

Technical paper

# Chromatographic Behavior of Cationic and Nonionic Surfactants on Silica Gel Impregnated with Paraffin Oil Using Aqueous Formamide Mobile Phase Systems

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## Abstract

The migration behavior of cationic and nonionic surfactants on silica gel impregnated with paraffin oil, tertiary butyl phosphate and silicon oil using aqueous dimethyl formamide (DMF) was examined. The mobility of surfactants at different concentration levels of DMF in double distilled water was investigated on silica gel impregnated with 1% paraffin oil. The most suitable mobile phase for the mutual separation of cationic and nonionic surfactants was the mixture of DMF and double distilled water in 6:4 ratios. The separation of cetylpyridinium chloride (CPC) from Brij-35 was successfully achieved on silica gel impregnated with 1% paraffin oil. The mobility pattern of cationic as well as nonionic surfactants on silica gel impregnated with (1, 3, 5, 7 and 10%) paraffin oil, 1% tertiary butyl phosphate and 1% silicon oil was examined. The solvent effect on the  $R_F$  values of surfactants, with protic solvent (DMF and tetrahydrofuran i.e. THF) and aprotic (Dimethylsulfoxide i.e. DMSO) was performed on silica gel impregnated with 1% paraffin oil. The migration behavior of surfactants on stationary phases (alumina, kieselguhr and cellulose) impregnated with 1% paraffin oil was also studied. The results show reasonable reproducibility ( $R_F$  values differ by a factor of 10%). The limits of detection of CPC and BJ-35 were 0.73 and 0.75  $\mu\text{g}$  respectively. To widen the applicability of the method, separation of CPC and BJ-35 from a sample of fabric softener was also investigated. The influence of metal cations as well as anionic impurities in the separation of CPC and Brij-35 was also examined.

**Keywords:** TLC, silica gel, paraffin oil, surfactants, dimethyl formamide

## 1. Introduction

Thin layer chromatography (TLC) is a useful method for identifying and testing the purity of surfactants. Surfactants have wider applicability in soaps for domestic use, industrial, petroleum industry, concrete additives, agro and food processing and in cosmetic and pharmaceutical purposes<sup>1</sup>. Mostly commercial surfactants containing products are mixtures of several components and hence simple and rapid methods for separation are always required for their identification. TLC is a useful technique because it is relatively quick and requires small quantities of material. Some cationic and nonionic surfactants are known to affect environment as they are routinely deposited in numerous ways on land and enter into water system as industrial and household wastes.

Several methods have been used for the separation, detection and quantification of surfactants. Gas chromatography,<sup>2,3</sup> reversed-phase and normal phase high-performance liquid chromatography (HPLC),<sup>4-7</sup> liquid chromatography combined with atmospheric-pressure ionization mass spectrometry,<sup>8,9</sup> IR and UV spectrometry,<sup>10,11</sup> ion-pair chromatography,<sup>12</sup> ion exchange chromatography,<sup>13</sup> microbial sensors,<sup>14</sup> amperometric biosensors,<sup>15</sup> capillary electrophoresis<sup>16</sup> and flow-injection techniques.<sup>17,18</sup> These techniques are expensive and require special equipments except thin layer chromatography.

Reversed phase thin layer chromatography (RPTLC) of surfactants using undecane, silicon oil, and cholesterol as impregnant silica layers in combination with aqueous methanol or methanol plus ethyl acetate as mobile phases has been generally used for the analysis of surfactants.<sup>19,20</sup>

Alumina layers impregnated with 5% paraffin oil in hexane have been used to investigate the interaction of surfactants with peptides using methanol-water mixture (10 and 90% v/v) as mobile phase.<sup>21</sup> The work reported from our laboratory<sup>22–25</sup> deals with the separation of cationic and nonionic surfactants by normal phase TLC. Therefore, we decided to explore the separation possibilities of mixture of surfactants by reversed-phase TLC.

