

Application of the Retention Index Concept in Micellar Electrokinetic Capillary Chromatography

Citation for published version (APA):

Muijselaar, W. G. H. M., Claessens, H. A., & Cramers, C. A. (1994). Application of the Retention Index Concept in Micellar Electrokinetic Capillary Chromatography. *Analytical Chemistry*, 66(5), 635-644.
<https://doi.org/10.1021/ac00077a009>

DOI:

[10.1021/ac00077a009](https://doi.org/10.1021/ac00077a009)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Application of the Retention Index Concept in Micellar Electrokinetic Capillary Chromatography

Pim G. H. M. Muljselaar,* Henk A. Claessens, and Carel A. Cramers

Laboratory of Instrumental Analysis, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The application of the retention index concept in micellar electrokinetic capillary chromatography (MECC) was evaluated for the identification of neutral species. Homologous series of alkylbenzenes and alkylaryl ketones were applied as retention index standards and also for the calculation of the micelle migration time by an iteration procedure. The relationship between retention indexes, I , and octanol-water partition coefficients is discussed, and ΔI values were calculated from retention indexes, obtained with both anionic and cationic surfactant systems, to study the separation mechanism for solutes with different functionalities in MECC. The influence of the phase ratio is treated theoretically, and it is demonstrated that the capacity factor is linearly related to the surfactant concentration, whereas the retention index is independent of the surfactant concentration. The temperature dependence of the retention index was investigated and the standard enthalpy, entropy, and Gibbs free energy for micellar solubilization of the sample compounds were determined, showing that the hydrophobic interaction plays a significant role in MECC analysis.

Micellar electrokinetic capillary chromatography (MECC) has proved to be a highly efficient separation technique with a great variety of applications. Because of the lipophilic character of the micelles, usually applied in aqueous electrolyte systems, neutral compounds can be separated, even if they are almost insoluble in water. Since the introduction of MECC by Terabe et al.^{1,2} many different components have been analyzed using this technique, including phenols, amino acids, oligonucleotides, and several pharmaceuticals.³⁻⁸ Also attention has been paid to the application of different surfactants or mixed micelles to improve the selectivity in MECC.^{9,10} Analogous to other chromatographic techniques, the capacity factor is most frequently used as a parameter for peak identification. Ackermans et al.¹¹ introduced the pseudo

effective mobility for identification purposes, which also can be calculated if the migration time of the micelles is unknown.

In gas chromatography (GC) retention indexes have found widespread application for the identification of substances in complex matrices, because they are considered to express the retention with the best reproducibility and precision.¹²⁻¹⁴ In 1958, Kovats described the fundamental concept and derived the basic equations for the retention index system. Retention indexes in GC are not only applied for peak identification but also as an aid in structure analysis and for the evaluation of stationary phases. In reversed-phase high-performance liquid chromatography (HPLC) retention indexes have found use in peak identification, the investigation of structure-activity relationships and the characterization of different eluents and reversed-phase stationary phases.¹⁵⁻¹⁹ In this paper we describe the applicability of the retention index system for neutral species in MECC.

THEORY

The separation mechanism of neutral species in MECC is based on the partitioning of the sample components between an aqueous mobile phase and a micellar phase, of which the interior is lipophilic. Migration data in MECC are mostly expressed by means of the capacity factor, k , which can be calculated according to the equation^{1,2}

$$k = \frac{\eta_{MC}}{\eta_{AQ}} = \frac{t_S - t_{EOF}}{t_{EOF}(1 - t_S/t_{MC})} \quad (1)$$

where η_{MC} and η_{AQ} are the number of moles of the solute in the micellar phase and the aqueous phase, respectively, and t_S , t_{EOF} , and t_{MC} are the migration times of the solute, a neutral insoluble component to determine the electroosmotic flow (EOF), and a component completely solubilized by the micelles (micelle marker), respectively. In contrast to most other chromatographic techniques, in MECC, two moving phases can be distinguished, viz., an electroosmotically pumped aqueous phase and a pseudostationary micellar phase. Hence both the velocity of the EOF and the velocity of the micelles

- (1) Terabe, S.; Otsuka, K.; Ichikawa, K.; Tsuchiya, A.; Ando, T. *Anal. Chem.* **1984**, *56*, 111.
- (2) Terabe, S.; Otsuka, K.; Ando, T. *Anal. Chem.* **1985**, *57*, 834.
- (3) Otsuka, K.; Terabe, S.; Ando, T. *J. Chromatogr.* **1985**, *348*, 39.
- (4) Otsuka, K.; Terabe, S.; Ando, T. *J. Chromatogr.* **1985**, *332*, 219.
- (5) Cohen, A. S.; Terabe, S.; Smith, J. A.; Karger, B. L. *Anal. Chem.* **1987**, *59*, 1021.
- (6) Burton, D. E.; Sepaniak, M. J.; Maskarinec, M. P. *J. Chromatogr. Sci.* **1986**, *24*, 347.
- (7) Wernly, P.; Thormann, W. *Anal. Chem.* **1991**, *63*, 2878.
- (8) Nishi, H.; Fukuyama, T.; Matsuo, M.; Terabe, S. *J. Pharm. Sci.* **1990**, *79*, 519.
- (9) Wallingford, R. A.; Curry, P. D.; Ewing, A. G. *J. Microcolumn Sep.* **1989**, *1*, 23.
- (10) Little, E. L.; Foley, J. P. *J. Microcolumn Sep.* **1992**, *4*, 145.
- (11) Ackermans, M. T.; Everaerts, F. M.; Beckers, J. L. *J. Chromatogr.* **1991**, *585*, 123.

- (12) Kovats, E. *Helv. Chim. Acta* **1958**, *41*, 1915.
- (13) Budahegyi, M. V.; Lombosi, E. R.; Lombosi, T. S.; Mészáros, S. Y.; Nyiredy, Sz.; Tarján, G.; Timár, I.; Takács, J. M. *J. Chromatogr.* **1983**, *271*, 213.
- (14) Pacáková, V.; Feltl, L. *Chromatographic Retention Indices*; Ellis Horwood: New York, 1992.
- (15) Baker, J. K. *Anal. Chem.* **1979**, *51*, 1693.
- (16) Smith, R. M. *J. Chromatogr.* **1982**, *236*, 313.
- (17) Smith, R. M. *Anal. Chem.* **1984**, *56*, 256.
- (18) West, S. D. *J. Chromatogr. Sci.* **1989**, *27*, 2.
- (19) Smith, R. M. Retention Indices in Reversed-Phase HPLC. In *Advances in Chromatography*; Giddings, J. C., Keller, R. A., Eds.; Dekker: New York, 1987; Vol. 26, p 277.

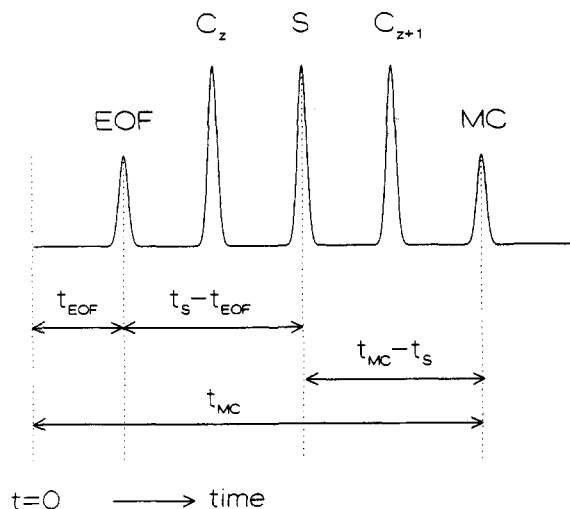


Figure 1. Schematic illustration of an electrokinetic chromatogram of an EOF marker (EOF), a neutral solute (S), and a micelle marker (MC) with the corresponding ratios of the migration times. C_z and C_{z+1} are the two neighboring members of a homologous series for solute S with z and $z + 1$ carbon atoms, respectively.

are characteristic for an MECC analysis. These two velocities determine the elution window t_{MC}/t_{EOF} , which influences the resolution. The capacity factor of a neutral solute can be regarded as the migration time of the solute, related to both t_{EOF} and t_{MC} , according to

$$k = \frac{((t_s - t_{EOF})/t_{EOF})}{((t_{MC} - t_s)/t_{MC})} = \frac{t_s - t_{EOF}}{t_{MC} - t_s} \frac{t_{MC}}{t_{EOF}} \quad (2)$$

This is illustrated in Figure 1.

