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Capillary electrophoresis of herbicides[1] II. Evaluation of alkylglucoside chiral surfactants in the enantiomeric separation of phenoxy acid herbicides

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Abstract

Two chiral alkylglucoside surfactants, namely *n*-octyl-(OG) and *n*-nonyl-β-D-glucopyranoside (NG), were evaluated in the enantiomeric separation of phenoxy acid herbicides. The enantiomeric resolution could be manipulated readily by adjusting the surfactant concentration, ionic strength, pH and separation temperature. The optimum surfactant concentration needed for maximum enantiomeric resolution varied among the different analytes and was an inverse function of the hydrophobicity of the phenoxy acid herbicides, with the most hydrophobic solute requiring less surfactant concentration for attaining a baseline enantiomeric resolution. Due to the ionic nature of the phenoxy acid herbicides, increasing the pH of the running electrolytes increased the degree of ionization of the acidic herbicides thus decreasing their association with the chiral micelles and in turn their enantiomeric resolution. Increasing the ionic strength seems to enhance both the solubilization of the solute in the micelle and the chiral interaction of the solute with the micelle with a net increase in enantiomeric resolution. Performing the separation at a sub-ambient temperature favoured an enhanced solute–micelle association and improved enantiomeric resolution.

Keywords: Enantiomer separation; Pesticides; Surfactants; Alkylglucosides; Phenoxy acid herbicides

1. Introduction

Chiral capillary electrophoresis (CCE) is increasingly employed in the enantiomeric separation of various kinds of racemic mixtures. This is due to the fact that CCE is a simple, rapid and practical method yet it provides high separation efficiency, and requires small sample and reagent volumes. Various direct and indirect CCE approaches have been exploited in enantiomeric separation. One direct approach involves inclusion complexation in the presence of cyclodextrins (CDs) either in an open tubular format [1–10] or CDs immobilized in gel-filled capillaries [11,12] or CDs bonded to the walls of fused-silica capillaries [13,14]. Also, inclusion complexation was performed in the presence of crown ethers [15]. A second direct approach for CCE is based on solubilization by chiral micelles [16–18] or microemulsions [19]. Other direct approaches include: (i) affinity interaction in the presence of proteins [20,21] or polysaccharides [22], and (ii) ligand-exchange complexation [23,24]. Finally, derivatization to diastereoisomers forms the basis for

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indirect methods for chiral separation by CE [25,26]. The details of these various methods have been described in several recent reviews on the CE of enantiomers [27].

Very recently, our laboratory has introduced novel chiral micellar systems based on steroidal–glycoside surfactant–borate complexes [28] for the separation of several optical isomers including binaphthyl, Troger's base, dansyl amino acid and silvex herbicide enantiomers. In a more recent report we evaluated the use of mixed CDs in the separation of fluorescently labelled phenoxy acid herbicide enantiomers [29].

Thus far, all chiral separation involving micellar phases were performed with charged chiral micelles [30,31], in situ charged micelles [28], mixed achiral charged micelles/CDs [18,32] or mixed achiral charged micelles/chiral micelles [16,33]. This article, which is a continuation of our previous efforts in the area of CCE, reports for the first time the use of uncharged alkylglucoside chiral micelles in the separation of charged enantiomers, namely phenoxy acid herbicides. There are two major rationales for using phenoxy acid herbicides as model chiral solutes for evaluating the alkylglucoside chiral surfactants under investigation: (i) they are important agrochemicals, especially in the control of weeds in cereal crops [34], and (ii) they have systematic structural differences, e.g., nature, location and number of substitution on the benzene ring, as well as a structural similarity (i.e., the chiral center) which make them attractive enantiomeric solutes for evaluating chiral selectors.

As will be shown in this report, the use of uncharged micelles in the CCE of charged enantiomers offers a great deal of advantages in terms of manipulating the enantioselectivity by various operational variables such as the surfactant concentration, the ionic strength and pH of the running electrolyte and the capillary temperature.

2. Experimental

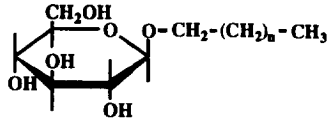
2.1. Capillary electrophoresis instrument

A Beckman P/ACE instrument (Beckman Instruments, Fullerton, CA, USA) Model 5510 equipped with a diode-array detector and a data-handling system comprising an IBM personal computer and System Gold software was used in this study. Detection was performed at 230 nm and the resulting signal was fed to the computer for archiving and real-time display of the electropherograms. The fused-silica capillaries were obtained from Polymicro Technology (Phoenix, AZ, USA) and had the dimensions of 50 cm (to detection window) and 57 cm (total length) with an I.D. of 50 μm and an O.D. of 365 μm. Unless otherwise stated, the temperature of the capillary was maintained at 15°C by the instrument thermostatting system. Samples were pressure injected as methanol–water solutions at 0.034 bar (i.e., 3.5 kPa) for various lengths of time.