In the present paper analysis of nonionic and cationic surfactants has been performed on silica gel layer impregnated with paraffin oil using different aqueous protic (e.g. DMF) mobile phase systems. Cationic surfactants are widely used as fabric softeners. The presence of nonionic surfactants influences their performance and hence the removal of nonionic surfactant is important before their use as fabric softener. Therefore we have successfully separated CPC (a cationic surfactant) from BJ-35 (a nonionic surfactant). Mutual separation of CPC and BJ-35 is also important because of their wider use in different fields of applications.<sup>26–31</sup>

## 2. Experimental

All experiments were performed at  $30 \pm 2$  °C. All chemicals were of analytical reagent grade. N, N-Dimethyl formamide was purchased from Merck (Mumbai, India). Paraffin oil was purchased from Qualigens where as petroleum ether, Brij-35 (BJ-35), Brij-57 (BJ-57), Brij-98 (BJ-98), Tween-20 (TW-20), Cween-40 (CW-40), Cween-60 (CW-60), cetylpyridinium chloride (CPC), tetradecylammonium bromide (TTAB), hexadecyltrimethylammonium chloride (HDTAC) and dodecyltrimethylammonium bromide (DTAB) were purchased from CDH (India). Solutions of the surfactants were prepared in methanol to give concentration of 0.5% (w/v).

Surfactants spots were detected by spraying Dragendorff reagent which was prepared by mixing two solutions. Solution A was prepared from two solutions, a solution of bismuth subnitrate ( $\text{BiONO}_3 \cdot \text{H}_2\text{O}$ ; 1.7 g) in acetic acid (20 mL), diluted to 100 mL with water, and a solution of potassium iodide (65 g) in water (200 mL). These solutions were transferred to a 1 L flask, acetic acid (200 mL) was added, and the solution was diluted to one liter with water. Solution B was prepared by dissolving barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; 290 g) in water (1 L). Solutions A and B were mixed in the ratio 2:1. A glass sprayer was used to apply the reagents to the plates.

Metallic cationic species [ $\text{Th}^{4+}$  (thorium nitrate),  $\text{Cd}^{2+}$  (cadmium chloride),  $\text{Cu}^{2+}$  (copper sulphate) and  $\text{Ag}^+$  (silver nitrate) and inorganic anions [ $\text{SO}_4^{2-}$  (zinc sulphate),  $\text{CrO}_4^-$  (sodium chromate),  $\text{Cr}_2\text{O}_7^{2-}$  (potassium dichromate),  $\text{PO}_4^{3-}$  (calcium phosphate)  $\text{MoO}_4^{2-}$  (sodium molybdate),  $\text{SCN}^-$  (potassium thiocyanate) and  $\text{Cl}^-$  (sodium chloride) were used as foreign substances to study their effect on the separation of CPC and BJ-35 from their mixture.

The TLC plates were prepared by mixing silica gel 'G' with double distilled water in 1:3 ratio with constant shaking until homogenous slurry was obtained. The resultant slurry was applied on the glass plates with the help of a TLC applicator to give a 0.25 mm thick layer. The plates were dried in air at room temperature and then activated by heating for 1h at  $100 \pm 2$  °C in an electrically controlled oven. After activation, the plates were cooled at room temperature. For the preparation of impregnated silica gel plates, post coating method has been used. In this method the activated silica gel plates were impregnated with desired concentration of paraffin oil (1, 3, 5, 7 and 10%, v/v), in petroleum ether by dipping silica gel plates in solution of impregnant for a specific time period followed by drying of the plates at room temperature (60 °C). The same method was used for the preparation of tertiary butyl phosphate and silicon oil (in petroleum ether) impregnated TLC plates. The stationary and mobile phases used in this experiment are listed in Tables 1 and 2.

