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# A study of dye–surfactant interactions. Part 2. The effect of purity of a commercial cationic azo dye on dye–surfactant complex formation.

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## Abstract

The interactions between the cationic azo dye C.I. Basic Yellow 25 and the cationic surfactant cetylpyridiniu chloride have been studied by potentiometry, UV/VIS spectrophotometry and $^1$H NMR. The effect of the purity of t commercial sample of the dye on the dye–surfactant interactions has been investigated. The results show that t cetylpyridinium chloride forms a complex with one of the components of the commercial sample of the dye in aqueo solution. The concentration of this component is decreased by purification of the commercial dye sample. The resu also indicate that there are no dye–surfactant interactions in solutions of the cationic and nonionic components of t dye. According to this observation, we conclude that the surfactant cetylpyridinium chloride does not form a compl with the dye component in the commercial sample of C.I. Basic Yellow 25, and that the reduction of the free surfacta cation concentration in the solution causes reduction of the levelling action of the surfactant in the system involving t same charged dye and surfactant. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Cationic azo dye; Cationic surfactant; Interactions; Potentiometry; Spectrophotometry; $^1$H NMR

## 1. Introduction

Many studies in the interactions between dyes and surfactants in aqueous solutions have been performed, especially in dyeing systems, where level dyeing is controlled by surfactants [1–7]. Ionic surfactants, which are used as levelling agents, operate in two main mechanisms depending on the ionic type of the dye [8,9]. When t charge of the surfactant is opposite of that of dye, the attractive forces between the dye a surfactant lead to dye-surfactant complex form tion in the solution, resulting in level dyeing. cases where the surfactant is of the same ionic ty as the dye used, competition between the dye a the surfactant for the sorption sites in the fib causes level dyeing.

The main reason for this research work was o recent discovery that the cationic surfactant cety pyridinium chloride (CPC) forms a complex wi

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one of the components in the solution of a commercial sample of the cationic dye C.I. Basic Yellow 25. The obtained results were quite unusual, because there are no reports in the literature about the attractive interactions between the same charged surfactants and dyes. One of the explanations of these results could be that CPC, which has a planar structure containing 16 carbon atoms in the alkyl chain and the aromatic benzene ring, forms strong attractive hydrophobic and van der Waals forces with the cations of C.I. Basic Yellow 25 (BY25), and that these forces are stronger than the repulsive electrostatic interactions between the same charged ions. The results could also mean that there is a non-cationic component in the commercial sample which forms the complex with the surfactant cations. To ascertain which component interacts with CPC, a series of potentiometric, UV/VIS spectrophotometric and $^1$H NMR measurements have been carried out on solutions of the commercial and purified samples of BY25, as well as on solutions of the different separated dye components of BY25.

## 2. Experimental

### 2.1. Materials

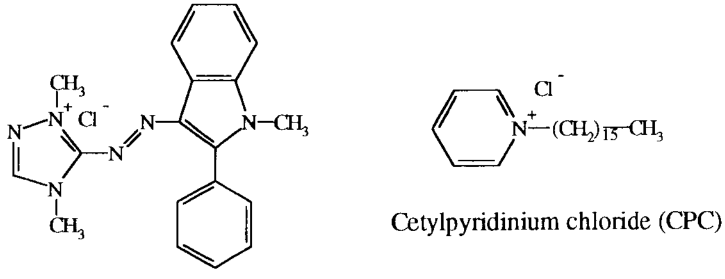
The commercial sample of the dye BY25 (CS-BY25) was purified by extraction with acetone and by several recrystallizations from a DMF–benzene mixture. Column chromatography was used for the separation of the purified sample (PS-BY25) into the cationic and nonionic dye components, using silica gel ($d < 65\,\mu$m) as adsc bent and acetone as eluent. The nonionic comp nent (NC-BY25) was eluted from the column a the cationic component (CC-BY25) remained the column.

