Evaluation and Characterization of Pseudo-stationary Phases in Micellar Electrokinetic Chromatography

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Previously we demonstrated that the retention index, I, is a good migration parameter to compare different surfactant systems since I is independent of the concentration, molar volume and critical micelle concentration of the applied surfactant [8]. For a given sample compound in a specific surfactant system, SF, a \( \Delta I_{SF} \) value can be calculated according to:

\[
\Delta I_{SF} = I_{SF} - I_{SDS}
\]

where \( I_{SF} \) is the retention index obtained with that specific surfactant system and \( I_{SDS} \) is the retention index obtained with sodium dodecylsulphate (SDS). Here SDS is chosen as reference system because this is the most widely used surfactant system in MEKC. These \( \Delta I_{SF} \) values yield information about the influence of different solute functionalities and micelle characteristics on solute-micelle interactions.

Analogous to the Rohrschneider-McReynolds scale in GC [3], \( \Delta I_{SF} \) values can be applied for the classification of pseudo-stationary phases in MEKC. From the LSER models, reported by Yang and Khaledi [6, 7], and from our own measurements it can be concluded that for several surfactant systems differences in selectivity are primarily due to their hydrogen bonding abilities. Hence for these surfactant systems differences in retention indices of a solute can be expressed in terms of two parameters, representing the hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) strength of both the solute and the micellar phase, according to:

\[
\Delta I_{SF} = \beta x + \alpha y
\]

where \( \beta \) and \( \alpha \) are physical quantities which represent the HBA and HBD strength of the solute, and \( x \) and \( y \) are system constants which represent the HBD and HBA strength of the micellar pseudo-stationary phase, respectively. In order to evaluate these system constants...
Table II. System constants x and y for five anionic and two cationic micellar systems.

<table>
<thead>
<tr>
<th>Surfactant system</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mM sodium dodecyl sulphate</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50 mM TRIS dodecyl sulphate</td>
<td>5</td>
<td>-3</td>
</tr>
<tr>
<td>50 mM sodium dodecyl sulphate + 2 mM Brij 35</td>
<td>-39</td>
<td>36</td>
</tr>
<tr>
<td>50 mM sodium dodecyl sulphate + 5 mM Brij 35</td>
<td>-87</td>
<td>48</td>
</tr>
<tr>
<td>50 mM sodium dodecyl sulphate + 10 mM Brij 35</td>
<td>-154</td>
<td>105</td>
</tr>
<tr>
<td>50 mM sodium dodecyl sulphate + 10 mM Brij 35</td>
<td>-180</td>
<td>135</td>
</tr>
<tr>
<td>50 mM cetyltrimethylammonium bromide</td>
<td>-185</td>
<td>300</td>
</tr>
<tr>
<td>50 mM dodecyltrimethylammonium bromide</td>
<td>-185</td>
<td>293</td>
</tr>
</tbody>
</table>

Table I. Solvatochromic parameters β and α for acetophenone and phenol in Eq. (2). [9]

<table>
<thead>
<tr>
<th>Standard</th>
<th>β</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>0.49</td>
<td>0.04</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.33</td>
<td>0.61</td>
</tr>
</tbody>
</table>

two standard compounds were selected, viz. acetophenone (a strong HBA) and phenol (a strong HBD). The solvatochromatic parameters for their HBA and HBD ability were used as the physical quantities β and α, respectively [9]. These values are listed in Table I. From the retention indices of these two standards in a specific surfactant system and in an SDS system, ΔIFS values can be calculated according Eq. (1) and the system constants x and y can be calculated applying Eq. (2). For five anionic and two cationic surfactant systems these constants x and y were calculated which are listed in Table II. With these constants the applied micellar systems can be classified according to their HBD strength (x) as follows:

TDS = SDS > SDSo > SDS/Brij 35 = CTAB = DTAB

and according to their HBA strength (y) as

CTAB = DTAB > SDS/Brij 35 > SDSo > SDS = TDS

Here the mixed micellar system of 50 mM SDS/10 mM Brij 35 was used. These results are comparable to a classification based on LSER models.

In order to illustrate the differences in selectivity between 50 mM SDS and a mixed 50 mM SDS/10 mM Brij 35 micellar system, in Table III the contributions to ΔIFS/Brij 35 of the hydrogen bonding terms βx and cy are listed for 13 sample compounds possessing different functionalities. The negative values for βx clearly illustrate the generally observed decrease in retention (i.e. negative ΔIFS/Brij 35) for strong HBA compounds in a mixed SDS/Brij 35 micellar system.

The reported approach has several advantages from a practical point of view. First, ΔIFS values are calculated directly from MEKC migration data. Therefore these values provide a good insight into the influence of a specific micellar phase on MEKC migration behaviour and the expected position of the peaks in the electrokinetic chromatogram. Second, only for the standards retention indices must be determined. Consequently a relative small amount of experiments is required for the classification of pseudo-stationary phases. Third, only for the limited number of standard compounds solvatochromic parameters are required.

These results demonstrate that retention indices can be used for the quantitative characterization and classification of pseudo-stationary phases in MEKC in a similar way as the Rohrschneider-McReynolds scale in GC. We assume that this kind of classification may be helpful in the fast selection of an optimum composition of the micellar system for a given separation problem.

References

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