Table 1. List of stationary phases used

| Code           | Stationary phase  |
|----------------|---|
| S <sub>1</sub> | silica gel G impregnated with 1% Paraffin oil             |
| S <sub>2</sub> | silica gel G impregnated with 3% Paraffin oil             |
| S <sub>3</sub> | silica gel G impregnated with 5% Paraffin oil             |
| S <sub>4</sub> | silica gel G impregnated with 7% Paraffin oil             |
| S <sub>5</sub> | silica gel G impregnated with 10% Paraffin oil            |
| S <sub>6</sub> | silica gel G impregnated with 1% Tertiary butyl phosphate |
| S <sub>7</sub> | silica gel G impregnated with 1% Silicon oil              |

Table 2. List of mobile phases used

| Code            | Mobile phase                 | composition |
|-----------------|------------------------------|-------------|
| M <sub>1</sub>  | Double distilled water (DDW) |             |
| M <sub>2</sub>  | DMF-DDW                      | 1:9         |
| M <sub>3</sub>  | DMF-DDW                      | 2:8         |
| M <sub>4</sub>  | DMF-DDW                      | 3:7         |
| M <sub>5</sub>  | DMF-DDW                      | 4:6         |
| M <sub>6</sub>  | DMF-DDW                      | 5:5         |
| M <sub>7</sub>  | DMF-DDW                      | 6:4         |
| M <sub>8</sub>  | DMF-DDW                      | 7:3         |
| M <sub>9</sub>  | DMF-DDW                      | 8:2         |
| M <sub>10</sub> | DMF-DDW                      | 9:1         |
| M <sub>11</sub> | DMF                          |             |

Test solutions (1  $\mu\text{L}$ ) were applied on plates with the help of Tripette (Gmbh, Werthlim, Germany) at about 1 cm above the lower edge of the plates. The solvent ascent was fixed to 10 cm in all cases for the determination of  $R_F$  value of individual surfactants. Development of plates was carried out in glass jars and dried at  $30 \pm 2$  °C followed by spraying with freshly prepared Dragendorff reagent. All surfactants were visualized as orange spots. The surfactants were identified on the basis of their  $R_F$  values; calculate from the  $R_L$  ( $R_F$  of leading front) and  $R_T$  ( $R_F$  of trailing front) of each spot.

$$R_F = 0.5 (R_L + R_T)$$

For the separation of surfactant mixtures, equal volumes of surfactants were mixed and 1  $\mu$ L of the resultant mixture was applied on TLC plate. The plate was developed with  $M_7$ , the spots were detected and the values of separated spots of surfactants were calculated.

To observe the effect of nature of impregnant, silica gel layers were impregnated with 1% paraffin oil, tertiary butyl phosphate and silicon oil separately and the mobility of surfactants on these layers was examined using DMF-DDW (6:4) as mobile phase.

For investigating the interference of metal cations as well as anions as impurities on the separation of CPC and BJ-35, an aliquot (1.0  $\mu$ L) of 0.1% of impurity solution was spotted along with the mixture (1.0  $\mu$ L) of surfactants (CPC and Brij-35) and chromatography was performed as described above with  $M_7$ . The spots were detected and the  $R_F$  values of separated surfactants were determined.

The reproducibility (or precision) of  $R_F$  values for individual surfactant was checked by determining the  $R_F$  values of the same sample by the same analyst on different days under identical experimental conditions. The variation in  $R_F$  values for five repeats differs by a factor of  $\pm 0.10$  (i.e.  $\pm 10\%$ ) from the average value indicating a good reproducibility. However, this variation is higher for the mixture of surfactants due to certain mutual interactions.