Analogue to the Kovats retention index scale in GC,¹² a retention index scale in MECC can be derived, based on a homologous series with an increasing number of methylene groups.²⁰ The members of the homologous series are assigned retention index values equal to 100 times the number of their carbon atoms, z ; i.e., benzene has a retention index equal to 600, toluene 700, ethylbenzene 800, etc. The retention index of a solute can be calculated by the logarithmic interpolation between the two neighboring members of the homologous series, according to the equation

$$I = 100z + 100 \frac{\log k_s - \log k_z}{\log k_{z+1} - \log k_z} \quad (3)$$

where k_z and k_{z+1} are the capacity factors of the homologues with z and $z + 1$ carbon atoms, respectively, and k_s is the capacity factor of the solute. From eq 3 it can be seen that the retention index, just as the capacity factor, is independent of the elution window. Combination of eqs 2 and 3 leads to an expression for the retention index as a function of the migration times:

$$I = 100z + 100 \frac{\log\left(\frac{t_s - t_{EOF}}{t_{MC} - t_s}\right) - \log\left(\frac{t_z - t_{EOF}}{t_{MC} - t_z}\right)}{\log\left(\frac{t_{z+1} - t_{EOF}}{t_{MC} - t_{z+1}}\right) - \log\left(\frac{t_z - t_{EOF}}{t_{MC} - t_z}\right)} \quad (4)$$

Compared to capacity factors, retention indexes of hydrophilic components are less sensitive to uncertainties in the

determination of t_{EOF} and retention indexes of hydrophobic components are less sensitive to uncertainties in the determination of t_{MC} . Moreover, the retention index is not influenced by the phase ratio, i.e., is independent of the surfactant concentration. Therefore retention indexes provide more accurate qualitative data in MECC. Calculation of ΔI values from retention indexes obtained with different surfactant systems can also provide information about the interaction phenomena between sample molecules with different functionalities and micelles in MECC experiments. For these reasons, retention indexes are a valuable way of expressing migration data in MECC.

EXPERIMENTAL SECTION

Chemicals. Benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, sodium dodecyl sulfate (SDS), and decyltrimethylammonium bromide (DTAB) were obtained from Aldrich (Steinheim, Germany); acetophenone, propiophenone, butyrophenone, valerophenone, and hexanophenone from Pierce (Rockford, IL), and cetyltrimethylammonium bromide (CTAB) and tris(hydroxymethyl)aminomethane (TRIS) from Merck (Darmstadt, Germany). All other chemicals were of analytical-reagent grade.

Instrumentation. For all MECC experiments, a BioFocus 3000 capillary electrophoresis system (Bio Rad, Hercules, CA) was used. All separations were carried out in 50- μ m-i.d. fused-silica capillaries from Chrompack (Middelburg, The Netherlands). For the experiments with the anionic surfactant SDS, the total length was 50.05 cm and the distance between injection and detection was 45.45 cm. For the experiments with the cationic surfactants CTAB and DTAB, the total length was 50.55 cm and the distance between injection and detection was 45.90 cm. The wavelength of the UV detector was set at 200 or 225 nm.

Conductivity measurements were carried out with a CDM 83 conductivity meter (Radiometer, Copenhagen, Denmark), equipped with a type CDC 314 conductivity cell. The SDS solutions for conductivity measurements were thermostated with a water bath (Ultra Thermostat, Colora, Germany).

Separation Conditions. All analyses were carried out at 25 °C in an electrolyte system of 0.02 M TRIS adjusted to pH 8.5 by adding boric acid, with 50 mM of the appropriate surfactant, unless otherwise noted. Samples were introduced by pressure injection with an injection constant of 2 psi·s. For all experiments, a constant voltage of 20 kV was applied, except for the experiments with different temperatures, where a constant current of 10 μ A was applied. With the anionic surfactant SDS, the anode was placed at the inlet side and the cathode at the outlet side of the capillary, and vice versa with the cationic surfactants CTAB and DTAB.

Samples and Solutions. Besides the reference compounds, nine benzene derivatives with different functionalities were selected as the sample compounds. Resorcinol, phenol, and naphthalene were dissolved at a concentration of 0.0005 M and all other sample compounds at a concentration of 0.15 μ L/mL in a 50 mM solution of the appropriate surfactant, unless otherwise noted. Formamide was used as a neutral EOF marker. All CTAB solutions were stored at 30 °C. Water was purified by a Milli-Q water purification system

(20) Smith, D. M.; Strasters, J. K.; Khaledi, M. G. 16th International Symposium on Column Liquid Chromatography, Baltimore, MD, 1992; Poster 344.

Table 1. Average Values of the Capacity Factors, k , and Retention Indexes, I , with Standard Deviations (in Parentheses) for the Alkylbenzenes and the Alkylaryl Ketones with the Three Different Surfactants ($n = 5$)

compound	SDS		CTAB		DTAB	
	k	I	k	I	k	I
benzene	1.081(0.005)	598.2(0.1)	2.294(0.018)	601.1(1.0)	1.061(0.009)	598.3(0.2)
toluene	3.108(0.025)	704.6(0.2)	6.252(0.038)	701.7(0.9)	2.749(0.019)	705.1(0.2)
ethylbenzene	7.656(0.054)	795.5(0.2)	15.333(0.232)	791.8(1.3)	6.087(0.030)	794.3(0.3)
propylbenzene	21.685(0.185)	900.4(0.2)	46.328(2.972)	902.5(1.3)	15.784(0.060)	901.2(0.2)
butylbenzene	58.223(0.550)	1000.0(0.0)	122.415(9.011)	1000.0(0.0)	38.075(0.265)	1000.0(0.0)
acetophenone	1.844(0.011)	802.6(0.1)	1.656(0.012)	800.2(0.5)	0.837(0.009)	798.9(0.2)
propiophenone	3.957(0.023)	896.7(0.2)	4.048(0.019)	900.6(0.4)	1.894(0.028)	902.0(0.2)
butyrophenone	8.970(0.081)	997.6(0.3)	9.529(0.066)	996.7(0.9)	4.049(0.067)	998.0(0.2)
valerophenone	20.846(0.240)	1101.5(0.2)	23.957(0.707)	1100.2(0.8)	9.054(0.155)	1099.6(0.2)
hexanophenone	46.376(0.711)	1200.0(0.0)	58.286(1.892)	1200.0(0.0)	20.050(0.417)	1200.0(0.0)

(Waters Millipore, Milford, MA). All buffer solutions were filtered through a 0.45- μ m filter prior to use.

RESULTS AND DISCUSSION

Selection of a Homologous Series. Standard reference compounds for the determination of retention indexes in MECC should satisfy a number of requirements: (1) relationship between $\log k$ and the number of carbon atoms in the molecules of the homologues must be linear; (2) lowest homologue should be reasonably polar, in order to obtain a wide scale of retention indexes, covering the greater part of the elution window; (3) should contain a strong chromophore to detect them spectrophotometrically, as most capillary electrophoresis instruments apply on-column UV detection; (4) should not possess an electrophoretic mobility; i.e., they should be uncharged; (5) should be readily available at reasonable price; (6) should be chemically stable in common electrolyte systems; (7) should not interact with the fused-silica capillary wall.