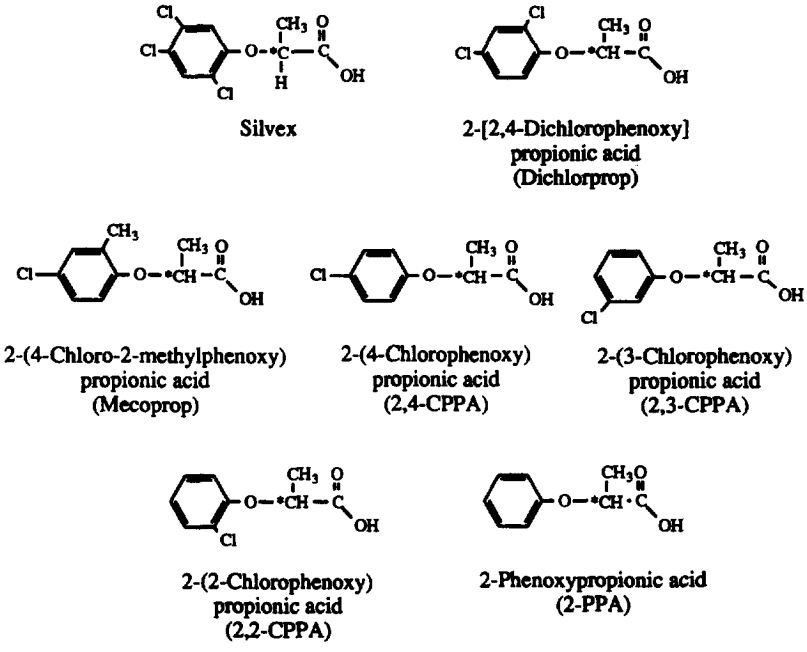
2.2. Reagents and materials

n-Octyl-β-D-glucopyranoside (OG) surfactant was purchased from Anatrace (Mumee, OH, USA) and *n*-nonyl-β-D-glucopyranoside (NG) surfactant was obtained from Sigma (St. Louis, MO, USA). The structures and the critical micellar concentration (CMC) of these surfactants are shown in Table 1. Phenoxy acid herbicides including silvex, 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop), 2-(4-chloro-2-methylphenoxy)propionic acid (mecoprop), 2-(4-chlorophenoxy)propionic acid (2,4-CPPA), 2-(3-chlorophenoxy)propionic acid (2,3-CPPA), 2-(2-chlorophenoxy)propionic acid (2,2-CPPA), and 2-phenoxypropionic acid (2-PPA) were purchased from Aldrich (Milwaukee, WI, USA) and from Chem Service (West Chester, PA, USA). The structures of the phenoxy acid herbicides used in this study are given in Scheme 1.

Table 1
Structures and CMCs of the alkylglucopyranosides used in this study

Structure and name of surfactant	Abbreviation	CMC (m*M*)[a]
		
n=6: Octyl-β-D-glucopyranoside	OG	25
n=7: Nonyl-β-D-glucopyranoside	NG	6.5

[a]Obtained from Ref. [38].



Scheme 1.

All chemicals used in the preparation of the separation electrolytes were obtained from Fisher Scientific (Pittsburgh, PA, USA).

3. Results and discussion

3.1. Effect of surfactant concentration and description of the separation principles

In aqueous solutions, and above their CMC, the alkylglucoside surfactants exist as micellar phases with the D-glucopyranoside chiral head group protruding from the micelle, (for structures of surfactants, see Table 1). Fig. 1 illustrates the electropherograms of phenoxy acid herbicides obtained at three different OG concentrations. As shown in Fig. 1, chiral resolution is achieved only at surfactant concentration above CMC, indicating that the presence of the chiral surfactant in the micellar form is critical for chiral recognition. In other words, solute–micelle association via polar and hydrophobic interactions are important components for the enantiomeric separation. On this basis, the enantiomeric resolution is achieved when the two enantiomers exhibit different association constants with the chiral micelles.

A schematic of the separation principles of anionic solutes (e.g., phenoxy acid herbicides) in the presence of the alkylglucoside micellar phases is depicted in Fig. 2. While the neutral micelles of the alkylglucoside surfactants migrate at the velocity of the electroosmotic flow (EOF), the electrophoretic mobility of an anionic analyte is opposite in direction to the cathodal EOF. Thus, the effective electrophoretic mobility, and, in turn, the migration time of an anionic solute (e.g., a phenoxy acid herbicide) will decrease as the magnitude of its association with the neutral micelle increases. In other words, the stronger the interaction between the analyte and the micelle the higher the apparent mobility of the anionic analyte, and, consequently, the faster its migration toward the cathode. This is seen in Fig. 1 where the migration time of silvex decreases from ca. 23 min to ca. 13 min when going from 10 m*M* OG to 60 m*M* OG while the migration time of the least interacting herbicide 2-PPA was slightly affected by the presence or the absence of the micelle, and decreased from ca. 31 min to ca. 27 min when the OG concentration increased from 10 to 150 m*M*. The slight increase in the migration time of 2-PPA when going from 10 to 60 m*M* OG can be attributed to the

