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Metal Complex Dyes of Nickel with Schiff Bases

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ABSTRACT

Nickel complexes with Schiff bases 2-(2-pyridylmethyleneamino)phenol (PMAP) and 2-(2-quinolylmethyleneamino)phenol (QMAP) were prepared and the composition of the crystalline complexes was determined by elemental analysis, solubility, UV–Vis, IR and mass spectrometry. It was found that, for the Ni–PMAP complex, two ligands were bonded to one metal ion, giving a neutral complex with one molecule of water probably bonded in the inner sphere of the complex. With QMAP, nickel forms cationic complexes with a metal-to-ligand ratio of 2:2 and two molecules of acetate as anions. The solution properties of Ni–QMAP were investigated at different pH. The chromophoric properties of the complex were enhanced with increase in pH, while stability decreased with time. The application of QMAP as a spectrophotometric reagent for the determination of small amounts of nickel was investigated. Adherence to Beer's law was observed from 0·00 to 5·00 μg/ml at pH 8, the most appropriate pH in respect to sensitivity and acceptable time stability of the complexes. Dyeing properties of both complexes were investigated on polyamide 66 and the influence of the addition of another phenyl ring to the ligand molecule on the dyeing properties of the complex is discussed.

INTRODUCTION

In previous work we have investigated the syntheses of a number of azomethine compounds and their metal complexes, as well as their

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applicability as spectrophotometric reagents or as metal complex dyes.[1–9] We found that 2-(2-pyridylmethyleneamino)phenol (PMAP) reacts with Mn(II) ion in solution giving ML_2 stoichiometry.[1] The isolated crystalline Mn–PMAP complex offers some potential as a dye for wool and nylon 6.6, with both fibers showing increased exhaustion at higher pH values, and wool showing a better color yield. The chromium (III)–PMAP dye[2] was used for wool dyeing and studies were made on the estimation of the stability of the bonding between the dye and wool fiber at pH 4·5 and 5·5. Since effluents in the dye and textile industry are a potential ecological problem, the decolorization of chromium(III)–PMAP dye under aerobic conditions has also been investigated.[3] PMAP was successfully used as a sensitive reagent for the simultaneous determination of chromium(III) and zirconium(IV),[4] zinc(II) and nickel(II),[5] and nickel(II) and manganese(II)[6] by first-derivative spectrophotometry. The composition and stability constants for Ni–PMAP and Co–PMAP complexes have been determined by three methods[7] at constant temperature (25 ± 1°C), ionic strength, $I = 0{\cdot}5$ M ($NaNO_3$) in a methanol/water volume ratio of 0.1 and at different pH. The composition and stability constants using the model of the single predominant complex species have been determined by two methods, viz. the mole fraction variation method and the mole ratio variation method. The third method, using the model of consecutive complexes simultaneously present in the solution, was the method of corresponding solutions. The results obtained using these three methods are discussed.

2-(2-Quinolylmethyleneamino)phenol (QMAP) ligand has been investigated in respect of its chelating properties for cobalt(II) and manganese(II) ions.[8] It was found that the QMAP complex with cobalt(II) is of an ionic type, while that for manganese(II) is a neutral complex. In solution, both metal ions form complexes of the ML_2 type. Complexes with cobalt are more stable than those with manganese.

In this paper we have studied the synthesis and characterization of nickel with PMAP and QMAP as a chelating azomethine ligand. The solution properties of the the PMAP complex, and the possibility of using QMAP as a spectrophotometric reagent for the determination of nickel have also been investigated. Properties of the Ni–PMAP and Ni–QMAP complexes for dyeing of polyamide 66 fabric are reported.

2 EXPERIMENTAL

PMAP was prepared from 2-pyridinecarbaldehyde and 2-hydroxyaniline according to the previously described procedure.[9,10] QMAP was prepared from *o*-aminophenol and 2-quinolinecarbaldehyde.[8,11] CHN analyses of the ligands gave good agreement with the literature values.

2.1 2-(2-Pyridylmethyleneamino)phenol nickel(II), Ni-PMAP

The nickel–PMAP complex was prepared by addition of 2-(2-pyridylmethyleneamino)phenol (1·50 g) to a stirred methanolic solution (40 ml) of Ni(II) acetate tetrahydrate. After stirring for 10 h at room temperature, excess solvent was evaporated and the resulting mixture was then allowed to cool. The filtered brown–orange crystals were rinsed several times with methanol and finally dried *in vacuo* (m.p. 339°C).