### 3. Results and Discussions

Reversed phase thin layer chromatography of cationic as well as nonionic surfactants was performed using eleven aqueous mobile phases. The mobility pattern of ten

surfactants (four cationic and six nonionic) on silica gel layers impregnated with 1% paraffin oil ( $S_1$ ) was examined using double distilled water ( $M_1$ ), aqueous dimethyl formamide at nine different concentration levels (10–90%) and pure DMF ( $M_{11}$ ). As evident from the data listed in Table 3, all cationic as well as nonionic surfactants remain at the point of application on  $S_1$  developed with  $M_1$ . All cationic surfactants show lower  $R_F$  value at all concentrations of aqueous dimethyl formamide except  $M_6$ . Interestingly, none of the cationic surfactants was detected on TLC plates developed with  $M_6$  (50% aqueous DMF). The failure of observing colored spot on TLC plate is probably due to diminishing of color in certain mobile phases or on some stationary phases. Similarly DTAB could not be detected with  $M_8$ ,  $M_9$  and  $M_{10}$ . Tailed spots for CPC in  $M_{11}$  and for HDTAC in  $M_8$  and  $M_{10}$  were observed. As regards to nonionic surfactants, they produced tailed spots in most of the mobile phase systems. Similarly, depending upon the composition of mobile phase, certain surfactants produce double spots. For example BJ-35 produces tailed spots with  $M_2$  and  $M_3$  whereas double spots ( $R_F = 0.03$  and  $0.42$ ) were observed with  $M_4$ . The formation of double spots shows the presence of two species of the surfactants which are resolved with 40% aqueous DMF. With  $M_8$ , BJ-35 and BJ-57 were not detected. Similarly, the detection of TW-20 and CW-60 was difficult at various concentrations of aqueous formamide. Amongst aqueous mobile phase systems tested,  $M_7$  (DMF-DDW, 6:4) was found promising for further study.

Silica gel layers impregnated with (1,3,5,7 and 10%) paraffin oil, 1% tertiary butyl phosphate and 1% silicon oil were used to examine the mobility of surfactants using DMF-DDW (6:4) as mobile phase with the aim to select most favorable TLC system for the analysis of surfactants.

**Table 3.**  $R_F$  values of cationic and nonionic surfactants using  $S_1$  stationary phase with different solvent systems

| Surfactants          | Mobile phases |                   |                                   |                                   |       |       |                    |                   |                   |                    |                   |
|----------------------|---------------|-------------------|-----------------------------------|-----------------------------------|-------|-------|--------------------|-------------------|-------------------|--------------------|-------------------|
|                      | $M_1$         | $M_2$             | $M_3$                             | $M_4$                             | $M_5$ | $M_6$ | $M_7$              | $M_8$             | $M_9$             | $M_{10}$           | $M_{11}$          |
| Cationic surfactants |               |                   |                                   |                                   |       |       |                    |                   |                   |                    |                   |
| CPC                  | 0.00          | 0.04              | 0.06                              | 0.03                              | 0.05  | ND    | 0.06               | 0.00              | 0.10              | 0.17               | 0.20 <sup>T</sup> |
| TTAB                 | 0.00          | 0.03              | 0.04                              | 0.04                              | 0.10  | ND    | 0.10               | 0.07              | 0.06              | 0.06               | ND                |
| HDTAC                | 0.00          | 0.05              | 0.04                              | 0.02                              | 0.04  | ND    | 0.03               | 0.02              | 0.26 <sup>T</sup> | 0.17 <sup>T</sup>  | 0.00              |
| DTAB                 | 0.00          | 0.04              | 0.05                              | 0.05                              | 0.23  | ND    | 0.25               | ND                | ND                | ND                 | 0.00              |
| Nonionic surfactants |               |                   |                                   |                                   |       |       |                    |                   |                   |                    |                   |
| Brij-35              | 0.00          | 0.30 <sup>T</sup> | 0.40 <sup>T</sup><br>(0.03, 0.42) | DS                                | 0.90  | 0.96  | 0.90               | ND                | 0.94              | 0.74               | 0.98              |
| Brij-57              | 0.00          | 0.04              | 0.03                              | 0.05                              | 0.91  | 0.95  | 0.92               | ND                | 0.81              | 0.22 <sup>T</sup>  | 0.85              |
| Brij-98              | 0.00          | 0.07              | 0.17 <sup>T</sup>                 | 0.37 <sup>T</sup><br>(0.05, 0.95) | DS    | 0.82  | DS<br>(0.07, 0.96) | 0.69 <sup>T</sup> | 0.89              | 0.97               | 0.93              |
| Tween-20             | 0.00          | 0.32              | 0.48                              | 0.46 <sup>T</sup><br>(0.05, 0.92) | DS    | ND    | DS<br>(0.03, 0.94) | 0.75 <sup>T</sup> | ND                | ND                 | 0.98              |
| Cween-40             | 0.00          | 0.17 <sup>T</sup> | 0.78                              | 0.43 <sup>T</sup><br>(0.05, 0.82) | DS    | 0.06  | DS<br>(0.02, 0.85) | 0.93              | ND                | ND<br>(0.05, 0.82) | DS                |
| Cween-60             | 0.00          | 0.27 <sup>T</sup> | 0.08                              | 0.31 <sup>T</sup><br>(0.04, 0.80) | DS    | 0.04  | 0.87               | 0.00              | 0.89              | ND<br>(0.05, 0.86) | DS                |