Dye BY25 was also separately synthesised coupling diazotized 3-amino-1,2,4-triazole with methyl-2-(4′-tolyl)indole followed by alkylati [10]. The cationic and nonionic dye componen obtained by the synthesis, as well as diazo a coupling components, were also included in t study. The surfactant CPC was purified by sever recristalizations from acetone. The structural fo mulae of the dye BY25 and the surfactant C are shown in Fig. 1.

### 2.2. Measurements

Potentiometric measurements were carried o using a surfactant-selective membrane electro cell; the electrode membrane was prepar according to the established method [11] and h been described previously [7,12].

The electrochemical cell was constructed as fo lows: Ag I AgCl I reference solution; $1\times10^{-4}$ CPC in 0.1 m NaCl I polymer membrane surfa tant–surfactant complex I test solution; $x$ $m$ without and with $m_D$ II KCl (satd.) I $Hg_2Cl_2$ I H where $m_S$ represents the molal concentration CPC, and $m_D$ the molal concentration of BY added in the test solution. The relationsh between e.m.f. ($E$) of the cell and the CPC co centration ($m_S$) were carried out in the concentr tion range $1\times10^{-6}$ to $1\times10^{-2}$ mol kg$^{-1}$ at 25°C. calibration plot of $E$ vs log $m_S$ of CPC was ma



C.I. Basic Yellow 25 (BY25)

Cetylpyridinium chloride (CPC)

Fig. 1. The structural formulae of the dye and the surfactant investigated.

in water without dye and the experiment was repeated in the presence of CS-BY25, PS-BY25, CC-BY25, NC-BY25 and of the coupling component *N*-methyl-2-(4′-tolyl)indole (MTI) under the same conditions.

The visible absorption spectra of solutions of CS-BY25, PS-BY25, CC-BY25 and NC-BY25 were recorded at 25°C on a Varian Cary 1E UV-Visible Spectrophotometer using 1 cm cells and the $^1$H NMR spectra were determined in DMSO using a Bruker AVANCE 300 DPX Spectrophotometer using TMS as reference.

## 3. Results and discussion

Fig. 2. shows plots of $E$ vs log $m_S$ of the surfactant CPC in CS-BY25 and PS-BY25 solutions of different concentrations at 25°C.

It is apparent that all the plots of CPC obtain
in CS-BY25 and PS-BY25 are completely differe
from the calibration plot, which is linear over t
concentration range $5\times10^{-5}$ to $2.5\times10^{-3}$ m CP
with a slope of 59.0 ± 0.2 mV per decade. T
straight line obtained as calibration plot indicat
that according to the Nernstian equation [1
$E = E^o \pm k \log m_{S,F}$ the concentration of free su
factant cations ($m_{S,F}$), that is measured directly
the electrode, is equal to the stochiometric co
centration $m_S$, of CPC. The plots obtained in t
solution of CS-BY25, which lie below the calibr
tion curve in the whole measured concentratio
range, clearly show that the CPC-selective ele
trode could not detect the total amount of CP
ions in the test solutions, and that the concentr
tion of free surfactant cations is lower than t
stochiometric concentration. This means th
some of the surfactant cations are bound to t

