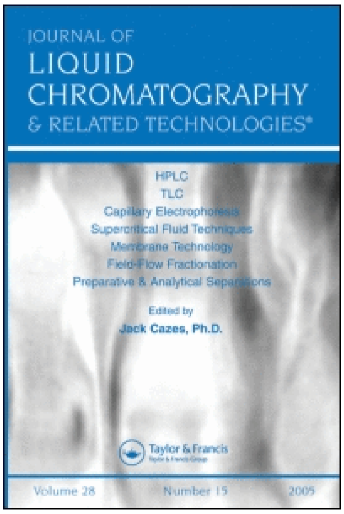

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CHROMATOGRAPHIC RETENTION OF Ni(II), Co(II) AND Cu(II) AS DIETHYLDITHIOCARBAMATE COMPLEXES IN PRESENCE OF SURFACTANT/n-PROPANOL/WATER SYSTEMS: DETERMINATION OF MICELLAR BINDING CONSTANTS

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ABSTRACT

This paper presents the values of the micellar binding constants of Ni(II), Co(II) and Cu(II) as complexes with sodium diethyldithiocarbamate, DDTC, in presence of hexadecyltrimethylammonium bromide, CTAB, and sodium dodecylsulphate, SDS, with larger amounts of n-Propanol as organic modifier, by High Performance Liquid Chromatography. Binding constants have been obtained from two equations: a) Arunyanart's treatment, very used for organic compounds but that is not take into account the influence of modifier and b) a multiple regression analysis that permits to consider the high quantities of n-Propanol.

INTRODUCTION

Surfactants which possess both hydrophilic and hydrophobic moieties may associate in aqueous media to form dynamic aggregates commonly called normal micelles. Above a certain concentration, termed the critical micelle concentration, CMC, which is unique for every surfactant, the molecules self-aggregate such that the hydrocarbon tails are oriented toward the center of the aggregate and the polar head groups point outward.[1-4] This self-aggregation serves largely to eliminate the hydrocarbon-water interface and is then energetically favorable. The repulsion of the head groups from each other, however, is the force controlling the size and shape of micelles. For these reasons, micelle structure is somewhat dependent on solution properties, changes in ionic strength, addition of an organic solvent, and even some solutes can affect micelle shape and size.[5-8]

Surfactants also can associate in nonaqueous media forming reverse micelles, but now the polar head groups are oriented toward the interior of the aggregate, and the hydrophobic chains are in contact with the solvent.[9-11] The size and characteristics of these structures are critically dependent upon the water content of the solution, the water present tends to accumulate within the core to form an isolate pool of water which may exhibit unique properties. These reverse micelles are more complex and less studied and understood than normal micelles.

The utilization of micellar solutions as the mobile phase in liquid chromatography has generated a new chromatographic variety that is the Micellar Liquid Chromatography, MLC.[12-16] Armstrong et al[12,13] first effectively demonstrated the usefulness of replacing traditional organic modifiers used in reverse phase liquid chromatography with an aqueous micelle solution and developed a three-phase model to allow a theoretical description of MLC

In this model, three equilibria are involved, the first is the solute distribution between the mobile micellar pseudophase and the bulk mobile phase; the second is the solute partitioning between the stationary phase and the mobile micellar pseudophase and the last equilibrium is the distribution of the solute between the bulk mobile phase and the stationary phase.

According to these equilibria, Arunyanart and Cline Love[17] have derived an equation that correlates the capacity factor, k', with the micellized surfactant concentration, C_M, in the form:

$$\frac{1}{k'} = \frac{K_S}{\Phi\,[L_S]\,K_1}\,C_M + \frac{1}{\Phi\,[L_S]\,K_1} \qquad (1)$$

where K_S is the association or binding constant of a solute to micelles, Φ is the phase ratio (V_S/V_M), V_S and V_M are the total stationary phase volume and the dead column volume respectively, [Ls] is the stationary phase concentration, K_1 the binding constant for the solute between the stationary phase and the bulk solvent and C_M is given by the total surfactant concentration minus the CMC. If plots of 1/k' vs C_M are lineal it is possible to calculate the binding constant K_S from the slope:intercept ratio.