Each value is mean of five measurements. (T= Tailed spot with  $R_L - R_T \geq 0.3$ , DS= Double spot).

The results presented in Table 4 clearly indicate that all cationic surfactants show lower mobility compared to nonionic surfactants on all stationary phases. HDTAC on  $S_3$ ,  $S_4$ ,  $S_5$  and  $S_6$  produces tailed spots, DTAB on  $S_2$ ,  $S_3$ ,  $S_4$  and  $S_5$  could not be detected and most of the nonionic surfactants yield double spots. Silica gel impregnated with paraffin oil (3–10%) was found not suitable from the separation point of view as silica plates impregnated with high degree of paraffin oil causes several problems including more time for plate development, absence of spot compactness and difficulty in drying of the plate. Stationary

**Table 4.** Mobility patterns (in terms of  $R_F$  value) of surfactants on different stationary phases using  $M_7$  mobile phase

| Surfactants          | Stationary phase   |                    |                    |                    |                      |                   |                    |
|----------------------|--------------------|--------------------|--------------------|--------------------|----------------------|-------------------|--------------------|
|                      | $S_1$              | $S_2$              | $S_3$              | $S_4$              | $S_5$                | $S_6$             | $S_7$              |
| Cationic surfactants |                    |                    |                    |                    |                      |                   |                    |
| CPC                  | 0.06               | 0.07               | 0.05               | 0.06               | 0.07                 | 0.06              | 0.04               |
| TTAB                 | 0.10               | 0.00               | 0.03               | 0.05               | 0.09                 | 0.08              | 0.00               |
| HDTAC                | 0.03               | 0.27               | 0.16 <sup>T</sup>  | 0.15 <sup>T</sup>  | 0.16 <sup>T</sup>    | 0.19 <sup>T</sup> | 0.20               |
| DTAB                 | 0.25               | ND                 | ND                 | ND                 | ND                   | 0.86              | 0.00               |
| Nonionic surfactants |                    |                    |                    |                    |                      |                   |                    |
| BJ-35                | 0.90               | 0.98               | 0.93               | DS<br>(0.04, 0.89) | DS<br>(0.06, 0.92)   | ND                | 0.94               |
| BJ-57                | 0.92               | 0.93               | 0.91               | DS<br>(0.05, 0.90) | DS<br>(0.04, 0.88)   | 0.83              | DS<br>(0.04, 0.84) |
| BJ-98                | DS<br>(0.05, 0.96) | 0.42 <sup>T</sup>  | DS<br>(0.02, 0.68) | DS                 | 0.11<br>(0.02, 0.74) | 0.98              | DS<br>(0.03, 0.80) |
| TW-20                | DS<br>(0.04, 0.94) | 0.91               | DS<br>(0.03, 0.84) | 0.40               | 0.98                 | ND                | DS<br>(0.02, 0.72) |
| CW-40                | DS<br>(0.02, 0.85) | DS<br>(0.03, 0.87) | DS<br>(0.02, 0.73) | DS<br>(0.03, 0.84) | DS<br>(0.03, 0.80)   | ND                | 0.94               |
| CW-60                | 0.87               | 0.49               | DS<br>(0.05, 0.90) | DS<br>(0.03, 0.85) | 0.94                 | ND                | 0.88               |