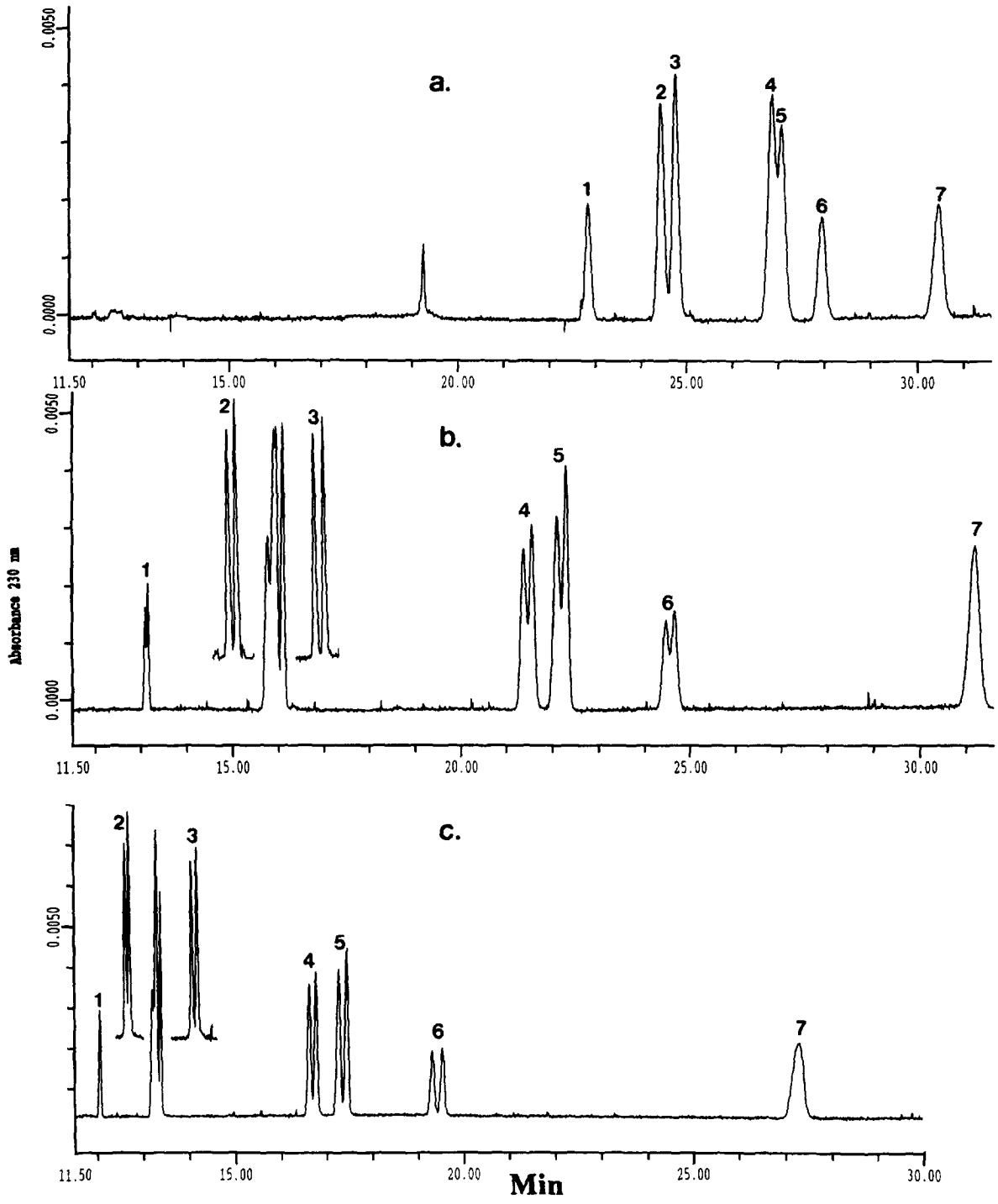


Fig. 1. Electropherograms of phenoxy acid herbicides depicting the effect of OG concentration on enantiomeric resolution. Conditions: running electrolyte, 200 m*M* sodium phosphate, pH 6.5, containing: (a) 10 m*M* OG, (b) 60 m*M* OG, and (c) 150 m*M* OG; capillary, 57 cm (50 cm to detection window)×50 μm I.D.; voltage, 20 kV; temperature 15°C. Peaks: 1=silvex, 2=dichlorprop, 3=mecoprop, 4=2,4-CPPA, 5=2,3-CPPA, 6=2,2-CPPA, 7=2-PPA.

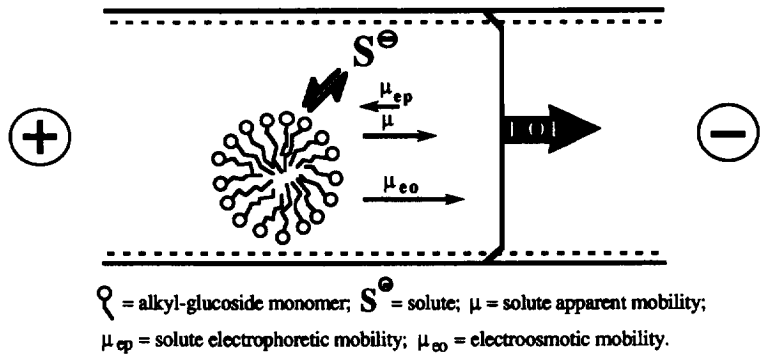


Fig. 2. Scheme illustrating the separation principles of charged species in the presence of neutral micelles.

increase in the viscosity of the running electrolyte.