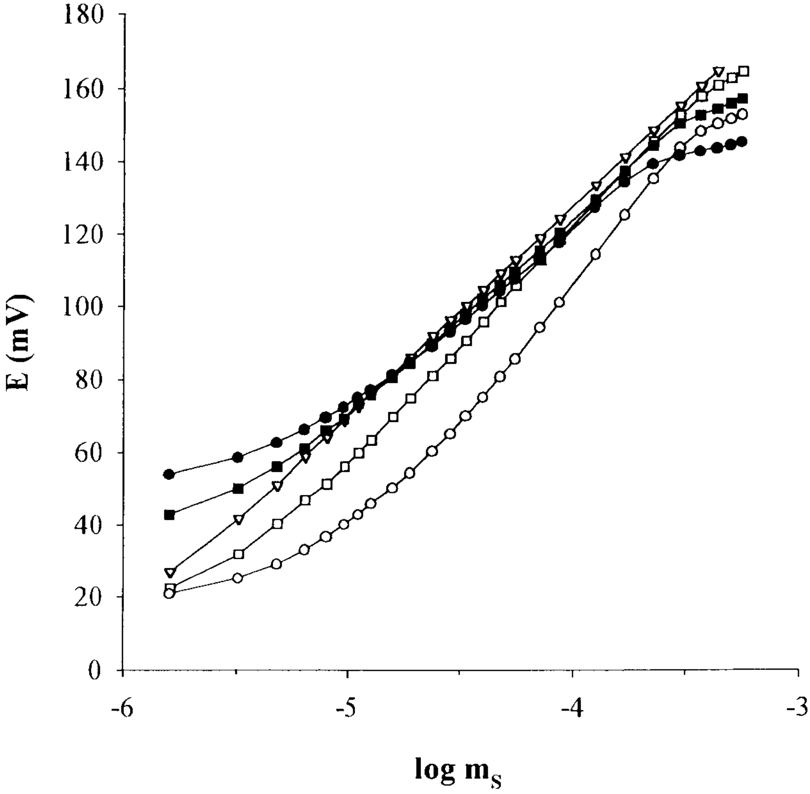


Fig. 2. Plots of $E$ vs log $m_S$ of the surfactant CPC in solutions of CS-BY25 and PS-BY25 at different concentrations at 25°C. -▽-▽ calibration curve, -□-□-: $5.094\times10^{-4}$ mol kg$^{-1}$ CS-BY25, -○-○-: $2.186\times10^{-3}$ mol kg$^{-1}$ CS-BY25, -■-■-: 5.108 × $10^{-4}$ mol kg PS-BY25, -●-●-: $2.156\times10^{-3}$ mol kg$^{-1}$ PS-BY25

complex and to which the electrode is not sensitive. Thus the measured $E$ values become smaller than they would be in the case where all surfactant cations in the solution were free. The concentration of bound surfactant cations increases with the increase of CS-BY25 concentration.

The plots of $E$ vs log $m_S$ in PS-BY25 shows that curves lie above the calibration curve at low surfactant concentrations, then cross the calibration curve and lie below the calibration curve at higher surfactant concentrations. The deviation from linear behaviour at low surfactant concentrations can be explained as a result of the selective behaviour of the CPC-selective electrode in the presence of interfering cations in the measured solution [13,14]. Because the purification of CS-BY25 leads to an increase of the cationic dye component concentration in the sample, dye cations in PS-BY25 can be interpreted as interfering cations that affect the normal electro response to CPC cations at low surfactant co centrations. The deviation from the line response noticeable at higher CPC concentratio suggests that complex formation takes place in t solution of PS-BY25 in this concentration rang It is seen from the extent of the deviation that t concentration of bound CPC cations in PS-BY is much lower compared to that of CS-BY25 at t same experimental conditions. From these resul one can say that the concentration of the comp nent which forms the complex with CPC decreas in PS-BY25. But on the other hand, we should n overlook the fact that the purification of the d results in the removal of a great amount of Na from the commercial sample and which cou affect the dye–surfactant interactions. The Na present in CS-BY25 apparently reduces the ele trostatic repulsion between the same charged d