Each value is mean of five measurements.

phase,  $S_1$  was found suitable for separation of cationic surfactants from nonionic surfactants. Silica gel layers impregnated with 1% tertiary butyl phosphate (TBP) or silicon oil were not found suitable for the analysis of surfactants because of (a) difficulty in detection of most nonionic surfactants except (BJ-57 and BJ-98) on TBP impregnated layer and the formation of tailed spot of HDTAC and (b) formation of double spots of nonionic surfactants.

We have successfully separated CPC (a cationic surfactant) from BJ-35 (a nonionic surfactant). Five other analytically important separations of nonionic from cationic surfactants were also experimentally achieved on  $S_1$  with  $M_7$  solvent system. The  $R_F$  values of separated spots were given in Table 5.

The mobility pattern of cationic as well as nonionic surfactants on using protic (DMF and THF) and aprotic (DMSO) solvent was also studied. Protic solvent (DMF) was found better solvent system because it activates the separation of cationic surfactants from nonionic surfactants. On the other hand, another protic solvent (THF) was not found as good as DMF because most of the nonionic

**Table 5.** Experimentally achieved separations on  $S_1$  sorbent layer with  $M_7$  mobile phase

| Separations ( $R_F$ values) |              |
|-----------------------------|--------------|
| CPC (0.06)                  | BJ-35 (0.97) |
| HDTAC (0.15)                | BJ-35 (0.89) |
| CPC (0.07)                  | BJ-57 (0.95) |
| HDTAC (0.16)                | BJ-57 (0.85) |
| CPC (0.06)                  | CW-60 (0.97) |
| HDTAC (0.11)                | CW-60 (0.93) |

Each value is mean of five measurements.

**Table 6.**  $R_F$  values of surfactants on  $S_1$  layer using 60% aqueous DMF, THF and DMSO as mobile phases

| Surfactants          | Mobile phase       |                   |      |
|----------------------|--------------------|-------------------|------|
|                      | DMF                | THF               | DMSO |
| Cationic surfactants |                    |                   |      |
| CPC                  | 0.06               | 0.08              | 0.00 |
| TTAB                 | 0.10               | 0.12              | 0.00 |
| HDTAC                | 0.03               | 0.11              | 0.10 |
| DTAB                 | 0.25               | 0.00              | 0.00 |
| Nonionic surfactants |                    |                   |      |
| Brij-35              | 0.90               | 0.89              | 0.00 |
| Brij-57              | 0.92               | 0.81              | 0.00 |
| Brij-98              | DS<br>(0.04, 0.96) | 0.76 <sup>T</sup> | 0.00 |
| Tween-20             | DS<br>(0.05, 0.94) | 0.90 <sup>T</sup> | 0.00 |
| Cween-40             | DS<br>(0.05, 0.85) | 0.60 <sup>T</sup> | 0.00 |
| Cween-60             | 0.87               | 0.71 <sup>T</sup> | 0.00 |

Each value is mean of five measurements.

surfactants show badly tailed spots with this system. Furthermore, aprotic solvent (DMSO) was unsuitable for the separation of surfactants. This may be due to the fact that, DMSO being dipolar solvent with hard oxygen and soft sulfur interacts strongly with the surfactant. All surfactants remain at the point of application (Table 6).