Found ($C_{24}H_{20}O_3N_4Ni$): C, 61·18; H, 4·28; N, 11·89; Ni, 12·46%.
Calcd.: C, 61·22; H, 4·32; N, 11·44; Ni, 12·51%.

2.2 2-(2-Quinolylmethyleneamino)phenol nickel(II), Ni–QMAP

The nickel–QMAP complex was prepared by addition of 2-(2-quinolylmethyleneamino)phenol (2·48 g) to 60 ml of a methanolic solution of $Ni(CH_3COO)_2 . 4H_2O$ (2·48 g) with vigorous stirring. The red solution was stirred for 6 h at room temperature and left to stand overnight. The dark red crystals were filtered and washed with methanol (m.p. 336°C).

Found ($C_{36}H_{28}O_6N_4Ni_2$): C, 60·00; H, 3·50; N, 7·82; Ni, 15·82%.
Calcd.: C, 59·22; H, 3·87; N, 7·68; Ni, 16·08%.

2.3 General

All chemicals and solvents were of reagent grade and were used without further purification.

A stock solution of Ni was prepared by dissolving $Ni(NO_3)_2$ (Merck) in doubly distilled water. The solution was standardized complexometrically. For pH adjustment, standard buffer solutions (Titrival, Kemika) were used.

Melting points were determined on a Koffler hot stage apparatus and they are given uncorrected. Samples for elemental analyses were dried for 6 h in vacuum, p = 533 Pa (0·04 mm Hg) at 100°C above phosphorus pentoxide.

The IR spectra were recorded on a Perkin-Elmer Model 257 using KBr pellets. Mass spectra were determined using a Hitachi/Perkin-Elmer Model RMU-60 mass spectrometer.

For potentiometric titrations a Metrohm E 436 apparatus was used. UV/Vis spectra were recorded on a Varian DMS-80 spectrophotometer and dye exhaustion was measured on a Pye Unicam SP 1800 spectrophotometer. The pH of the solution was measured on a microprocessor-controlled pH-meter (Iskra, Model MA 5740).

Data evaluations for stability constants were performed using an IBM compatible PC AT 486 computer.

A Linitest apparatus (Hanau) was used for the isothermal dyeing of polyamide 66 (dtex/34/2). Dyeing was carried out at 100°C and pH 6 (ammonium acetate buffer) with the addition of 1 g/liter of dispersing agent Sarabid 200 LL (TT. CHT). Dye exhaustion was carried out in Soxhlet apparatus with *N*,*N*'-dimethylformamide and followed spectrophotometrically after 10, 20, 30, 40, 50 and 60 min. In each dyeing process 2 g of fabric were treated at a liquor ratio of 80:1 with the complex applied at a level of 2% owf.

3 RESULTS AND DISCUSSION

The Ni–PAP complex is very soluble in dimethylformamide (DMF) and acetic and sulfuric acids, moderately soluble in chloroform and benzene and slightly soluble in water, acetone, methanol and ethanol (Table 1). Better solubility in nonpolar solvents indicates that the complex is of

TABLE 1

Solubility of the Ni–PMAP and Ni–Q MAP Complexes in Different Solvents

Solvent		*Ni–PMAP*			*Ni–QMAP*		
	ε	*Sol.*		*Col.*	*Sol.*		*Col.*
		c	*w*		*c*	*w*	
Water	80·2	−+	+−	Yellow	−+	+−	Orange
DMF	36·7	++	++	Wine red	++	++	Purple
Methanol	32·7	+−	+	Red–orange	+−	+−	Red
Ethanol	24·6	+−	+	Red–orange	+−	+−	Red
Acetone	20·7	−+	+−	Wine red	+−	+−	Red–brown
Acetic acid	6·2	++	++	Yellow	+	+	Orange
Chloroform	4·8	−+	+	Dark wine-red	−+	+	Purple
Ether	4·3	−	−	—	−	−	
Benzene	2·3	−+	+−	Light pink	−+	+−	Purple
Carbon tetrachloride	2·2	−	−+	Light violet	−	−	
Sulfuric acid		++	++	Orange–red			

Abbreviations: Sol. = solubility; c = cold; w = warm; Col. = solution color; − = insoluble; −+ = slightly soluble; +− = moderately soluble; + = soluble; ++ = very soluble.

a neutral type. The exception is DMF, which is a good solvent for a number of polar and nonpolar organic compounds. The Ni–QMAP complex is insoluble in diethyl ether and carbon tetrachloride, slightly soluble in chloroform and benzene and soluble in more polar solvents, confirming the ionic character of the molecule. The exception is water, where a very weak solubility is obtained. Because of the very weak hydrophilic character of nickel complexes the addition of a dispersing agent Sarabid 200 LL (1 g/litre) for the dyeing process was necessary.