According to the Martin equation,²¹ a homologous series with an increasing number of methylene groups shows a linear relationship between $\log k$ and the number of carbon atoms:

$$\log k = az + b \quad (5)$$

where z is the number of carbon atoms in the molecules of the homologues. The constant b is characteristic for the functional group of the homologues and depends on the phase ratio. Both the constants a and b depend on the nature of the aqueous phase and the micellar phase.²² The retention index, I , can be calculated by interpolation and for components migrating faster than the first homologue by extrapolation of the equation

$$\log k = a \frac{I}{100} + b \quad (6)$$

In first instance a number of alkan-2-ones were applied, but these compounds have only a weak chromophore and no reasonable UV signal was obtained. Therefore, homologous series of alkylbenzenes and of alkylaryl ketones were tested as possible retention index standards. Five members of each series were analyzed, applying three different surfactants, viz., SDS, CTAB, and DTAB. From the observed migration times the capacity factors, k , were calculated and linear graphs were constructed for $\log k$ versus carbon number of the

homologues. From these graphs the retention indexes were calculated, according to eq 6. All observed migration times and calculated capacity factors and retention indexes are listed in Table 1. The small deviations in the retention index values of the homologues from their nominal values give an indication of the precision of this method. For the last homologue, the retention index equals the nominal value exactly, due to the iteration procedure for the determination of t_{MC} (vide infra). From these results it can be seen that for SDS benzene is the first homologue with the lowest capacity factor, whereas for CTAB and DTAB acetophenone is the first homologue with the lowest capacity factor. Moreover, for all components the calculated capacity factors obtained with DTAB are smaller than those obtained with CTAB, due to the smaller interior of the DTAB micelles and a higher amount of free surfactant molecules in the aqueous phase; the critical micelle concentrations (cmc's) for DTAB and CTAB in water at 25 °C are 15.64 and 0.92 mM, respectively.²³ The linear graphs for $\log k$ versus carbon number of the homologues are shown in Figure 2. As can be seen from Figure 2, with all surfactants, higher capacity factors are obtained for the alkylbenzenes compared to the alkylaryl ketones with an equivalent carbon number. The electroosmotic mobility, m_{EOF} , the effective mobility of the micelles, m_{MC} , and the regression data for the graphs in Figure 2 are given in Table 2.

From these results it can be concluded that both the alkylbenzenes and the alkylaryl ketones show a linear relationship between $\log k$ and the carbon number of the homologues. Hence, both homologous series can be used as retention index standards in MECC. For the anionic surfactant SDS, the alkylbenzenes are to be preferred with respect to the scale of the capacity factors, whereas for the cationic surfactants CTAB and DTAB, the alkylaryl ketones are more favourable.

Determination of the Micelle Migration Time. According to eqs 1 and 4, both t_{EOF} and t_{MC} must be known in order to calculate the capacity factor and the retention index. Formamide proved to be a suitable EOF marker in MECC because it is a neutral compound that absorbs UV radiation and is not solubilized by the micelles. The micelle migration time can be determined by a compound which is completely solubilized by the micelles, such as Sudan III, anthracene, or timepidium

(21) Karger, B. L.; Snyder, L. R.; Horvath, C. *An Introduction to Separation Science*; Wiley & Sons: New York, 1973; p 55.

(22) Colin, M.; Guiochon, G. *J. Chromatogr. Sci.* **1980**, *18*, 54.

(23) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; National Bureau of Standards: Washington DC, 1971; NSRDS-NBS 36, p 51.

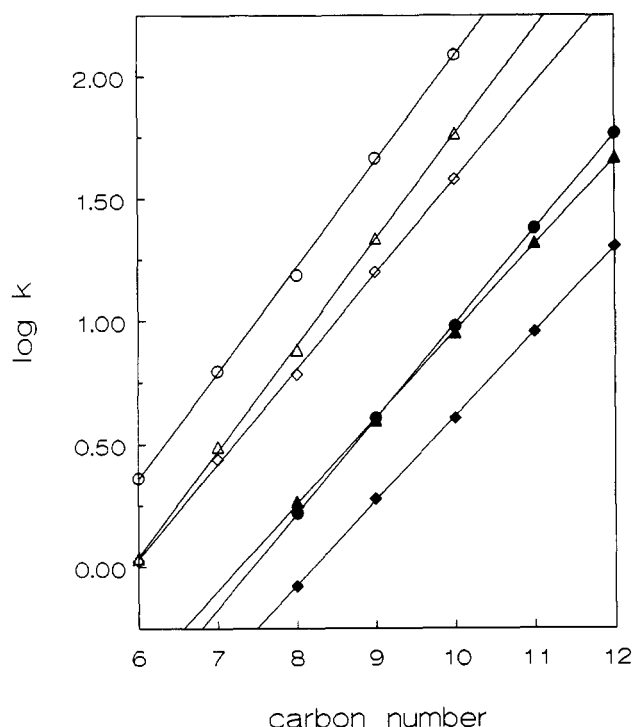


Figure 2. Relationship between $\log k$ and carbon number for the alkylbenzenes (open symbols) and the alkylaryl ketones (closed symbols) applying a background electrolyte containing (Δ) 50 mM SDS, (\circ) 50 mM CTAB, or (\diamond) 50 mM DTAB.

bromide.²⁴ In an alternative method, described by Bushey and Jorgenson,^{25,26} the migration data of a homologous series are used to determine t_{MC} by an iteration procedure. The migration time of the last homologue is used as an estimation for t_{MC} . With this t_{MC} , the capacity factors of the other homologues are calculated and a linear graph of $\log k$ versus carbon number is constructed for these components. From this graph, the capacity factor for the last homologue is determined and with the migration time a new t_{MC} is calculated, using eq 1. With this new t_{MC} , the capacity factors of the other homologues are recalculated. This iteration procedure is repeated until the difference in consecutive calculated t_{MC} values is considered negligible. It is obvious that the linear graph of $\log k$ versus carbon number of the homologous series, constructed for the determination of t_{MC} , can be applied for the calculation of the retention indexes, according to eq 6.

In order to compare these two methods for the determination of t_{MC} , experiments were carried out with the homologous series of alkylbenzenes and alkylaryl ketones with Sudan III as a micelle marker. In Figure 3 are shown the electrokinetic chromatograms of the separation of the alkylbenzenes and the alkylaryl ketones, applying a background electrolyte containing 50 mM SDS. The difference in the migration time of Sudan III in these electrokinetic chromatograms is a result of a small difference in the EOF. The t_{MC} was calculated from the observed migration times of the homologues, using a laboratory-written iteration program. The iteration procedure was continued until the difference between consecutive calculated t_{MC} values was smaller than

0.1%. All measured migration times and the calculated values for t_{MC} are listed in Table 3. In this table are included the calculated capacity factors, using the migration time of Sudan III as t_{MC} . As can be seen from these results, the values for t_{MC} , calculated with the iteration procedure, are higher than the migration time of Sudan III in both cases. The micellization of Sudan III probably causes a small decrease in the effective mobility of the micelles. As a consequence, the calculated capacity factors, using the migration time of Sudan III as t_{MC} , are higher than the calculated capacity factors, using the iterative obtained t_{MC} (see Table 1), especially for components migrating near t_{MC} . Although these differences are observed, both methods provide reproducible results and the differences between the calculated effective mobilities of the micelles are rather small; 0.16×10^{-5} and 0.33×10^{-5} $\text{cm}^2/\text{V}\cdot\text{s}$ for the alkylbenzenes and the alkylaryl ketones, respectively. Hence, both methods can be used for the determination of the micelle migration time in MECC with aqueous electrolyte systems. In all further experiments, the laboratory-written iteration program was used for the calculation of t_{MC} .

Determination of Capacity Factors and Retention Indexes.

In order to determine the capacity factors and retention indexes of the sample compounds, experiments were carried out with a sample mixture consisting of resorcinol, aniline, phenol, benzaldehyde, nitrobenzene, acetophenone, chlorobenzene, bromobenzene, naphthalene, and the five alkylbenzenes as the retention index standards with the anionic surfactant SDS. The electrokinetic chromatogram of this sample mixture in a background electrolyte containing 50 mM SDS is shown in Figure 4. To investigate the influence of a rinsing procedure, the experiments were performed with and without rinsing the capillary between analyses for 2 min with background electrolyte, respectively. The experiments were carried out 10 times and the capacity factors, k , and the retention indexes, I , were calculated from the observed migration times, t , using eqs 1 and 6. As can be seen from the results, listed in Table 4, both the capacity factor and the retention index can be used for peak identification in MECC. However, the retention index shows a better repeatability. This is mainly because it is a relative quantity that is less sensitive to small fluctuations in the experimental conditions than the capacity factor.¹⁴ Rinsing of the capillary with background electrolyte between analyses had no significant influence on the repeatability of the migration times.