Fig. 3 illustrates the variation in the average of the effective electrophoretic mobility of phenoxy acid herbicide enantiomers as a function of OG and NG concentrations. In all cases, the effective electrophoretic mobility of the analytes decreased as the concentration of the surfactant increased. This is due to the fact that by increasing the surfactant concentration [S], the micellized surfactant concentration ([S]-CMC) is increased, and, consequently, the number of micelles interacting with a given solute at any instant increases. The net result is an increase in the time the solute spends in the micellar phase. As shown in Fig. 3, silvex, dichlorprop and mecoprop exhibited a sharp decrease in their effective electrophoretic mobilities up to 60 m*M* OG and up to 30 m*M* NG, and this decrease became shallower at higher surfactant concentrations. The effective electrophoretic mobility of the other analytes, 2,4-CPPA, 2,3-CPPA and 2,2-CPPA, decreased almost monotonically with increasing OG and NG concentrations in the concentration range studied. It should be noted that the decrease in mobility at higher surfactant concentration is also partly due to the increase in the electrolyte viscosity.

Generally, and with uncharged surfactants, the magnitude of solute association with the micelle should increase with increasing solute hydrophobicity. Therefore, the order of the hydrophobicity of the different phenoxy acid herbicides seems to

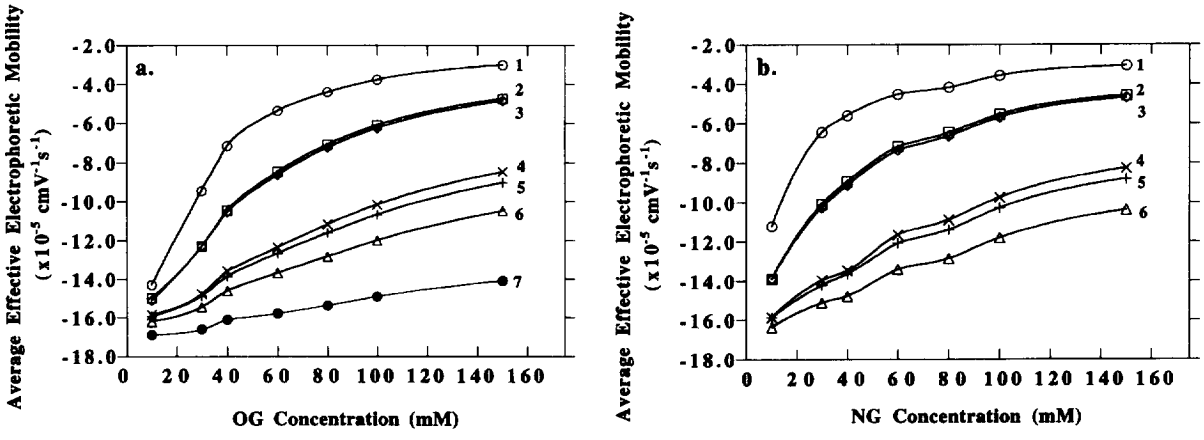


Fig. 3. Plots of the average effective electrophoretic mobility of phenoxy acid herbicides versus the concentration of: (a) OG, and (b) NG in the running electrolyte. Conditions: running electrolyte, 200 m*M* sodium phosphate, pH 6.5, containing various concentrations of: (a) OG, and (b) NG; capillary, 57 cm (50 cm to detection window)×50 μm I.D.; voltage, 20 kV; temperature 15°C. Lines: 1=silvex, 2=dichlorprop, 3=mecoprop, 4=2,4-CPPA, 5=2,3-CPPA, 6=2,2-CPPA, 7=2-PPA.

decrease in the following order, silvex ≫ dichlorprop>mecoprop ≫ 2,4 - CPPA>2,3 - CPPA> 2,2-CPPA ≫ 2-PPA, which is the same as the migration order. This correlates with the number of substituted nonpolar groups (i.e., Cl or CH_3) on the benzene rings. For 2,4-CPPA, 2,3-CPPA and 2,2-CPPA, the position of the chlorine atom seems to influence the net hydrophobicity of the solute. The closer the chloride atom to the oxygen atom the weaker the hydrophobicity of the phenoxy acid herbicides.