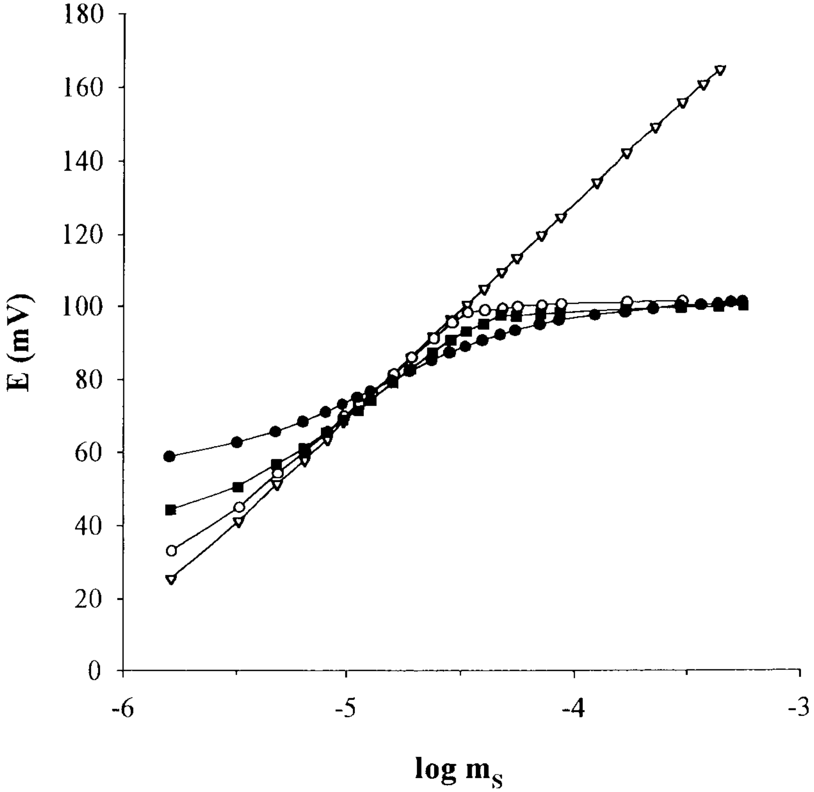


Fig. 3. Plots of $E$ vs log $m_S$ of the surfactant CPC in solutions of PS-BY25 in the presence of 0.1 m NaCl at 25°C. -▽-▽-: calibrati curve in pure water, -○-○-: calibration curve in 0.1 m NaCl, -■-■-: $5.677\times10^{-4}$ mol kg$^{-1}$ PS-BY25, -●-●-: $6.986\times10^{-3}$ mol kg$^{-1}$ PS-BY

and surfactant, which is opposed to the dye–surfactant complex formation in the solution. If attractive hydrophobic and van der Waals forces between the dye and the surfactant become stronger than the repulsion between the same charged cations, it could lead to dye–surfactant complex formation in the commercial sample of the dye. To check the influence of the NaCl on the dye–surfactant interactions a series of plots of $E$ vs log $m_S$ were carried out in mixtures of PS-BY25 and NaCl, shown in Fig. 3.

It is evident from the figure that the addition of NaCl in the PS-BY25 does not change the shape of the e.m.f. plots at low surfactant concentrations, which indicates that there is no dye-surfactant complex formation in the salt solutions of PS-BY25 in the submicellar concentration range CPC. The addition of NaCl only affects t change of the critical micelle concentration CPC, which appears at lower concentration th in pure water.

The electronic spectra data shown in Fig. shows the great difference in the composition CS-BY25 and PS-BY25, the increase of abs bance of PS-BY25 ($E$=0.9546) compared to C BY25 ($E$=0.1186) at 458 nm clearly showing th the purified sample contains a higher concentr tion of the dye component than the commerci one. The $^1$H NMR spectra of the commercial a purified dye samples (Fig. 5). also suggest th there are less impurities in PS-BY25 than in C BY25.