In Figure 5 is shown the electrokinetic chromatogram of the separation of the sample mixture in a background electrolyte containing 50 mM DTAB, with the five alkylaryl ketones as the retention index standards. Resorcinol, chlorobenzene, and naphthalene coeluted with propiophenone, butyrophenone, and hexanophenone, respectively. Therefore, these compounds were omitted in the sample mixture.

Correlation between Retention Indexes and Octanol-Water Partition Coefficients and Calculation of ΔI Values. In HPLC, the correlation between retention indexes and octanol-water partition coefficients has been used for the examination of structures and physical properties of the analytes and for the prediction of retention characteristics. Also, the octanol-water partition coefficients have proved to be useful for the quantitative correlation of biological activity with chemical

(24) Vindevogel, J.; Sandra, P. *Introduction to Micellar Electrokinetic Chromatography*; Hüthig: Heidelberg, 1992; p 55.

(25) Bushey, M. M.; Jorgenson, J. W. *Anal. Chem.* 1989, 61, 491.

(26) Bushey, M. M.; Jorgenson, J. W. *J. Microcolumn Sep.* 1989, 1, 125.

Table 2. Slope, Intercept, and Correlation Coefficient for the Graphs shown in Figure 2, Electroosmotic Mobility, m_{EOF} (10^{-5} cm²/V s), and Effective Mobility of the Micelles, m_{MC} (10^{-5} cm²/V s), with Standard Deviations (in Parentheses) for the Three Different Surfactants and Measured Electric Current (μ A) ($n = 5$)^a

surfactant	compd ^a	slope	intercept	corr coeff	m_{EOF}	m_{MC}	measd current
SDS	I	0.43	-2.54	0.999 76	53.40(0.13)	-38.82(0.13)	13.1
	II	0.35	-2.56	0.999 83	55.46(0.07)	-39.25(0.06)	13.2
CTAB	I	0.43	-2.24	0.999 11	-72.26(0.36)	41.22(0.28)	11.7
	II	0.39	-2.87	0.999 81	-72.20(0.40)	40.75(0.24)	11.5
DTAB	I	0.39	-2.29	0.999 67	-54.96(0.25)	35.19(0.24)	20.0
	II	0.34	-2.82	0.999 85	-57.08(0.56)	35.41(0.07)	20.0

^a I, homologous series of alkylbenzenes; II, homologous series of alkylaryl ketones.

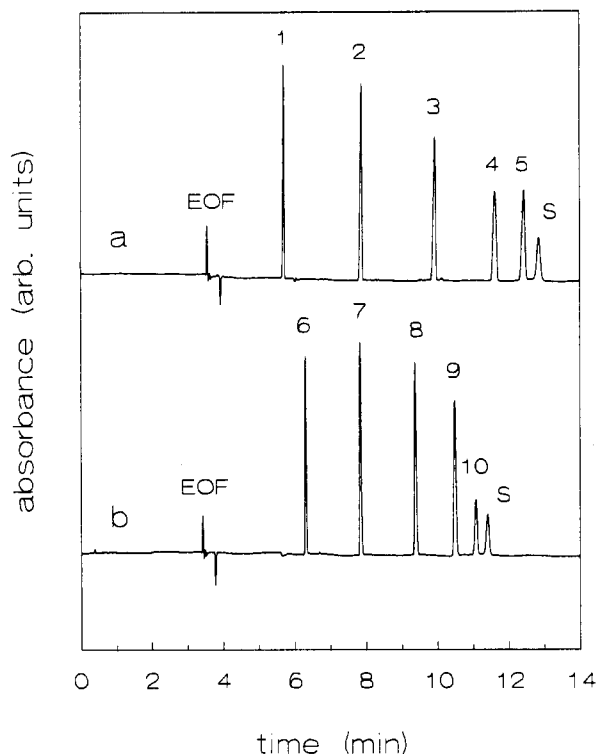


Figure 3. Electrokinetic chromatograms of the separation of (a) the alkylbenzenes (1) benzene, (2) toluene, (3) ethylbenzene, (4) propylbenzene, and (5) butylbenzene and (b) the alkylaryl ketones (6) acetophenone, (7) propiophenone, (8) butyrophenone, (9) valerophenone, and (10) hexanophenone with Sudan III (S) as t_{MC} marker applying a background electrolyte containing 50 mM SDS. Detection wavelength, 200 nm. The concentrations of the alkylbenzenes and the alkylaryl ketones were 0.50 and 0.06 μ L/mL, respectively.

structure. Baker¹⁵ and Veith et al.²⁷ observed a linear relationship between the retention index and the logarithm of the octanol-water partition coefficient ($\log P$) for several organic compounds. The octanol-water partition coefficient is usually measured by UV spectroscopy. In Table 5 are listed $\log P$ values, taken from the literature, for the alkylbenzenes and the nine benzene derivatives with different functionalities.

If the distribution mechanism of the analytes in MECC follows the same free energy relationship as the distribution in the octanol-water system, both $\log k$ and I will be linearly related to $\log P$. In order to determine the correlation between the retention index and the octanol-water partition coefficient, a graph was constructed of the retention indexes, listed in Table 4 (I), versus the $\log P$ values, listed in Table 5. As can be seen from this graph, shown in Figure 6, a linear relationship is obtained between I and $\log P$ for the homologous series of

Table 3. Average Migration Times, t (min), and Calculated Capacity Factors, k , Using Sudan III as the Micelle Marker with Standard Deviations (in Parentheses) for the Alkylbenzenes and the Alkylaryl Ketones in a Background Electrolyte Containing 50 mM SDS ($n = 5$)

compound	t	k
formamide (EOF)	3.55(0.01)	0
benzene	5.70(0.01)	1.091(0.005)
toluene	7.89(0.02)	3.163(0.026)
ethylbenzene	9.94(0.03)	7.948(0.058)
propylbenzene	11.63(0.03)	23.994(0.210)
butylbenzene	12.44(0.03)	77.766(1.199)
Sudan III	12.85(0.03)	∞
MC (calcd) ^a	13.00(0.03)	
formamide (EOF)	3.42(0.00)	0
acetophenone	6.32(0.02)	1.890(0.011)
propiophenone	7.87(0.03)	4.157(0.044)
butyrophenone	9.41(0.04)	9.803(0.076)
valerophenone	10.53(0.04)	25.618(0.195)
hexanophenone	11.12(0.05)	77.804(0.908)
Sudan III	11.46(0.05)	∞
MC (calcd) ^a	11.69(0.05)	

^a MC is the calculated value for t_{MC} according to the iteration procedure.

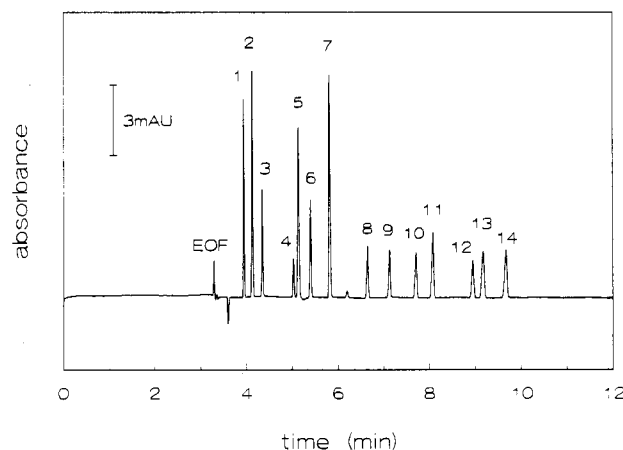


Figure 4. Electrokinetic chromatogram of the separation of (1) resorcinol, (2) aniline, (3) phenol, (4) benzene, (5) benzaldehyde, (6) nitrobenzene, (7) acetophenone, (8) toluene, (9) chlorobenzene, (10) bromobenzene, (11) ethylbenzene, (12) naphthalene, (13) propylbenzene, and (14) butylbenzene applying a background electrolyte containing 50 mM SDS. Detection wavelength, 200 nm.

the alkylbenzenes. The nonpolar compounds chlorobenzene, bromobenzene, and naphthalene also follow this relationship. The polar compounds, however, show a deviation from the curve. These results indicate that nonpolar and polar compounds are solubilized in different ways. In aqueous solutions, it is generally accepted that nonpolar compounds are solubilized in the hydrophobic interior of the micelle and polar compounds are solubilized by adsorption on the micelle

(27) Veith, G. D.; Austin, N. M.; Morris, R. T. *Water Res.* 1978, 13, 43.