The results of elemental analyses show that, for the Ni–PMAP complex, two molecules of PMAP are bonded to one metal ion and that one molecule of water is also bonded to the complex. Results obtained for the Ni–QMAP complex show that two molecules of QMAP are bonded to two nickel ions, giving a cationic complex with two molecules of acetate as anions.

The composition of the complexes is further confirmed by IR spectroscopy (Table 2). Instead of the sharp band at 3385–3360 cm^{-1} observed in the IR spectrum of the PMAP ligand,[1] which corresponds to the O—H vibrations of the OH group present in the ligand, a weak broad band at 3650–3200 cm^{-1} was observed in the IR spectrum of the Ni–PMAP complex. The metal–oxygen covalent bond, i.e. disappearance of the O—H stretching vibration of the OH group, cannot be seen in this region of the spectra, because of the presence of water. In the IR spectrum of the Ni–QMAP complex the ν(O—H) band found in the region 3200–3020 cm^{-1} for the QMAP ligand was not apparent, indicating coordination of the oxygen atom of the phenoxy group to the nickel ion.[12] This coordination is further confirmed by the shift of ν(C—O) in the phenolic moiety from 1250 cm^{-1} (PMAP) and 1240 cm^{-1} (QMAP) to 1282 cm^{-1} (Ni–PMAP) and 1260 cm^{-1} (Ni–QMAP). The carbon–nitrogen double bond in the azomethine found at 1630 cm^{-1} for PMAP shifted to a lower wavenumber, i.e. 1585 cm^{-1}, for the Ni–PMAP complex, and broadening of the peak occurred due to the coordination of the metal atom to the nitrogen atom of the azomethine group. In the IR spectra of the Ni–QMAP complex, the stretching of the central C=N band is shifted to higher frequencies on complexation, from 1600 cm^{-1} for QMAP to 1690 cm^{-1} for the complex, probably due to the perturbing effect of the coordinated metal ion.[13] The vibration of the C—N bond in the pyridine ring, which appears at 1350 cm^{-1} in PMAP, is also shifted to about 1325 cm^{-1}, indicating that the hetero N atom is involved in bonding to the metal ion. The coordination of the N atom from the quinoline ring is not clearly seen because of the overlapping of C—O, C—N and C—C bands. The absorption peaks due to the stretching modes of the aromatic C—H bonds occur in the 3050–2920 cm^{-1} region. Typical in-plane C—H

TABLE 2
IR Spectra Data of the Ni–PMAP and Ni–QMAP Complexes

Absorption band wavenumbers (cm^{-1})		*Assignments*
Ni–PMAP	*Ni–QMAP*	
3650–3200(w)	—	ν(OH) water
3050(w)	3050(w)	ν(aromatic C—H)
2920(w)	2920(w)	ν(aromatic C—H)
1585(s)	1690(m)	ν(C=N azomethine)
	1550(m)	ν(COO in acetate)
1560(w)	1540(w)	ν(C=C in heterocyclic compound)
1530(w)	1510(w)	
1480; 1455(s)		
	1430(m)	ν(COO in acetate)
1325(m)	1300(m)	ν(C—N in conjugated cyclic system)
1300(m)		
1282(s)	1260(s)	ν(C—O)
1183(m)	1180(m)	δ(C—H in plane)
1144(s)	1140(s)	δ(C C)
1100(w)	1020(w)	δ(C—H in plane)
1049; 1014; 1010(w)		δ(C—H in plane)
950; 920; 910(w)	990; 940; 880(w)	
867(m)	820(s)	
807(w)		
753(s)	760(m); 770(m); 780(s)	δ(C—H out of plane)
671(w)	660(w)	
588(w)		
517(m)		
415(w)		
393(m)		
375(vs)		δ(H—O of water)

Abbreviations: vs = very strong; s = strong; m = medium; w = weak.