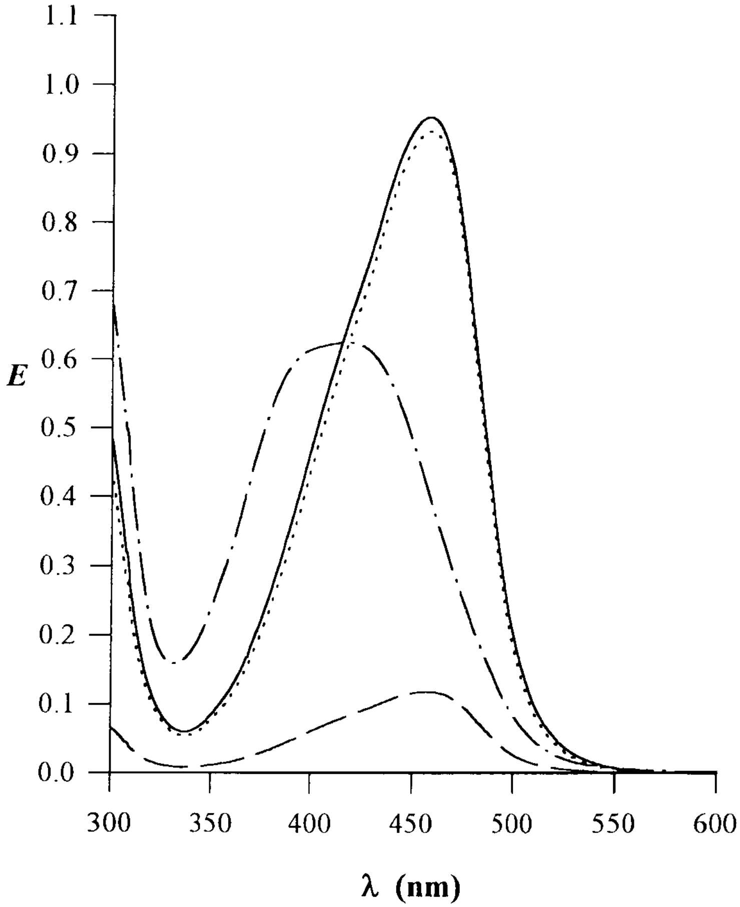


Fig. 4. UV/VIS spectra of dye solutions at 25°C. — — — : 3.593×10$^{-5}$ mol kg$^{-1}$ CS-BY25, ·······: 3.534×10$^{-5}$ mol kg$^{-1}$ PS-BY
————: 3.506×10$^{-5}$ mol kg$^{-1}$ CC-BY25, - · - · - ·: NC-BY25