Table 4. Average Migration Times, t (min), Capacity Factors, k , and Retention Indexes, I , with Standard Deviations (In Parentheses) for the Different Sample Compounds in a Background Electrolyte Containing 50 mM SDS ($n = 10$) (Standards, Alkylbenzenes)

compound	I ^a			II ^a		
	t	k	I	t	k	I
EOF	3.29(0.00)	0		3.30(0.01)	0	
resorcinol	3.93(0.01)	0.325(0.004)	477.7(1.6)	3.95(0.01)	0.324(0.002)	475.6(1.6)
aniline	4.13(0.01)	0.436(0.003)	507.3(0.6)	4.17(0.01)	0.450(0.004)	508.7(0.7)
phenol	4.34(0.01)	0.570(0.004)	534.3(0.5)	4.38(0.01)	0.583(0.004)	534.6(0.5)
benzene	5.04(0.01)	1.076(0.010)	598.4(0.2)	5.09(0.02)	1.101(0.011)	598.6(0.1)
benzaldehyde	5.15(0.01)	1.169(0.010)	606.8(0.3)	5.20(0.02)	1.195(0.011)	606.9(0.2)
nitrobenzene	5.41(0.02)	1.412(0.013)	625.7(0.2)	5.47(0.02)	1.443(0.013)	625.9(0.3)
acetophenone	5.81(0.02)	1.846(0.018)	652.7(0.2)	5.88(0.02)	1.883(0.016)	652.7(0.3)
toluene	6.65(0.02)	3.080(0.028)	704.3(0.1)	6.72(0.02)	3.138(0.027)	704.1(0.2)
chlorobenzene	7.12(0.02)	4.097(0.039)	733.0(0.3)	7.20(0.03)	4.182(0.036)	733.0(0.3)
bromobenzene	7.70(0.02)	5.910(0.055)	769.9(0.2)	7.78(0.03)	6.035(0.048)	769.9(0.3)
ethylbenzene	8.06(0.03)	7.620(0.076)	795.5(0.3)	8.14(0.03)	7.762(0.070)	795.2(0.2)
naphthalene	8.92(0.03)	16.377(0.189)	872.6(0.3)	9.00(0.03)	16.766(0.098)	872.8(0.4)
propylbenzene	9.14(0.03)	21.607(0.270)	900.5(0.2)	9.22(0.03)	22.149(0.212)	900.8(0.2)
butylbenzene	9.63(0.03)	57.992(0.743)	1000.0(0.0)	9.71(0.04)	59.353(0.617)	1000.0(0.0)
MC (calcd)	9.96(0.03)	∞		10.04(0.04)	∞	

^a I, rinsing of the capillary between analyses with background electrolyte for 2 min; II, no rinsing of the capillary between analyses.

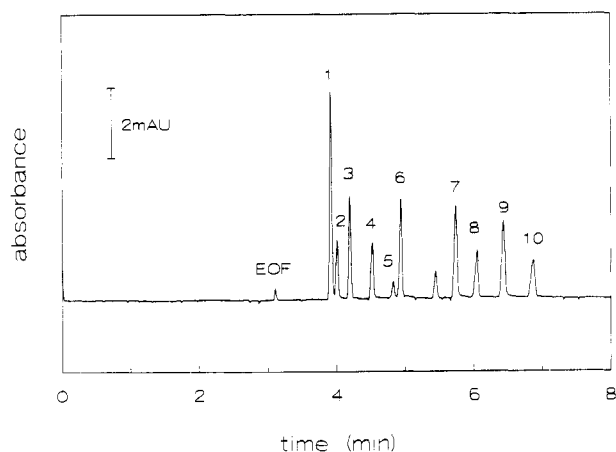


Figure 5. Electrokinetic chromatogram of the separation of (1) aniline, (2) benzaldehyde, (3) acetophenone, (4) nitrobenzene, (5) phenol, (6) propylphenone, (7) butylphenone, (8) bromobenzene, (9) valerophenone, and (10) hexanophenone applying a background electrolyte containing 50 mM DTAB. Detection wavelength 225 nm.

surface, oriented with their hydrophobic moieties inside the micelle and their polar groups toward the aqueous phase.^{30,31} Therefore the distribution coefficients of nonpolar compounds are mainly influenced by the alkyl chain length of the surfactant whereas the distribution coefficients of polar compounds are mainly influenced by the hydrophilic group of the surfactant.²

In order to get more insight into this phenomenon, ΔI values were determined from the retention indexes obtained with the three different surfactants for all sample compounds, with the alkylbenzenes as the retention index standards. The calculated retention indexes and ΔI values for all sample compounds are listed in Table 5. Since the cationic surfactants CTAB and DTAB differ only in the alkyl chain length and the retention index is a relative quantity, the values for ΔI_3 are small for all sample compounds. For resorcinol, aniline,

and phenol, positive values were obtained for ΔI_1 and ΔI_2 . These compounds were shown to have more interaction with the cationic micelles than with the anionic micelles. Here it should be noted, however, that at the pH of the electrolyte systems the acidic compounds resorcinol and phenol ($pK_a = 9.81$ and $pK_a = 9.89$, respectively) and the basic compound aniline ($pK_b = 9.42$) are partly ionized. This probably accounts for the high values of ΔI_1 and ΔI_2 obtained for resorcinol and phenol. Although these compounds are ionized to some extent, their migration behavior is mainly based on micellar solubilization. For benzaldehyde and acetophenone, both containing a polar carbonyl group, and for nitrobenzene, containing an electron-withdrawing group, negative values were obtained for ΔI_1 and ΔI_2 . These polar compounds were shown to have more interaction with the anionic micelles than with the cationic micelles. The positive values of ΔI_1 and ΔI_2 , obtained for the nonpolar compound naphthalene, are not yet understood.

Besides the approach described above, it is obvious that by calculation of ΔI values within one surfactant system information can also be obtained about the interaction of different molecular functionalities with this specific micellar phase.

Influence of Surfactant Concentration. The capacity factor is related to the distribution coefficient, K , and the phase ratio, V_{MC}/V_{AQ} , according to

$$k = K(V_{MC}/V_{AQ}) \quad (7)$$

where V_{MC} and V_{AQ} are the volume of the micellar phase and the aqueous phase, respectively. The phase ratio can be calculated according to

$$\frac{V_{MC}}{V_{AQ}} = \frac{\bar{v}(C_{SF} - cmc)}{1 - \bar{v}(C_{SF} - cmc)} \quad (8)$$

where \bar{v} is the partial molar volume of the micelles, C_{SF} is the concentration of the surfactant, and cmc is the critical micelle concentration. If the volume of the micellar phase is small compared to the volume of the aqueous phase, the denominator of eq 8 equals 1 and then the capacity factor is linearly related

(28) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. *J. Chem. Eng. Data* **1982**, *27*, 451.

(29) Iwasa, J.; Fujita, T.; Hansch, C. *J. Med. Chem.* **1965**, *8*, 150.

(30) Shinoda, K.; Nakagawa, T.; Tamamushi, B.; Isemura, T. *Colloidal Surfactants*; Academic Press: New York, 1963; p 140.

(31) Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilization by Surface-Active Agents*; Chapman and Hall: London, 1968; p 67.