The effect of OG concentration on the enantiomeric resolution of the phenoxy acid herbicides under investigation is illustrated in Fig. 4. Resolution was calculated from the electropherogram using the equation $R_s=(t_{E2}-t_{E1})/[2(\sigma_{E2}+\sigma_{E1})]$ where t_{E2} and t_{E1} are the migration times of enantiomers 2 and 1, respectively, and σ_{E2} and σ_{E1} are the peak standard deviations of enantiomers 2 and 1, respectively. The optimum surfactant concentration for maximum enantiomeric resolution seems to decrease as the extent of the analyte solubilization in the OG micelle increases, which in the case of phenoxy acid herbicides seems to correlate with the hydrophobicity of the analyte. Generally, solute solubilization is believed to occur at a number of different sites in the micelle [35]: (i) on the surface of the micelle, i.e., at the micelle–solvent interface; (ii) between the hydrophillic head groups; (iii) in the so-called palaside layer of the micelle between the hydrophillic groups and the first few carbon atoms of the hydrophobic tails that comprise the outer core of the micellar interior; (iv) more deeply in the palaside layer; and (v) in the inner core of the micelle. Due to their ionic nature, the phenoxy acid herbicides are likely to be solubilized mainly in locus (iii) between the individual molecules of the surfactant in the palaside layer, with the polar group of the solute, which is also the chiral center, oriented toward the polar, chiral group of the alkylglucoside surfactant and the nonpolar portion oriented toward the interior of the micelle. Depth of penetration in the palaside layer depends on the ratio of polar to nonpolar structures in the phenoxy acid herbicide molecules, with the less-polar compounds penetrating more deeply than the more polar (i.e., less substituted) phenoxy acid herbicides. The depth of penetration will affect the enantioselectivity of the system. The deeper the solute will penetrate, the more its optical center will be pulled away from interacting with the chiral head group of the surfactant molecule, and, consequently, there will be a decreased enantioselectivity. On the other extreme of the spectrum, the weaker the solubilization of the solute in the micelle, the less probable is the association between the micelle and the solute chiral centers, and the enantiomeric resolution is lower. Silvex, the most hydrophobic species among the analytes used in this study, attained maximum enantiomeric resolution at 40 m*M* OG, while the enantiomeric resolution of the weakly hydrophobic solutes, namely 2,4-CPPA, 2,3-CPPA and 2,2-CPPA, improved as OG concentration increased. Increasing the surfactant concentration results in an increase of the concentration of the chiral centers in the overall micellar phase as well as an increase of the nonpolar phase ratio in the electrolyte system. Thus, for silvex, increasing OG concentration beyond 40 m*M* would have provided more chiral centers in the micellar phase than the optimum value for maximum resolution and/or increasing the OG concentration has resulted in the solute interacting more with the nonpolar portion than with the sugar chiral head groups in the palaside layer of the micelle. For the solutes of intermediate hydrophobicity, e.g., mecoprop and dichlorprop, the enantiomeric resolution of these two solutes reached maximum values at 60 and 80 m*M*, respectively. The optimum surfactant concentration for maximum resolution is in the low range for hydrophobic solutes and in the high range for the less hydrophobic ones.

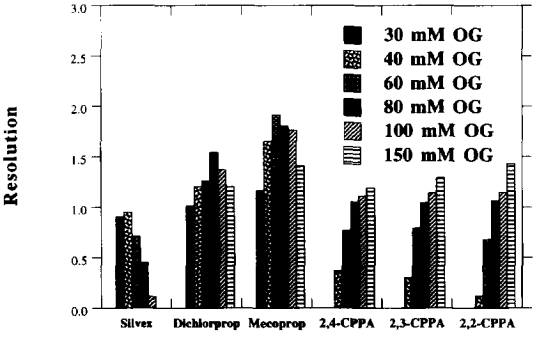


Fig. 4. Bar graphs of the enantiomeric resolution of phenoxy acid herbicides at different OG concentrations. Experimental conditions as in Fig. 1.

The alkyl chain of NG has one more carbon atom

than the alkyl chain of OG, and the CMC value of NG is four times lower than that of OG (see Table 1). As a result, the NG concentration needed to attain enantiomeric resolution is less than that needed for OG (compare Fig. 4 to Fig. 5). However, the dependence of the enantiomeric resolution on NG concentration followed the same trend as that observed with OG. In other words, optimum enantiomeric resolution was attained for silvex at low NG concentration, for dichlorprop and mecoprop at intermediate NG concentration, and for 2,4-CPPA, 2,3-CPPA and 2,2-CPPA at high NG concentration. Again, no enantiomeric resolution of 2-PPA was observed even at 150 m*M* NG. The electropherograms of the phenoxy acid herbicides obtained at various NG concentrations are illustrated in Figs. 6a–c. Note, silvex, dichlorprop and mecoprop were enantiomerically separated using 10 m*M* NG, since the CMC value of NG is 6.5 m*M*. Moreover, at this low surfactant concentration, 2,4-CPPA and 2,3-CPPA as well as dichlorprop and mecoprop co-migrated. Again, as the concentration of the surfactant increased the migration time of the analytes decreased in a proportion that reflected the hydrophobicity of the analytes. The migration time of 2-PPA exceeded 45 min at 10 and 60 m*M* NG and decreased substantially to ca. 27 min at 150 m*M* NG.

In summary, the chiral selectivity of the alkylglucoside surfactants is based on the interaction between the analyte and the optically active glucopyranoside residue of the surfactant in the micellar phase. This was deduced from the fact that the enantiomeric selectivity toward the phenoxy acid herbicides was not achieved using the alkylglucoside surfactants at concentrations below CMC. In the concentration range above CMC, increasing the concentration of the surfactant increases the micellized surfactant concentration, i.e., [S]-CMC, thus ensuring an increasing number of chiral sites in the micellar form. However, optimum enantiomeric resolution is attained at a certain surfactant concentration, which is inversely proportional to the hydrophobicity of the analytes. As expected, and because of the lower CMC value, increasing the length of the alkyl tail of the surfactant leads to an optimum enantiomeric resolution at lower surfactant concentrations. Other factors were also found to influence the enantiomeric resolution, including the ionic strength of the buffer as well as the separation temperature; see below.

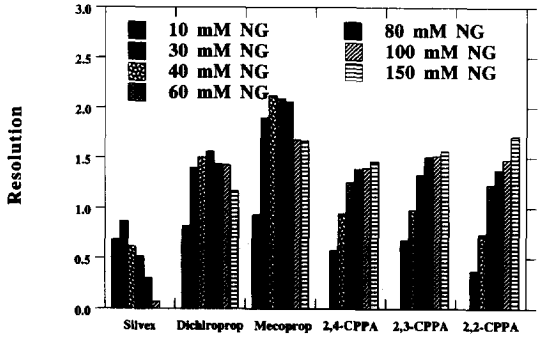


Fig. 5. Bar graphs of the enantiomeric resolution of phenoxy acid herbicides at different NG concentrations. Conditions: running electrolyte, 200 m*M* sodium phosphate, pH 6.5, containing various NG concentrations. Other experimental conditions as in Fig. 3.