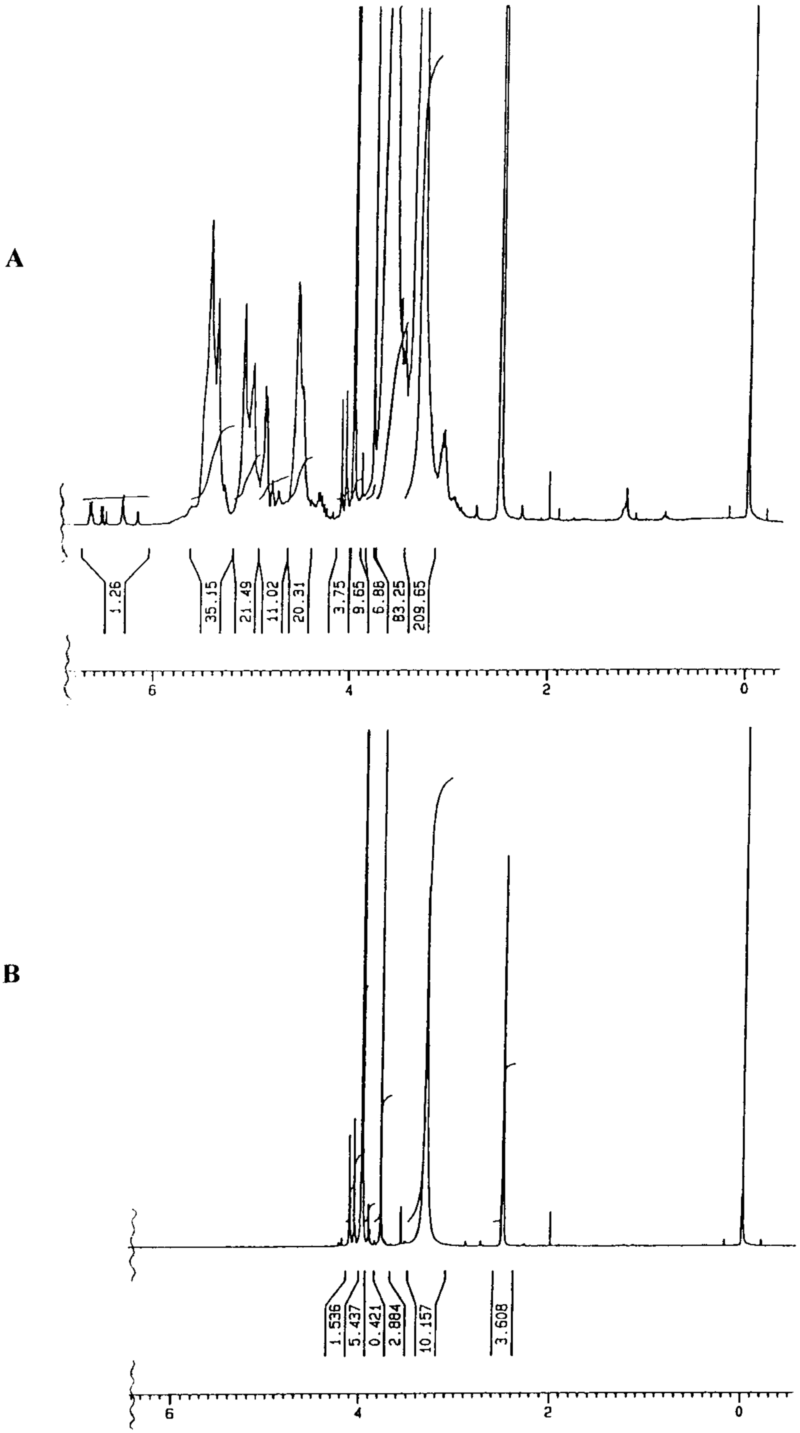


Fig. 5. $^1$H NMR spectra of the methyl group protons of the commercial and purified dye samples at 25°C. A: CS-BY25, B: BY25.