Table 5. Functionalities, Octanol–Water Partition Coefficients, log P, and Calculated ΔI Values Obtained with the Three Surfactants for the Different Sample Compounds (Standards, Alkylbenzenes)

compound	functionality	log P ^a	I _{SDS}	I _{CTAB}	I _{DTAB}	ΔI_1^d	ΔI_2^d	ΔI_3^d
resorcinol	OH, OH	0.80	477.7	670.4	658.0	192.7	180.4	12.3
aniline	NH ₂	0.98	507.3	540.2	531.2	32.9	23.9	9.0
phenol	OH	1.46	534.3	656.0	652.2	121.7	117.9	3.8
benzene		2.13	598.4	604.4	598.4	6.0	0.1	5.9
benzaldehyde	COH	1.48	606.6	552.7	546.3	-54.0	-60.3	6.4
nitrobenzene	NO ₂	1.86	625.7	616.9	615.7	-8.8	-10.0	1.2
acetophenone	COCH ₃	3.18	652.7	574.0	573.7	-78.8	-79.0	0.3
toluene	CH ₃	2.65 ^b	704.3	698.9	704.7	-5.3	0.4	-5.7
chlorobenzene	Cl	2.84 ^c	733.0	740.3	748.4	7.3	15.4	-8.1
bromobenzene	Br	2.99 ^c	769.9	774.3	792.9	4.4	22.9	-18.5
ethylbenzene	C ₂ H ₅	3.13 ^b	795.5	786.6	794.1	-9.0	-1.5	-7.5
naphthalene	C ₄ H ₄	3.37	872.6	914.3	925.8	41.7	53.2	-11.6
propylbenzene	C ₃ H ₇	3.69 ^b	900.5	904.9	901.0	4.4	0.4	3.9
butylbenzene	C ₄ H ₉	4.28 ^b	1000.0	1000.0	1000.0	0.0	0.0	0.0

^a From ref 27. ^b Reference 28. ^c Reference 29. ^d $\Delta I_1 = I_{CTAB} - I_{SDS}$; $\Delta I_2 = I_{DTAB} - I_{SDS}$; $\Delta I_3 = I_{CTAB} - I_{DTAB}$.

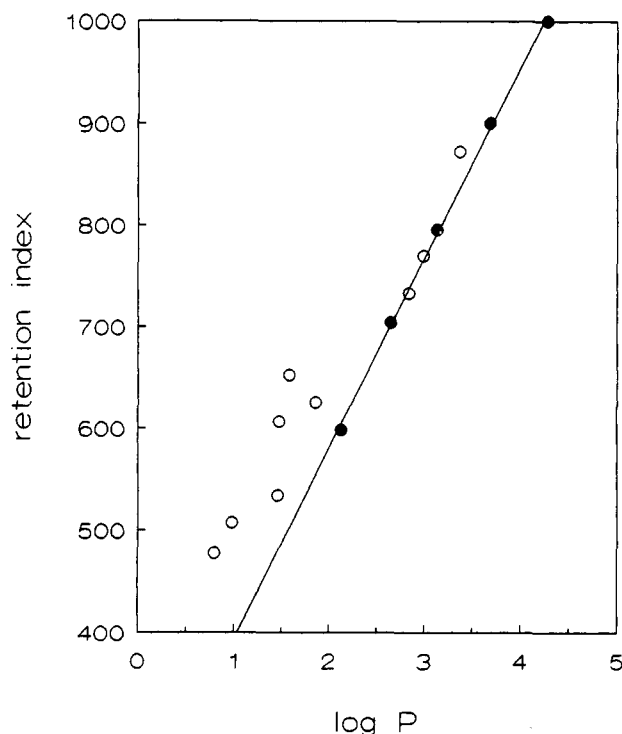


Figure 6. Relationship between retention index and log P for (●) the alkylbenzenes and (○) the sample compounds with different functionalities obtained with a background electrolyte containing 50 mM SDS.

to the surfactant concentration according to

$$k = K_{\bar{v}}(C_{SF} - cmc) \quad (9)$$

The retention index, however, is independent of the phase ratio as it is a relative quantity for expressing migration data. Hence the retention index will be independent of the surfactant concentration. This can be clearly seen after combination of eqs 3 and 7, leading to

$$I = 100z + 100 \frac{\log K_S - \log K_z}{\log K_{z+1} - \log K_z} \quad (10)$$

Of course the relative retention, which relates the capacity factor of a neutral solute to that of a standard substance, will also be independent of the phase ratio.¹⁴

In order to demonstrate the influence of the surfactant concentration on both the capacity factor and the retention

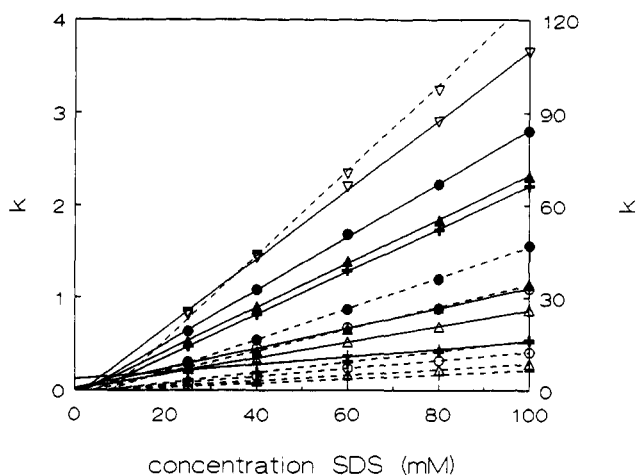


Figure 7. Capacity factor versus the concentration of SDS for (drawn lines) (+) 1, (Δ) 2, (○) 3, (+) 4, (▲) 5, (●) 6, and (▽) 7 and (dotted lines) (+) 8, (Δ) 9, (○) 10, (+) 11, (▲) 12, (●) 13, and (▽) 14. Drawn lines for the left and dotted lines for the right ordinate, respectively. See the legend of Figure 4 for the names of the components.

index, experiments were carried out with electrolyte systems containing different amounts of SDS, ranging from 25 to 100 mM. All experiments were carried out five times and from the observed migration times the average capacity factors and retention indexes were calculated, applying the alkylbenzenes as retention index standards. Linear graphs were obtained for the capacity factor versus surfactant concentration, as shown in Figure 7. The retention index was shown to be independent of the surfactant concentration, which is illustrated in Figure 8. This independence is advantageous for the comparison of experimental results obtained with different batches of electrolyte systems or in different laboratories. The decrease of the retention indexes of resorcinol, aniline, and phenol with increasing SDS concentration is probably because these compounds are partly ionized. For ionic species, not only the distribution between the micellar phase and the aqueous phase, but also the effective mobility of the species determines the separation mechanism in MECC.^{32,33} The contribution of the effective mobility, however, decreases with increasing surfactant concentration. In Table 6 are listed the average values for the retention indexes

(32) Khaledi, M. G.; Smith, S. C.; Strasters, J. K. *Anal. Chem.* 1991, 63, 1820.
 (33) Strasters, J. K.; Khaledi, M. G. *Anal. Chem.* 1991, 63, 2503.