3.2. Effects of pH and ionic strength

As expected, the pH of the running electrolyte influenced the electrophoretic system under investigation. The enantiomeric resolution decreased as the pH was increased due to the increasing ionization of the phenoxy acid herbicides which is believed to decrease the solute solubilization into the micelle (results not shown). On the other hand, as the pH increased the EOF increased too, and, consequently, the migration time decreased. Thus, pH 6.5 was a compromise in terms of obtaining satisfactory enantiomeric resolution and analysis time.

The effect of the ionic strength of the running electrolyte on the enantiomeric resolution is illustrated in Fig. 7. Increasing the ionic strength of the running electrolyte seems to improve the enantiomeric resolution of all analytes. Increasing the ionic strength of the separation electrolyte decreases the EOF as well as the effective electrophoretic mobility of the analytes with an overall decrease in the apparent mobility of the analytes, i.e., increasing the analysis time (results not shown). Also, increasing the ionic strength of the running electrolyte is known to cause a decrease in the CMC of the surfactant and an increase in the aggregation number [36,37]. This will increase the micellized surfactant concentration ([S]-CMC) and will also increase the concentration of chiral centers in the micellar form. In addition,

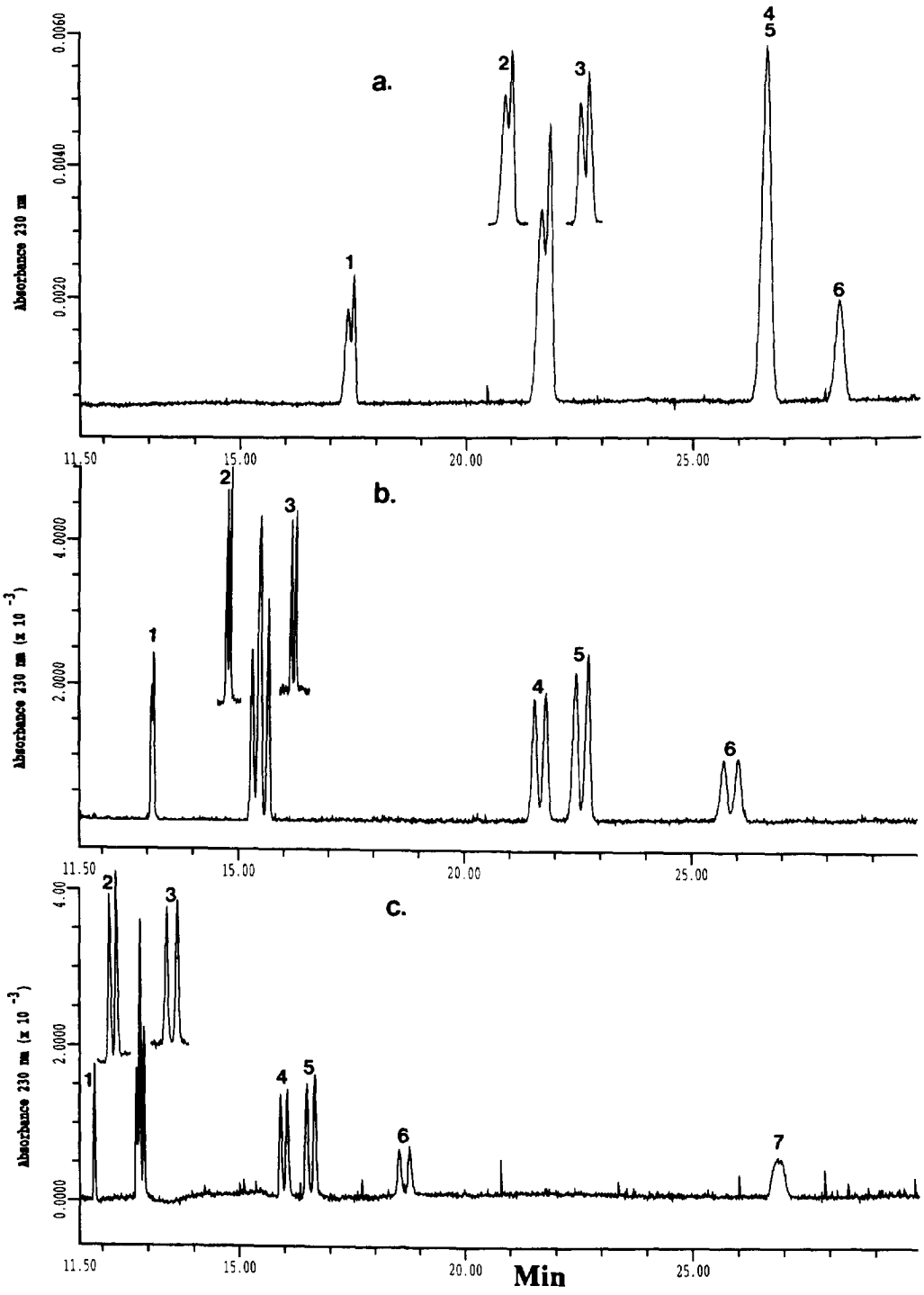


Fig. 6. Electropherograms of phenoxy acid herbicides depicting the effect of NG concentration on enantiomeric resolution. Conditions: running electrolyte, 200 m*M* sodium phosphate, pH 6.5, containing: (a) 10 m*M* NG, (b) 60 m*M* NG, and (c) 150 m*M* NG. Other conditions as in Fig. 3. Peaks: 1=silvex, 2=dichlorprop, 3=mecoprop, 4=2,4-CPPA, 5=2,3-CPPA, 6=2,2-CPPA, 7=2-PPA.