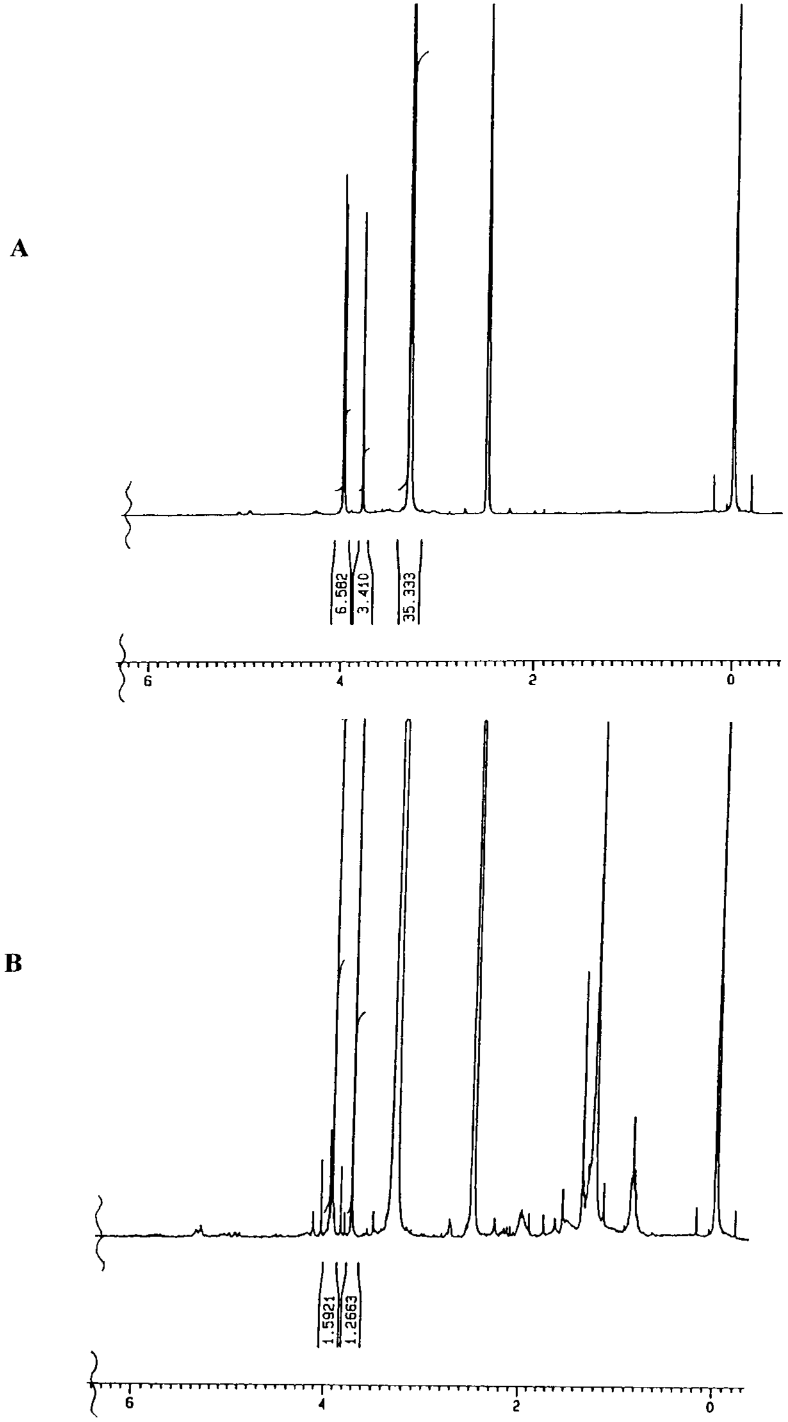


Fig. 6. $^1$H NMR spectra of the methyl group protons of the cationic and nonionic dye components at 25°C. A: CC-BY25, B: N
BY25.

Comparison of the spectra in Fig. 6. shows that CC-BY25 and NC-BY25 are of different ionic type. There are three signals for the methyl hydrogens of CC-BY25 (3.77, 3.96 and 3.98 ppm) but only two signals for NC-BY25 (3.73 and 3.93 ppm). The third chemical shift of CC-BY25, which is typical of the hydrogens in $-CH_3$ compounds bound to the quaternary N of the heteroaromatic ring, strongly indicates the presence of a cationic component. The visible absorption spectra (Fig. 4) also confirm the presence of two molecular species with different absorption behaviour, i.e. CC-BY25 with absorption maximum at 458 nm and NC-BY25 with absorption maximum at 417 nm. The shape of the spectrum of CC-BY25 is quite different from that of NC-BY25, but very similar to that of PS-BY25. These findings are in good agreement with the assumption obtained by potentiometric measur ments that the cationic dye component, of whi the concentration strongly increases in PS-BY2 is not the component that forms the complex wi CPC. The results of the potentiometric measur ments obtained in the solutions of CC-BY25 a NC-BY25, as well as in the solution of the no ionic coupling component MTI also confirm th conclusion.

The results shown in Fig. 7. indicate that no of the studied dye components forms a compl with the surfactant CPC. The titration curv obtained in CC-BY25, NC-BY25 and MTI a linear and in good agreement with the calibratio plot. The deviation from linear behaviour at lo surfactant concentrations is due to the detectio limit of the CPC-selective electrode in the solutio of CC-BY25.