Various stationary phases e.g. – alumina, kieselguhr and cellulose impregnated with 1% paraffin oil were used to study the mobility pattern of surfactants using  $M_7$  solvent system. Obtained  $R_F$  values of the surfactants are presented in Table 7. Surfactants on alumina layers impregnated with 1% paraffin oil show double spots as well as tailed spots whereas on kieselguhr and cellulose layer cationic and non-ionic surfactants show higher mobility. This observation indicates that the nature of supports for paraffin oil play minor role in modifying retention behavior of surfactants. It is a deviation from earlier belief that in reversed-phase TLC, the nature of support has no role and the partitioning of analyte between mobile phase and stationary phase (paraf-

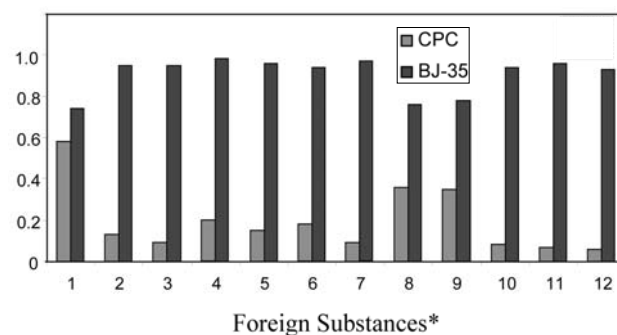
**Table 7.**  $R_F$  values of surfactants on different stationary phases (alumina, kieselguhr and cellulose) impregnated with 1% paraffin oil using  $M_7$  mobile phase

| Surfactants          | Impregnated with 1% paraffin oil |            |                    |
|----------------------|----------------------------------|------------|--------------------|
|                      | Alumina                          | Kieselguhr | Cellulose          |
| Cationic surfactants |                                  |            |                    |
| CPC                  | 0.11                             | 0.56       | 0.92               |
| TTAB                 | 0.21 <sup>T</sup>                | 0.60       | 0.93               |
| HDTAC                | 0.00                             | 0.20       | 0.89               |
| DTAB                 | 0.00                             | 0.36       | 0.94               |
| Nonionic surfactants |                                  |            |                    |
| Brij-35              | DS<br>(0.02, 0.88)               | 0.91       | 0.94               |
| Brij-57              | DS<br>(0.06, 0.90)               | 0.74       | 0.85               |
| Brij-98              | 0.00                             | 0.78       | 0.93               |
| Tween-20             | 0.82 <sup>T</sup>                | 0.83       | 0.91               |
| Cween-40             | DS<br>(0.02, 0.78)               | 0.90       | DS<br>(0.03, 0.88) |
| Cween-60             | DS<br>(0.03, 0.88)               | 0.94       | DS<br>(0.05, 0.90) |

Each value is mean of five measurements.

fin oil in present case) controls the separation mechanism. The reported TLC methods as listed in Table 8 clearly indicate the superiority of proposed reversed-phase technique over normal phase procedure. Better resolved spots have been obtained with present method as compared to the earlier reported methods as indicative by higher value of  $\Delta R_F$ .

Separation of CPC from BJ-35 was investigated in the presence of inorganic species which is shown in Fig. 1. The separation is hampered by the presence of  $\text{Th}^{4+}$ ,  $\text{PO}_4^{3-}$  and  $\text{MoO}_4^{2-}$  in the sample because of their specific interactions with the analyte. The lowest possible amount of CPC and BJ-35 on  $S_1$  stationary phase with  $M_7$  mobile phase was found 0.73 and 0.75  $\mu\text{g}$  respectively. To widen the applicability of the method, separation of CPC and BJ-35 from spiked sample of fabric softener (Godrej ezee) was investigated. The results show that CPC and BJ-35 can be easily identified and separated on  $S_1$  with  $M_7$  as mobile phase.