In the literature, there are many papers in regard to determine the solute-micelle binding constant using normal micelles and micellar systems modified with small percentages of some organic modifiers, like short and medium chain alcohol, for some organic solutes.[18-29] On the contrary, the use of micellar mobile phases in inorganic chromatography, metal-complexes, has been limited.[30-36] In a previous paper,[36] the separation and determination of Co(II), Ni(II) and Cu(II) as diethyldithiocarbamate complexes is achieved by HPLC using a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and a larger amount (45% v/v) of n-Propanol in the mobile phase.

In any case, the Arunyanart's expression (equation 1) is not applied when the surfactant mobile phase solutions contain a larger amount of an organic modifier.

In this paper, the equation 1 has been tested using two different surfactants, one cationic as hexadecyltrimethylammonium bromide,CTAB, and one anionic as sodium dodecylsulphate, SDS, in presence of increasing percentages of n-Propanol, PrOH.

EXPERIMENTAL

Materials

All reagents were of analytical grade. The Cu(II), Ni(II) and Co(II) solutions were prepared from the nitrates (Merck) of each one. The ligand, sodium diethyldithiocarbamate (DDTC), surfactants (CTAB, SDS) and n-Propanol (PrOH) from Merck were used as was received.

A Waters liquid chromatograph was used with a pump model 510, UV-Vis detector model 481, an integrator model 740 and an injection valve Rheodyne with an injection volume of 20 µl.

The separation columns were Lichrosorb RP-18, 150x3.9 mm, particle size 10µm from Sugelabor for CTAB and Bondclone RP-18, 150x3.9 mm, particle size 10µm from Phenomenex for SDS.

