. Conclusions

The addition of methanol to the running buffers used in CEC enhances selectivity, but the reduction of the EOF also produced, can be too great to be of practical use.

The selectivity and retention factor are the same in CEC and HPLC for the neutral compounds investigated in this study. Therefore any gains in resolution in CEC are wholly attributable to gains in efficiency.

Not all compounds demonstrate superior efficiency when analyzed by CEC, in fact the inherent increases in efficiency associated with CEC can be lost when high aqueous containing running buffers are used in circumstances where $\ln k' > 1$.

The control of flow-rate coupled with the advan-

tages offered by the ability to perform solvent gradients currently makes HPLC a more versatile technique than CEC for method development.

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