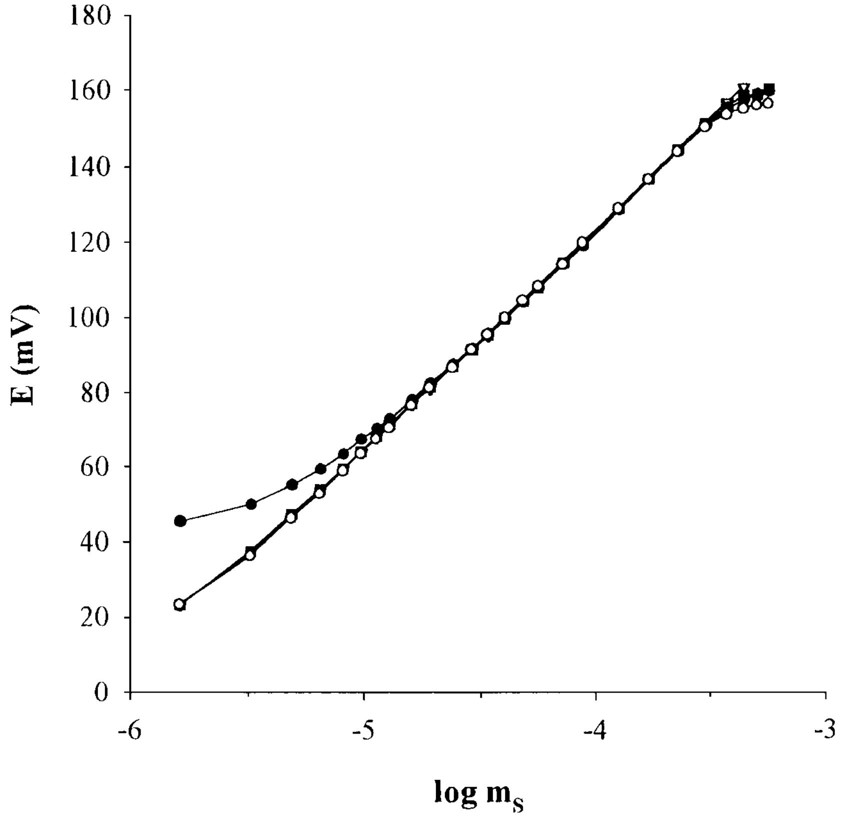


Fig. 7. Plots of $E$ vs log $m_S$ of the surfactant CPC in solutions of CC-BY25, NC-BY25 and MTI at 25°C. -▽-▽-: calibration cur -●-●-: $1.017 \times 10^{-3}$ mol kg$^{-1}$ CC-BY25, -■-■-: 2.312 $10^{-4}$ mol kg$^{-1}$ NC-BY25, -○-○-: $1.029 \times 10^{-3}$ mol kg$^{-1}$ MTI

## 4. Conclusion

There are no attractive interactions between the dye BY25 and the surfactant CPC in aqueous solution. It can be noted from the results that electrostatic repulsion between CPC and BY25 dominates in the solution and does not allow non-coulombic attractive van der Waals forces and hyrdophobic interactions to act between the cations. Complex formation in the mixture of CS-BY25 and CPC results in reduction in concentration of the free surfactant cations, which can compete with the dye cations for the sorption sites in the fibre, resulting in reduction of levelling action of CPC in the solution of CS-BY25.

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## References

[1] Barni E, Savarino P, Viscardi G. Acc Chem Res 1991;
98–103.
[2] Dutta RK, Bhat SN. Bull Chem Soc Jpn 1992;65:1089–
[3] Yamamoto K. Analytical Sciences 1992;8:299–305.
[4] Dutta RK, Bhat SN. Bull Chem Soc Jpn 1993;66:2457–
[5] Novicka G, Nowicki W. J Chim Phys 1994;91:247–57.
[6] Guo LN, Petit-Ramel M, Arnaud I, Gauthier R, Chev
lier Y. JSDC 1994;110:149–54.
[7] Simončič B, Špan J. Dyes and Pigments 1998;36:1–14.
[8] Datyner A. Surfactants in textile processing, Surfacta
Science Series, vol. 14. New York: Marcel Dekker, 198
[9] Shore J. Colorants and auxiliaries, organic chemistry a
application properties, Manchester: SDC, 1990.
[10] Zollinger H. Color chemistry: syntheses, properties a
applications of organic dyes and pigments. Weinhei
Germany: VCH. 1987.
[11] Cutler SG, Meares PJ, Hall DG. Electroanal Ch
1977;85:145–61.
[12] Simončič B, Špan J, Vesnaver G. Dyes and Pigme
1994;25:69–78.
[13] Morf WE. The principles of ion-selective electrodes and
membrane transport, Budapest: Akademiai Kiado, 198
[14] Covington AK. Ion-selective electrode methodology, v
1. Boca Raton, FL: CRC Press, 1979.