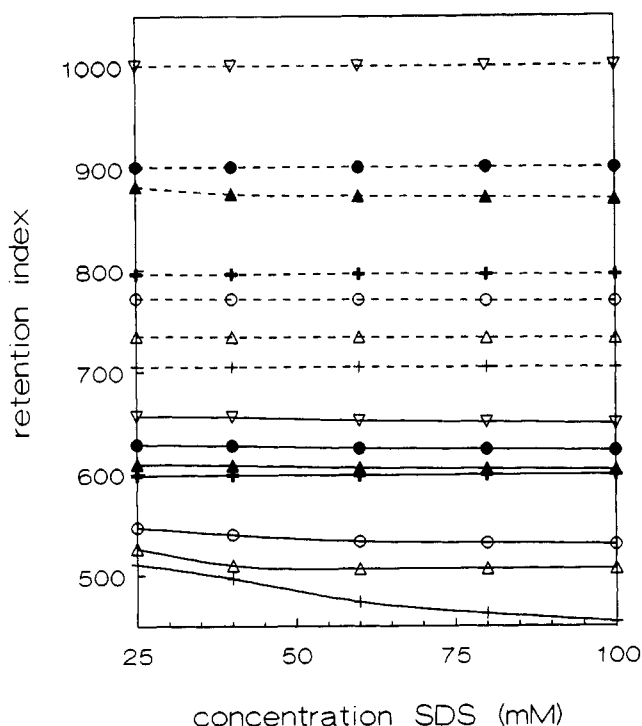


Figure 8. Retention index versus the concentration of SDS for (drawn lines) (+) 1, (Δ) 2, (O) 3, (+) 4, (\blacktriangle) 5, (\bullet) 6, and (∇) 7 and (dotted lines) (+) 8, (Δ) 9, (O) 10, (+) 11, (\blacktriangle) 12, (\bullet) 13, and (∇) 14. See the legend of Figure 4 for the names of the components.

Table 6. Average Values of the Retention Indexes, I , with Standard Deviations (in Parentheses) Obtained with Different SDS Concentrations ($n = 25$)

compound	I	compound	I
resorcinol	479.6(21.0)	toluene	704.2(0.4)
aniline	510.9(7.7)	chlorobenzene	733.3(1.0)
phenol	535.8(6.3)	bromobenzene	770.0(1.2)
benzene	598.5(0.3)	ethylbenzene	795.4(0.4)
benzaldehyde	606.2(2.2)	naphthalene	873.8(7.0)
nitrobenzene	625.3(2.2)	propylbenzene	900.6(0.3)
acetophenone	652.3(3.0)	butylbenzene	1000.0(0.0)

obtained with the different SDS concentrations. For all surfactant concentrations, linear graphs were obtained for $\log k$ versus carbon number of the alkylbenzenes, according to eq 5, which are shown in Figure 9. From Figure 9 it can be seen that the intercept (b) increases if the surfactant concentration increases, whereas the slope (a) remains fairly constant.

Influence of Temperature and Calculation of Thermodynamic Quantities. To investigate the dependence of the retention index on the temperature in MECC, experiments were carried out at different temperatures between 15 and 40 °C with a background electrolyte containing 50 mM SDS. At each temperature, a constant current of 10 μ A was applied in order to exclude differences in Joule heating. All experiments were carried out five times and the average capacity factors and retention indexes were calculated from the observed migration times, applying the alkylbenzenes as the retention index standards. The temperature dependence of the retention index, expressed as dI/dT , is listed in Table 7 for all sample compounds. As can be seen from these values, the retention index, based on the alkylbenzenes, decreases with increasing temperature for all analytes. Moreover, the temperature

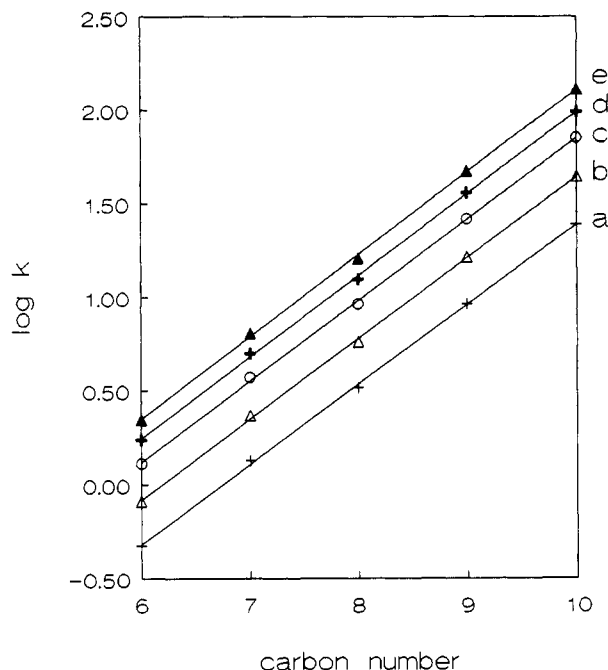


Figure 9. Relationship between $\log k$ and carbon number for the alkylbenzenes applying a background electrolyte containing (a) 25, (b) 40, (c) 60, (d) 80, and (e) 100 mM SDS.

Table 7. Temperature Dependence of the Retention Index, dI/dT , and the Distribution Coefficients, K , of the Sample Compounds and Measured Voltage Drop (kV) at Different Temperatures, T (°C)

compound	dI/dT	distribution coefficient					
		15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
resorcinol	-0.52	32.1	30.9	29.1	27.8	27.0	26.4
aniline	-0.47	44.8	43.2	40.6	39.6	38.3	36.7
phenol	-0.43	57.5	55.7	52.6	50.9	49.4	47.5
benzene	0.01	103	102	98.7	97.4	96.0	93.7
benzaldehyde	-0.42	119	114	108	104	101	97.0
nitrobenzene	-0.25	141	136	130	126	124	119
acetophenone	-0.44	190	180	170	164	158	152
toluene	-0.03	300	292	282	276	271	264
chlorobenzene	-0.13	407	392	377	366	358	347
bromobenzene	-0.21	595	569	545	526	512	494
ethylbenzene	0.01	747	722	699	682	670	652
naphthalene	-0.57	1760	1630	1530	1450	1380	1300
propylbenzene	-0.04	2160	2070	2000	1940	1890	1820
butylbenzene	0.00	5850	5480	5370	5180	5040	4850
voltage		17.8	16.8	15.8	14.8	14.2	14.2

dependence of the retention index is rather small, especially if the temperature working range for MECC experiments is taken into account (e.g., with our apparatus the capillary temperature can be varied between 15 and 40 °C).

The migration data of the sample compounds at different temperatures can be used for the determination of several thermodynamic quantities of micellar solubilization.³⁴ From the determined capacity factors, the distribution coefficient can be calculated with eqs 7 and 8, provided that the partial molar volume and the critical micelle concentration at the different temperatures are known. Literature data for \bar{v} and cmc at different temperatures in pure water are listed in Table 8. The partial molar volume of SDS was shown to be almost independent of the constituents of the buffer solution.³⁴ Since

(34) Terabe, S.; Katsura, T.; Okada, Y.; Ishihama, Y.; Otsuka, K. *J. Microcolumn Sep.* 1993, 5, 23.

Table 8. Partial Molar Volume, \bar{v} (mL/mol), and Critical Micelle Concentration (cmc) (mmol/L) for SDS at Different Temperatures, T ($^{\circ}\text{C}$)

T	\bar{v}^a	cmc ^b	
		I ^c	II
15	243.5	8.43	6.28
20	245.6	8.25	6.39
25	247.8	8.16	5.34
30	250.0	8.23	5.28
35	252.1	8.39	5.19
40	254.3	8.60	5.38

^a From ref 35. ^b I, in pure water; II, in a 0.02 M TRIS–borate electrolyte system at pH 8.5, from own measurements. ^c From ref 23.

the cmc generally decreases with increasing ionic strength of the surfactant solution, the cmc for SDS in the applied electrolyte system was determined by conductivity experiments as described by Saitoh et al.³⁶ The graphs of the specific conductivity versus the concentration SDS in the TRIS–borate electrolyte system at different temperatures are shown in Figure 10. From the inflection points of these graphs, the cmc's were determined, which are listed in Table 8. As can be seen from these results, at all temperatures the cmc in the electrolyte systems is lower than the cmc in pure water. The distribution coefficients of the sample compounds at the different temperatures were calculated from the determined capacity factors and the experimentally obtained cmc's using eqs 7 and 8. These values are listed in Table 7.