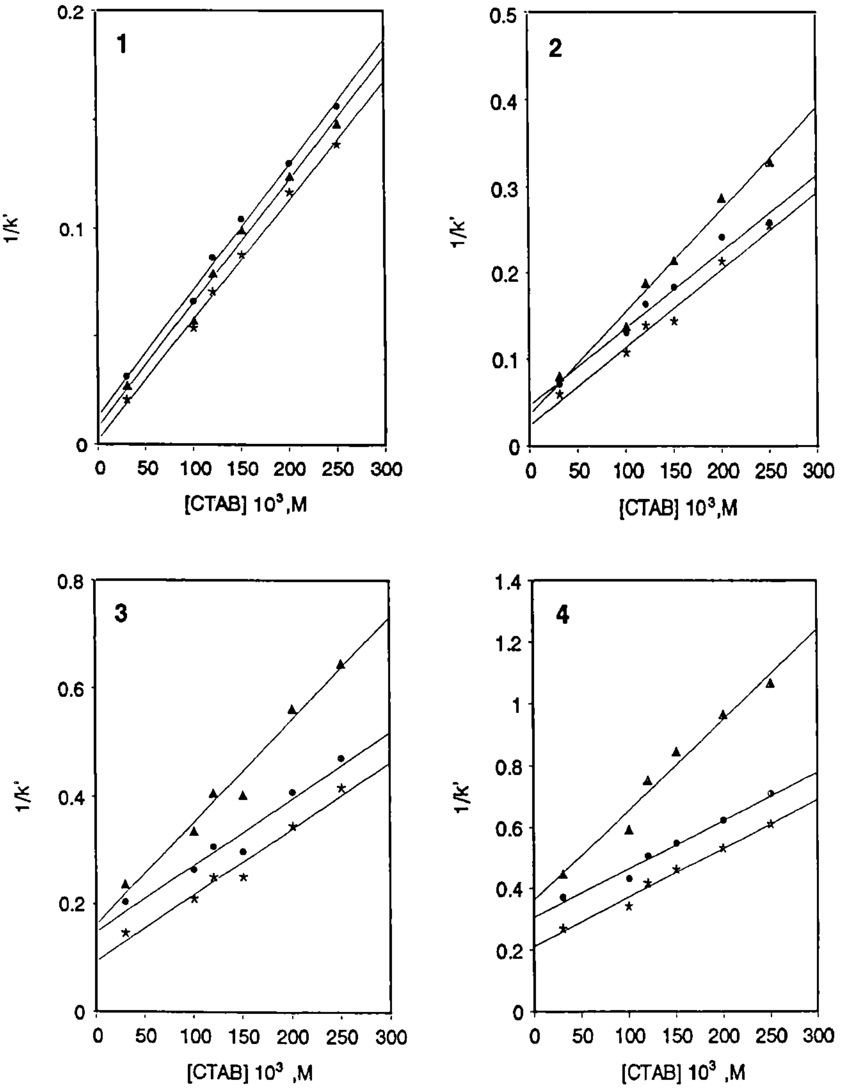

Figure 1. Variation of 1/k' in function of CTAB concentration at different percentages of n-Propanol (1, 20%; 2, 30%; 3, 40%; 4, 50%); ● Ni(II); ▲ Co(II); ✱ Cu(II).

Methods

The mobile phases used in this work were prepared with the cationic and

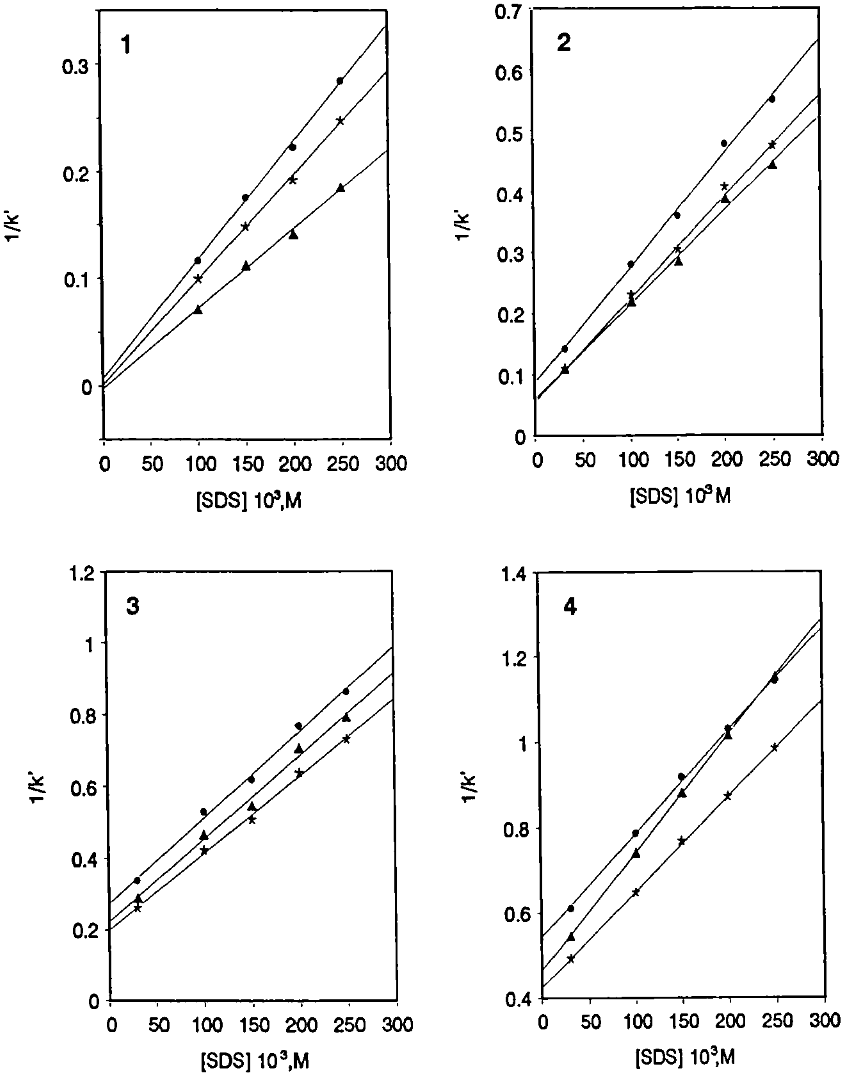

Figure 2. Variation of 1/k' in function of SDS concentration at different percentages of n-Propanol (1, 20%; 2, 30%; 3, 40%; 4, 50%); ● Ni(II); ▲ Co(II); ✳ Cu(II).