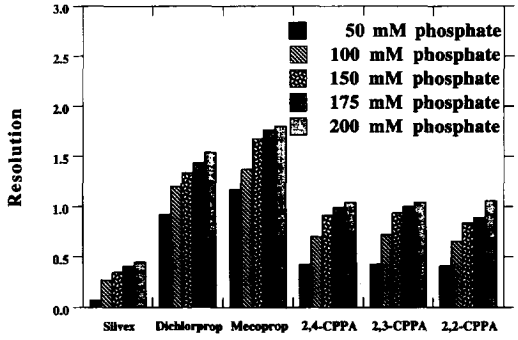


Fig. 7. Bar graphs of the enantiomeric resolution of phenoxy acid herbicides at different ionic strengths of the running electrolyte. Conditions: running electrolyte, various sodium phosphate concentrations, pH 6.5, containing 80 m*M* OG. Other experimental conditions as in Fig. 3.

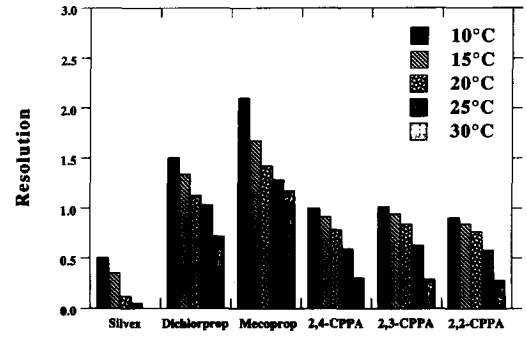


Fig. 8. Bar graphs of the enantiomeric resolution of phenoxy acid herbicides at different temperatures. There were various separation temperatures; running electrolyte, 150 m*M* sodium phosphate, pH 6.5, containing 80 m*M* OG. Other experimental conditions as in Fig. 3.

increasing the ionic strength has a salting out effect which should afford stronger nonpolar interaction between the solutes and the chiral micelles. Thus, increasing the ionic strength of the running electrolyte may result in enhancing both solute solubilization into the micelle and solute chiral association with the chiral micelle. These two effects are likely to explain the increase in the enantiomeric resolution of all analytes at high ionic strength. On the other hand, increasing the ionic strength resulted in longer analysis time from ca. 13 min at 50 m*M* sodium phosphate to ca. 30 min at 200 m*M* sodium phosphate. It should be noted that there is a limit for increasing the ionic strength due to the increase in conductivity, and, consequently, Joule heating at elevated ionic strength. Under the conditions of Fig. 7, 200 m*M* phosphate was the limit to which the ionic strength could be increased without introducing undesirable Joule-heating effects.

3.3. Effect of temperature

As shown in Fig. 8, decreasing the separation temperature increased the enantiomeric resolution of all analytes. Temperature has various influences on the electrophoretic system under investigation. The effect of temperature on the CMC of surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increases in temperature [35]. The minimum in the CMC–temperature dependence is around 50°C for nonionic surfactants such as those used in this study [35]. Increasing temperature causes decreased hydration of the hydrophillic group, which favours micellization. This, in principle, should increase the number of interacting micelles in the temperature range 10–30°C, and, in turn, the enantiomeric resolution. However, increasing temperature favours the partitioning of the solute in the aqueous phase, and this may explain the continuous decrease in the enantiomeric resolution as the temperature is increased from 10 to 30°C. Also,

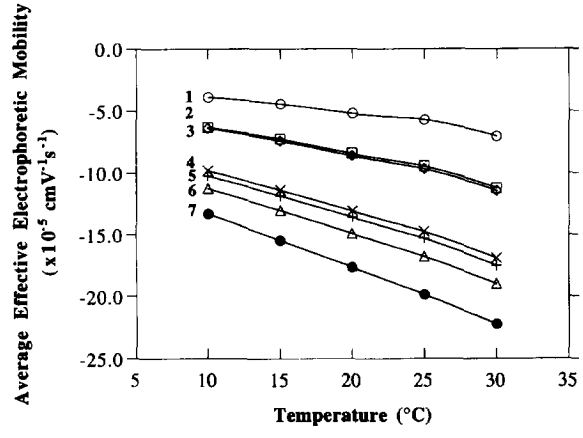


Fig. 9. Plots of the effective electrophoretic mobility of phenoxy acid herbicides versus separation temperature. Conditions: running electrolyte, 150 m*M* sodium phosphate, pH 6.5, containing 80 m*M* OG. Other experimental conditions as in Fig. 3. Curves: 1=silvex, 2=dichlorprop, 3=mecoprop, 4=2,4-CPPA, 5=2,3-CPPA, 6=2,2-CPPA, 7=2-PPA.