The standard enthalpy, ΔH° , and the standard entropy, ΔS° , for the micellar solubilization of the sample compounds can be calculated according to the van't Hoff equation:

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (11)$$

where R and T are the gas constant and the absolute temperature, respectively. The standard Gibbs free energy, ΔG° , for the micellar solubilization can be calculated according to

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (12)$$

The van't Hoff plots for all sample compounds are shown in Figure 11. From the slope and the intercept of these plots ΔH° and ΔS° and with eq 12 ΔG° at 25 $^{\circ}\text{C}$ were calculated. These values are listed in Table 9. The differences between these results and the results reported by Terabe et al.³⁴ may be due to differences in the applied electrolyte systems. As can be seen from Table 9, the enthalpy change of the alkylbenzenes decreases with an increase in the alkyl chain length. This indicates that the affinity for the micelles is stronger for alkylbenzenes with a longer alkyl chain, i.e., for more hydrophobic species. For the entropy change, however, an increase was observed with an increase of the alkyl chain length. Moreover, for all sample compounds a positive value for the entropy change was obtained, which seems rather contradictory to the apparent lower degree of freedom of the solutes incorporated in the micelles. This phenomenon can be explained by a strong contribution of the hydrophobic interaction, as described by Terabe et al.³⁴ From the entropy

(35) Shinoda, K.; Soda, T. *J. Phys. Chem.* **1963**, *67*, 2072.

(36) Saitoh, K.; Kiyohara, C.; Suzuki, N. *J. High Resolut. Chromatogr.* **1991**, *14*, 245.

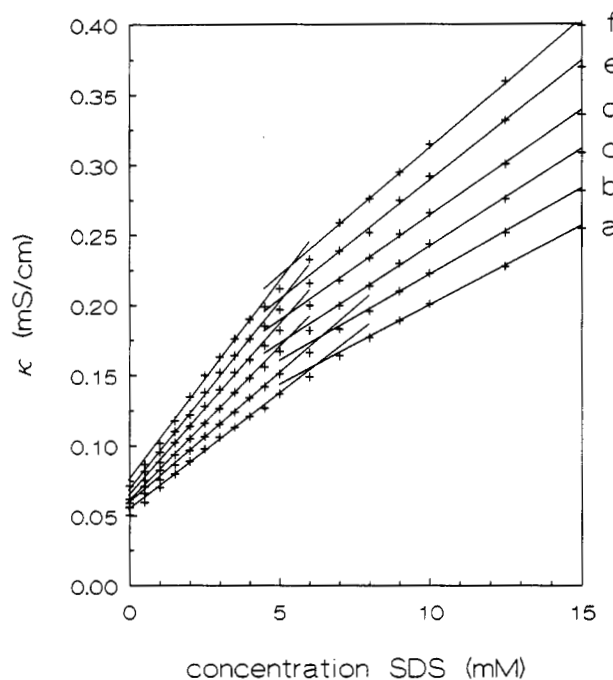


Figure 10. Specific conductivity, κ , versus the concentration of SDS in a TRIS–borate electrolyte system at pH 8.5 at (a) 15, (b) 20, (c) 25, (d) 30, (e) 35, and (f) 40 $^{\circ}\text{C}$.

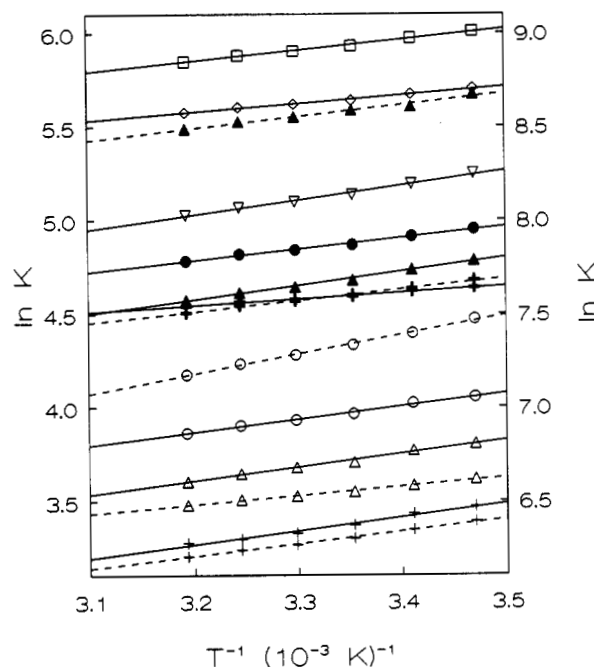


Figure 11. Van't Hoff plots for (drawn lines) (+) 1, (Δ) 2, (O) 3, (+) 4, (\blacktriangle) 5, (\bullet) 6, (∇) 7, (\diamond) 8, and (\square) 9 and (dotted lines) (+) 10, (Δ) 11, (O) 12, (+) 13, and (\blacktriangle) 14. Drawn lines for the left and dotted lines for the right ordinate, respectively. See the legend of Figure 4 for the names of the components.

changes, listed in Table 9, it can be concluded that the hydrophobic interaction plays a significant role in the micellar solubilization of sample compounds in MECC. The Gibbs free energy for micellar solubilization was shown to be consistent with the migration order of the sample compounds (see Figure 4).

CONCLUSIONS

Both the capacity factor and the retention index can be used as a parameter for peak identification in MECC. The

Table 9. Correlation Coefficients for the Graphs Shown in Figure 12 and the Standard Enthalpy, ΔH° (kJ/mol), Standard Entropy, ΔS° (J·mol⁻¹·K⁻¹), and Standard Gibbs Free Energy, ΔG° (kJ/mol) at 25 °C with Standard Deviations (In Parentheses) for the Micellar Solubilization of the Different Sample Compounds by the SDS Micelles

compound	corr coeff	ΔH°	ΔS°	ΔG°
resorcinol	0.985	-6.1(0.2)	7.5(0.7)	-8.4(0.3)
aniline	0.968	-6.0(0.3)	10.9(1.0)	-9.2(0.4)
phenol	0.982	-5.8(0.2)	13.6(0.7)	-9.8(0.3)
benzene	0.896	-2.9(0.3)	28.7(0.9)	-11.4(0.4)
benzaldehyde	0.976	-6.2(0.3)	18.3(0.9)	-11.6(0.4)
nitrobenzene	0.964	-5.0(0.3)	23.8(0.9)	-12.1(0.4)
acetophenone	0.977	-6.5(0.3)	20.8(0.9)	-12.8(0.4)
toluene	0.936	-3.8(0.3)	34.2(0.9)	-14.0(0.4)
chlorobenzene	0.958	-4.7(0.3)	33.6(0.9)	-14.7(0.4)
bromobenzene	0.971	-5.5(0.3)	33.9(0.9)	-15.6(0.4)
ethylbenzene	0.941	-4.0(0.3)	41.1(0.9)	-16.3(0.4)
naphthalene	0.988	-8.8(0.3)	31.5(0.9)	-18.2(0.4)
propylbenzene	0.946	-5.0(0.3)	46.6(1.1)	-18.8(0.5)
butylbenzene	0.882	-5.3(0.5)	53.7(1.8)	-21.3(0.7)

capacity factor provides fundamental information concerning the distribution coefficient of the analytes between the aqueous phase and the micellar phase and is linearly related to the phase ratio. However, the retention index shows a better repeatability, and as it is a relative quantity, the retention index is independent of the phase ratio, i.e., independent of the surfactant concentration.

Both the homologous series of alkylbenzenes and of alkylaryl ketones show a linear relationship between the

logarithm of the capacity factor and the carbon number of the homologues. Hence, both series can be applied as retention index standards in MECC. Moreover, this linear relationship can be used to calculate the micelle migration time by an iteration procedure. The alkylbenzenes are to be preferred with the anionic surfactant SDS with respect to the scale of the capacity factors, whereas the alkylaryl ketones are to be preferred with the cationic surfactants CTAB and DTAB.

The correlation between retention indexes and octanol-water partition coefficients and the calculation of ΔI values from retention indexes obtained with different surfactant systems can provide information about the interaction phenomena and the separation mechanism in MECC.

The temperature dependence of the retention index was found to be rather small. From the calculated thermodynamic quantities, it can be concluded that the hydrophobic interaction contributes significantly to the micellar solubilization of sample compounds in MECC.

ACKNOWLEDGMENT

The authors express their gratitude to the foundation for Chemical Research in the Netherlands (SON) for financial support of this investigation.

Received for review July 8, 1993. Accepted December 8, 1993.*

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.