**Fig. 1.** Resolved spots positions of CPC and BJ-35 from their mixtures on paraffin oil impregnated silica TLC plate in the presence of foreign substances

\* $\text{Th}^{4+}$  (1),  $\text{Cd}^{2+}$  (2),  $\text{Cu}^{2+}$  (3),  $\text{Ag}^+$  (4),  $\text{SO}_4^{2-}$  (5),  $\text{CrO}_4^{2-}$  (6),  $\text{Cr}_2\text{O}_7^{2-}$  (7),  $\text{PO}_4^{3-}$  (8),  $\text{MoO}_4^{2-}$  (9),  $\text{SCN}^-$  (10) and  $\text{Cl}^-$  (11), without impurity (12)

## 4. Conclusion

A new reverse phase thin layer chromatographic system comprising of silica gel impregnated with 1% paraffin oil as stationary phase and the mixture of dimethyl formamide and water (protic solvent) as mobile phase has been

**Table 8.** TLC methods used for the separation of CPC from BJ-35

| S. No. | Stationary phase                                  | Mobile phase   | $R_F$ value                | $\Delta R_F$ value | Reference        |
|--------|---|--|----------------------------|--------------------|------------------|
| 1.     | Silica gel  | THF–DDW<br>(6:4)                                     | CPC = 0.00<br>BJ-35 = 0.81 | 0.81               | 21               |
| 2.     | Silica gel  | 1M aqueous glutamic acid +<br>MeOH + Acetone (1:1:1) | CPC = 0.12<br>BJ-35 = 0.85 | 0.71               | 22               |
| 3.     | Kieselguhr 'G'                                    | 0.1% L-Methionine                                    | CPC = 0.12<br>BJ-35 = 0.87 | 0.75               | 24               |
| 4.     | Silica gel<br>impregnated with<br>1% paraffin oil | DMF + DDW<br>(6:4)                                   | CPC = 0.06<br>BJ-35 = 0.97 | 0.91               | Present<br>study |

Here  $\Delta R_F$  value is the difference in  $R_F$  values of BJ-35 and CPC ( $R_F$  BJ-35 minus  $R_F$  CPC)

the most suitable for separation of cationic surfactants from nonionic surfactants and their on-plate identification. The developed system is applicable for the mutual separation of cetylpyridinium chloride (CPC) and Brij-35 from spiked sample of fabric softener. The lowest possible amounts of CPC and Brij-35 that can be detected on 1% paraffin oil impregnated silica layers were 0.73 and 0.75  $\mu\text{g}$  respectively. Compared to other commercially available adsorbents (Alumina, Cellulose and Kieselguhr) as support for paraffin oil, the performance of silica gel was better.

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## Povzetek

Preučevana je bila vezava kationskih in neionskih surfaktantov na silikagel, ki je bil impregniran s parafinskim oljem, terciarnim butil fosfatom ter silikonskim oljem iz vodne raztopine dimetil formamida (DMF). Vezava surfaktantov iz vodnih raztopin z različnimi koncentracijami DMF je bila določena za silikagel, impregniran z 1 % parafinskim oljem. Najbolj primerna mobilna faza za ločitev kationskih ter neionskih surfaktantov je mešanica DMF in vode v razmerju 6:4. Na silikagelu, impregniranim z 1 % parafinskim oljem je bila dosežena ločitev cetilpiridinijevega klorida (CPC) iz Brij-35. Nadalje je bila določena vezava kationskih ter neionskih surfaktantov na silikagelu, impregniranim z (1, 3, 5, 7 in 10 %) parafinskim oljem, 1 % terciarnim butil fosfatom in 1 % silikonskim oljem. Testiran je vpliv različnih topil (DMF in tetrahidrofuran, dimetilsulfoksid) na  $R_F$  vrednosti surfaktantov ter vezava surfaktantov na druge stacionarne faze (aluminijev oksid, diatomejske zemlje-kieselguhr, celuloza), impregnirane z 1 % parafinskim oljem. Rezultati kažejo zadovoljivo ponovljivost ( $R_F$  vrednosti se razlikujejo za 10 %). Meje zaznave so 0.73 za CPC in 0.75  $\mu\text{g}$  za BJ-35. Opisana je ločba CPC in BJ-35 iz vzorca mehčalca ter določen vpliv kovinskih kationov in anionskih nečistoč na ločbo CPC in Brij-35.