bending appears at about 1180, 1100 and 1020 cm^{-1}, with the out-of-plane C—H bands at about 750 cm^{-1} characteristic for an *ortho*-disubstituted benzene ring. These characteristic absorptions for the adjacent hydrogen systems are also observed in substituted pyridines. Coordinated water in the Ni–PMAP spectrum can be recognized by the appearance of bands of the wagging, twisting and rocking modes of the M—OH_2 structural unit established by the coordination of an oxygen electron pair to the metal ion. A rocking vibration appears at about 900 cm^{-1}, and the M—O stretching vibration at 670 cm^{-1}. The stretching vibration of the bond between the metal and the oxygen of water appears at 375 cm^{-1}. For the Ni–QMAP complex, the two bands at 1550 and 1430 cm^{-1} can be attributed to carbonyl vibrations ν(C=0) and ν(C—O) from acetate ions. The frequencies and $\Delta\nu$ value of 120 cm^{-1} confirm the existence of the bridging acetate group in the complex.[14]

In order to elucidate the type of the chelate structures, the mass spectra of Ni–PMAP and Ni–QMAP were recorded (Table 3). The mass spectral data for ligands PMAP and QMAP have already been reported.[1,8] The mass histogram of most abundant fragments for the Ni–PMAP complex is given in Fig. 1 and confirms the 1:2 type of the chelate structure. The fragment ion at *m/z* 452 corresponds to the mass of two ligands and one nickel ion. The base peak (*m/z* 256) corresponds to nickel attachment to the ligand. The base peak (*m/z* 196) corresponds to the ligand fragment, while the peaks, smaller than that of the ligand ion, confirm the fragmentation pattern of the ligand.

The mass spectrum for the Ni–QMAP complex is given in Fig. 2. The molecular ion is observed at *m/z* 730, and the fragment ions at *m/z* 671 and 612 correspond to the fragmentation of the first and second acetate ions. The fragment ion at *m/z* 612 corresponds to a metal-to-ligand ratio of 2:2, while a further symmetrical split at *m/z* 306 gives the base peak in the spectrum corresponding to a metal-to-ligand ratio of 1:1. The ligand QMAP peak is observed at *m/z* 248, and further fragmentation corresponds to the ligand itself.[8]

On the basis of all data obtained for Ni–PMAP and Ni–QMAP, a structure for the complexes can be proposed. The characteristic shifts in the vibrational spectrum of the complexes compared to the spectrum of

TABLE 3
Mass Spectra Data for the Ni–PMAP and Ni–QMAP

Compound	M_r	*m/z* (*Rel. int.* (%))
Ni–PMAP	471·16	454(38·7), 453(32·1), 452(81·7), 258(72·5), 256(100·0), 197(66·7), 196(98·5), 181(24·8), 170(32·5), 142(9·1), 120(53·0), 106(8·6), 105(8·3), 93(43·9), 78(62·7), 64(39·5), 52(12·8), 51(15·1),
Ni–QMAP	730·00	730(20·0), 671(31·0), 612(45·0), 306(100·0), 248(82·0), 231(8·0), 220(34·0), 193(9·0), 155(39·0), 129(51·0), 120(19·0), 103(40·0), 93(7·0).