anionic surfactants (CTAB,SDS) in an appropriate concentration, the ligand (DDTC) and the organic modifier, PrOH, which was needed to reduce the retention

Table 1

Values of the Binding Constant for Metal(II)-DDTC Complexes at Different Percentages of n-Propanol in Presence of CTAB and SDS

K_S, M^{-1} in CTAB

%PrOH v/v	$[PrOH]_T$,M	Ni(II)	Co(II)	Cu(II)
20	2.66	48.9	58.9	147.3
30	3.99	15.5	23.9	36.1
40	5.32	8.1	11.1	12.5
50	6.66	4.8	5.0	6.8

K_S, M^{-1} in SDS

%PrOH v/v	$[PrOH]_T$,M	Ni(II)	Co(II)	Cu(II)
20	2.66	133.8	---	476.1
30	3.99	20.5	24.2	27.6
40	5.32	8.7	10.2	10.7
50	6.66	4.4	5.9	5.2

$[PrOH]_T$ is the total concentration of n-Propanol

times. A buffer wasn't used to modify the pH.

These mobile phases were prepared weighing the necessary quantities of surfactants (at concentrations between 0.03M and 0.25M) and DDTC 10^{-4}M and dissolving them in a mixture of n-Propanol and Milli-Q water with the percentage of alcohol varying from 20 to 50% v/v. All the mobile phases were filtered and placed in an ultrasound bath for twenty minutes for degasification before introduction to the chromatographic system.

The complexes were prepared dissolving the necessary quantity of each one of the salts directly in the mobile phase. These complexes were then injected into the chromatographic system.

The variation of the retention times of the three complexes as a function of the concentration of CTAB or SDS in the mobile phase with different percentages of propanol, as organic modifier, and DDTC in a concentration 10^{-4}M was determined.

Table 2

Equations Obtained for Multiple Regression with Confidence Level of 95% for CTAB in High Performance Liquid Chromatography for the Three Metal Ions (1/k' = a + b [CTAB] + c $[PrOH]_M$)

	a±C.I.	b±C.I.	c±C.I.	% Agreement
Ni(II)	-0.1552±0.0383	1.1805±0.1817	0.0871±0.0072	96.41

1/k' = 0.1552 ± 1.1805 [CTAB] + 0.0871 $[PrOH]_M$

	a±C.I.	b±C.I.	c±C.I.	% Agreement
Co(II)	-0.3153±0.0847	1.7318±0.4012	0.1412±0.0159	93.28

1/k' = -0.3153 + 1.7318 [CTAB] + 0.1412 $[PrOH]_M$

	a±C.1.	b±C.1	C±C.1	% Agreement
Cu(II)	-0.1249±0.0527	1.0866±0.2580	0.0700±0.0103	90.37

1/k' = -0.1249 = 1.0866 [CTAB] + 0.0700 $[PrOH]_M$

C.I. = Confidence interval.

The detection was carried out by UV-visible spectrophotometry with a wavelength of 326nm for Ni(II) and Co(II) complexes and 440nm for the Cu(II) complex.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of 1/k' vs. C_M for the three DDTC complexes in presence of CTAB and SDS, respectively, at four different percentages of n-Propanol. According to the high quantities of alcohol, the critical micelle concentration, CMC, is practically zero and C_M is the total surfactant concentration. In all cases, exists a good linear regression and thus it is possible to calculate the binding constants, K_S for the three metal complexes at different percentages of PrOH, for CTAB and SDS; Table 1 collects the K_S values.

For the Co(II)-DDTC complex is not possible to calculate the binding constant at 20% (v/v) PrOH in presence of SDS because in the linear regression, the intercept has a negative value. The found values of K_S show that for elevated percentages of PrOH the binding constants are very different for the three complexes, but at high PrOH concentrations (~up 30% v/v) the K_S values are low and similar for the Ni(II), Co(II) and Cu(II) DDTC complexes in presence of both surfactant systems. This behavior indicates that, the presence of organic modifier, PrOH, at high concentration provokes the same microenvironment to possible complexes interactions.