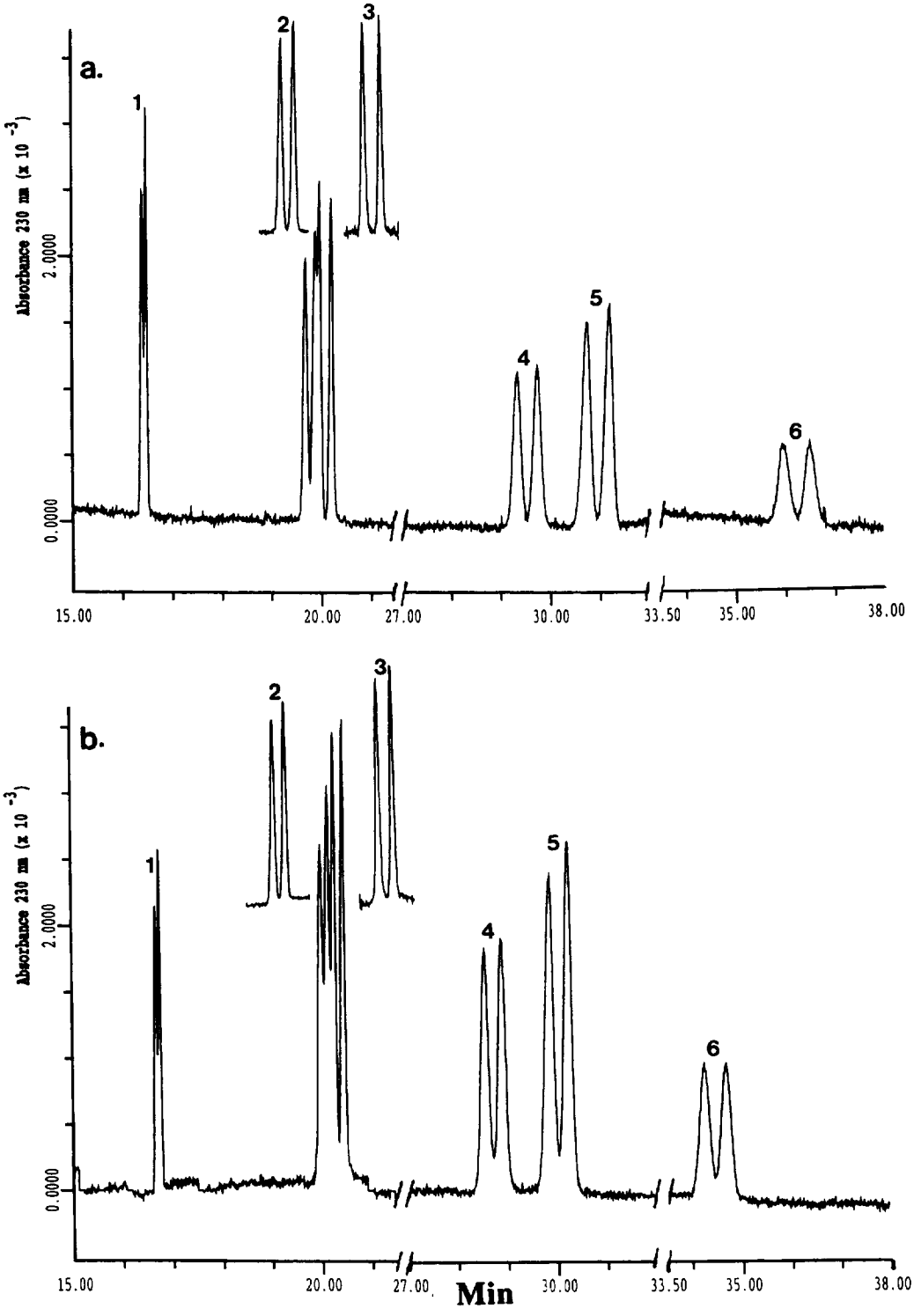


Fig. 10. Electropherograms of phenoxy acid herbicides depicting optimum enantiomeric resolution using: (a) NG, or (b) OG. Conditions: running electrolyte, 250 m*M* sodium phosphate, pH 6.5, containing: (a) 50 m*M* NG, and (b) 70 m*M* OG; temperature, 10°C. Other experimental conditions as in Fig. 3.

increasing temperature decreases the viscosity of the separation buffer. This effect combined with the decrease in the partitioning of the solute in the micelle may have resulted in increasing the effective electrophoretic mobility of all analytes as the separation temperature increased (Fig. 9).

3.4. Chiral separation under optimized conditions

Optimization of all of the aforementioned parameters (i.e., surfactant concentration, ionic strength and temperature) allowed the enantiomeric resolution of all analytes in a single run using NG (Fig. 10a) or OG (Fig. 10b). Baseline enantiomeric resolution of all analytes except silvex was attained by performing the separation at 10°C and using 250 m*M* sodium phosphate buffer, pH 6.5, containing 50 m*M* NG or 70 m*M* OG. Again, and as expected, higher enantiomeric resolution for all analytes except silvex were attained with NG. Also, with NG maximum enantiomeric resolution was attained at less surfactant concentration than with OG.

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