Despite this good correlation, in equation 1 the binding constant, K_S, according to the pseudophase micellar model,[37,38] is defined by:

$$K_S = \frac{[S]_M}{[S]_W\ C_M} \qquad (2)$$

where, S is the solute and the subscripts W and M denote the aqueous and micellar phases. In this equation the PrOH concentration is not considered. However, in presence of alcohol the binding constant can be defined by the following expression:

$$K_S = \frac{[S]_M}{[S]_W\ (C_M + [PrOH]_M)} \qquad (3)$$

since one fraction of micellized alcohol is a part of the micellar phase. The $[PrOH]_M$ is calculated from a distribution equilibrium defined by Gettins et al.[39] that gives the following equation:

$$K_{PrOH} = \frac{[PrOH]_M}{[PrOH]_W\ (C_M + [PrOH]_M)} \qquad (4)$$

To calculate the micellized concentration of n-Propanol it is necessary to know the equilibrium constants, K_{PrOH}, that according to the literature have the following values: 0.5 M^{-1} for CTAB[39] and 8.0 for SDS.[40]

In order to study the influence of the micellized concentration of PrOH upon the chromatographic retention, a multiple regression analysis has been realized according to the equation:

$$\text{RETENTION} = a + b\ C_M + c\,[PrOH]_M \qquad (5)$$

Table 3

Equations Obtained for Multiple Regression with Confidence Level of 95% for SDS in High Performance Liquid Chromatography for the Three Metal Ions ($1/k' = a + b\,[SDS] + c\,[PrOH]_M$)

	a±C.I.	b±C.I.	c±C.I.	% Agreement
Ni(II)	-0.6674±0.0774	2.1015±0.2546	0.19111±0.0129	98.49

$1/k' = 0.6674 + 2.1015\,[SDS] + 0.1911\,[PrOH]_M$

	a±C.I.	b±C.I.	c±C.I.	% Agreement
Co(II)	-0.7689±0.1193	2.0484±0.3920	0.2021±0.0199	96.75

$1/k' = -0.7689 + 2.0484\,[SDS] + 0.2021\,[PrOH]_M$

	a±C.1.	b±C.1	C±C.1	% Agreement
Cu(II)	-0.5099±0.1113	1.7132±0.3645	0.1522±0.0195	95.19

$1/k' = -0.5099 + 1.7132\,[SDS] + 0.1522\,[PrOH]_M$

C.I. = Confidence interval.

where the retention has been expressed by three ways: the capacity factor, k', the logarithm form, log k' and the opposite, 1/k'. The best results have been found by 1/k' for the three metal-DDTC complexes and both surfactants, CTAB and SDS.

Tables 2 and 3 show, for CTAB and SDS respectively, the obtained values of parameters a, b and c with the corresponding confidence intervals. As can be observed in these tables, the agreement of experimental values of 1/k'to Equation 5 is, in all cases, greater than 90%. To confirm this behavior, Figures 3,4 show the agreement between the experimental and calculate values in presence of CTAB and SDS, respectively.

According to these results and the linear relation between 1/k' and C_M (Figures 1,2), it is possible to arranged equation 5 in form:

$$\frac{1}{k'} = a' + b\ C_M \tag{6}$$

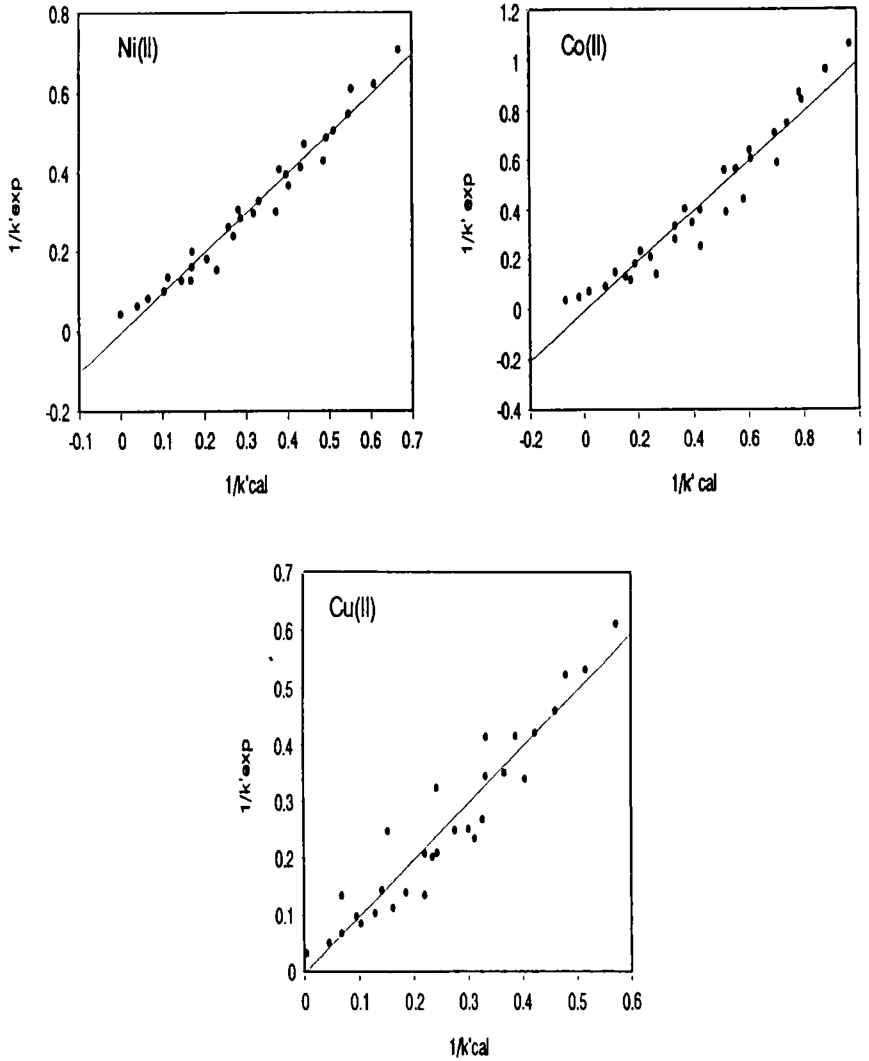

Figure 3. Experimental 1/k' *vs* calculated 1/k' using multiple regression equation in CTAB media.

so that the parameter a' is expressed like:

$$a' = a + c\,[\mathrm{PrOH}]_M \qquad (7)$$

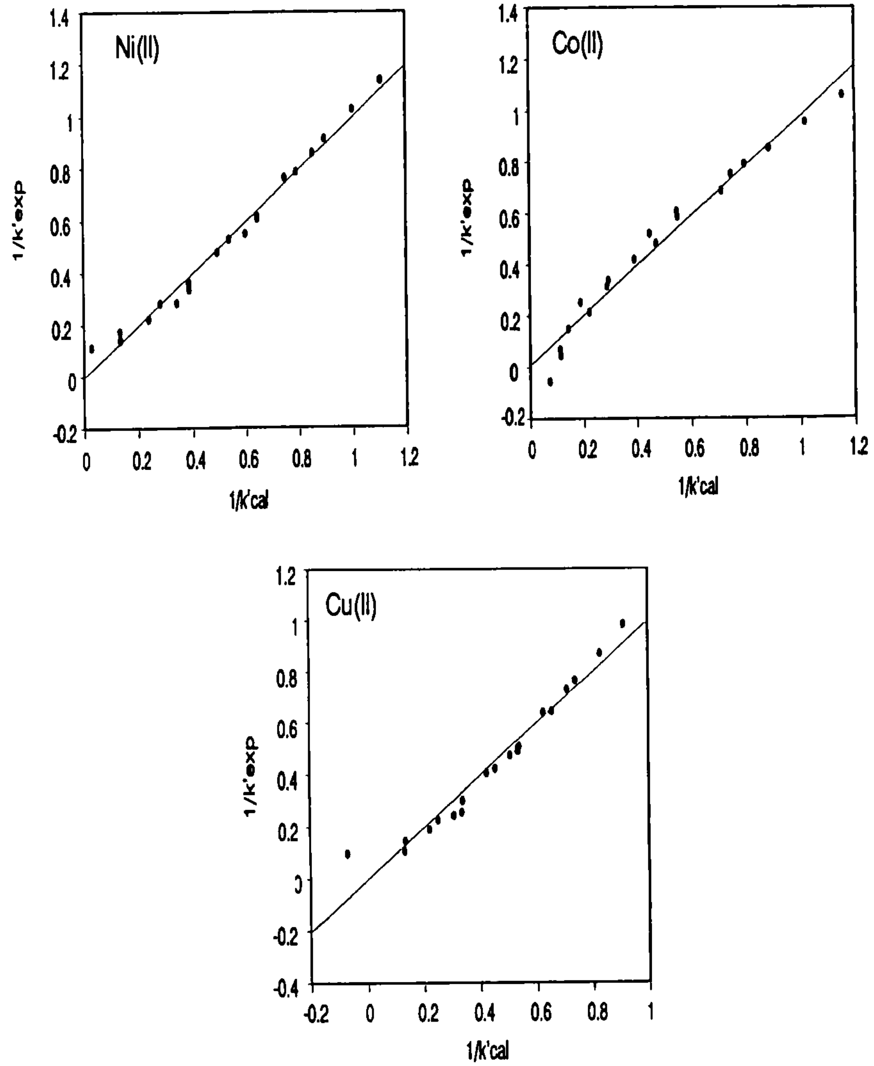

Figure 4. Experimental 1/k' *vs* calculated 1/k' using multiple regression equation in SDS media.

and in comparison to the Arunyanart's equation the parameter b would be K_S / a', so that a' includes the distribution constant of the complexes between the stationary phase and the hydroalcoholic extramicellar phase. In this way, it is possible to calculate the binding constants, K_S, but taking into account the micellized

Table 4

Binding Constants for the Complexes with CTAB and SDS at Different Concentrations of n-Propanol Using the Multiple Regression

K_S, M^{-1} (CTAB)

$[PrOH]_M$, M	Ni(II)	Co(II)	Cu(II)
2	62.1	----	72.0
3	11.1	16.0	12.8
4	6.1	6.9	7.0
5	4.2	4.4	4.8
6	3.2	3.3	3.7
7	2.6	2.6	3.0

K_S, M^{-1} (SDS)

$[PrOH]_M$, M	Ni(II)	Co(II)	Cu(II)
2	----	----	----
3	----	----	----
4	21.7	51.9	17.3
5	7.3	8.5	6.8
6	4.4	4.6	4.3
7	3.1	2.7	3.1

concentration of n-Propanol. For this calculation has been necessary to obtain, from the $[PrOH]_M$ calculated by equation 4, the total range of micellized concentration of n-Propanol for each surfactant and some values, have been introduced into equations 6,7 with the aim to obtain the K_S values.

Table 4 shows the calculated values of the binding constants for Ni(II), Co(II) and Cu(II) as DDTC complexes in CTAB and SDS. In some cases, it is not possible to obtain the K_S values because in equation 6 the parameter a' gives a negative value.

In presence of CTAB, if it is compared with Arunyanart's equation (Table 1), the multiple regression analysis gives, in all cases, K_S values more lower and at high micellized PrOH concentration, up to 4 M (~ 30% v/v) the three metal-DDTC complexes present the same values. According with the results obtained in our laboratory[41] that, confirm the presence of aggregates in these systems

CTAB/PrOH/water it is possible to think that the complexes interact in the same way with them, showing a similar behavior.

The results in SDS, indicate similar K_S values for the DDTC complexes, at more higher micellized PrOH concentrations than CTAB, $[PrOH]_M \geq 6$ M (~ 50% v/v). At micellized PrOH low concentrations there is a dispersion of K_S data, that agrees with the presence of mixed aggregates for this system SDS/PrOH/water.[41] Anyway, comparing the obtained results with those by Arunyanart's equation, the multiple regression analysis gives low binding constant values.

CONCLUSIONS

The variation of the opposite capacity factor, as chromatographic parameter, is linear with surfactant concentration in presence of larger percentages of n-Propanol, for Ni(II), Co(II) and Cu(II) as DDTC complexes.

According with this behavior, it is possible to obtain the micellar binding constants, K_S, by a multiple regression analysis where, it has been considered the micellized n-Propanol concentration.

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