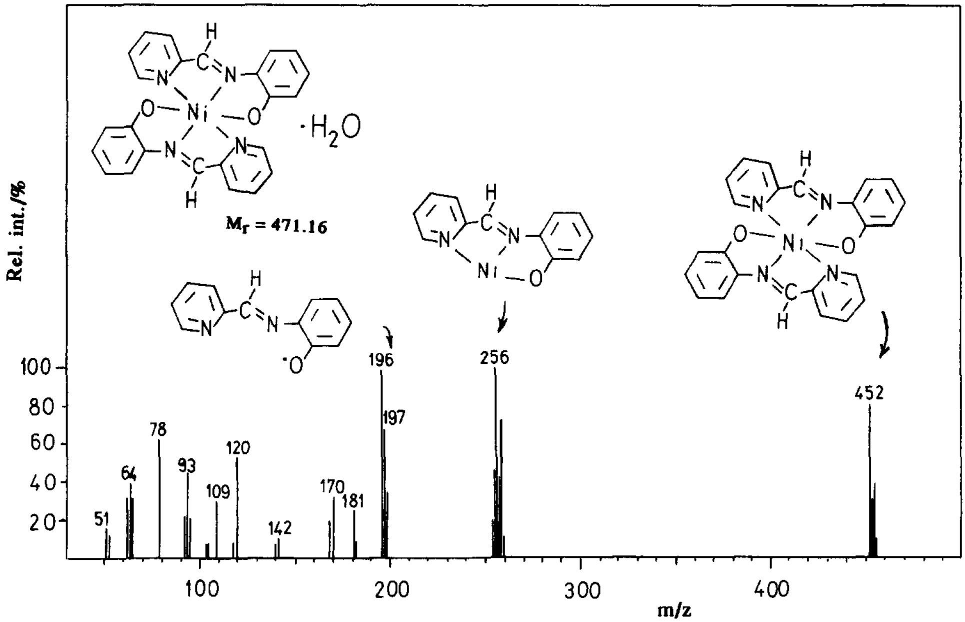

Fig. 1. Mass spectrum of Ni–PMAP complex.

the ligands allow conclusions to be drawn concerning the occurrence of the coordination in the chelate ring. Thus, the nickel ion occupies six coordination positions inside the complex zone, and, therefore, the coordination number is six. Confirming the 1:2 stoichiometry of the Ni–PMAP chelate, it is evident that the coordination can occur through the nitrogen atoms of two pyridine moieties and two azomethine groups,

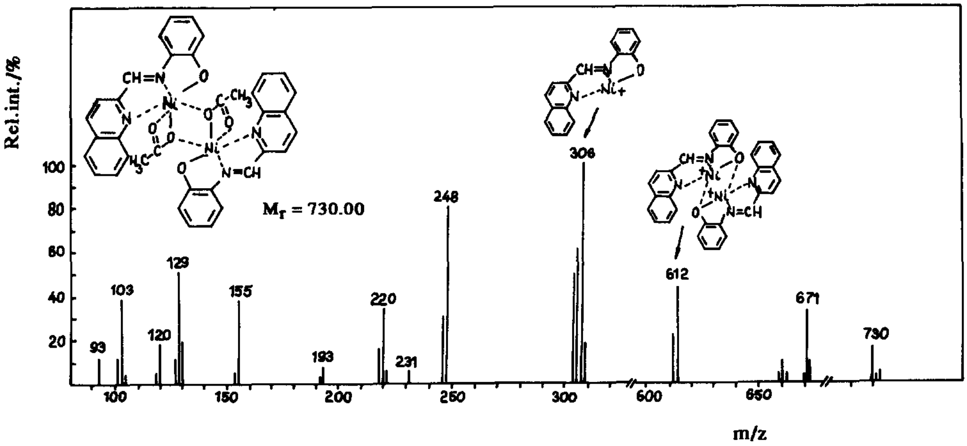

Fig. 2. Mass spectrum of Ni–QMAP complex.

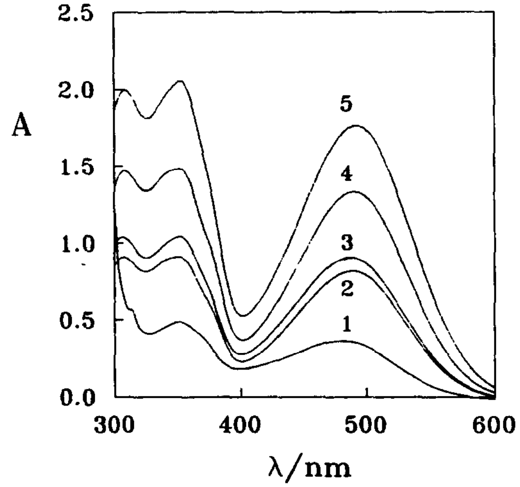

Fig. 3. UV–Vis absorption spectra of Ni–QMAP complex at different pH values. ϕ (Methanol) = 0·1, c(QMAP) = 2 mM, c(Ni) = 0·05 mM, t = 15 min; (1) pH 4, (2) pH 6, (3) no buffer, (4) pH 8, (5) pH 10.

and through the oxygen of two hydroxyl groups. The presence of water in the complex is confirmed by IR spectra and by elemental analyses. For the Ni–QMAP chelate, 2:2 stoichiometry is obtained with two acetate ions as anions.

The solution properties of the ligand PMAP and of the Ni–PMAP complex have been reported,[7,10] as well as the properties of QMAP.[8] The solution properties of the Ni–QMAP complex were investigated spectrophotometrically at different pH. From the absorption spectra presented in Fig. 3, it can be seen that the absorption of the Ni–QMAP complex increases with increase in pH (curves 1, 2, 4 and 5) and a bathochromic shift of up to 19 nm occurs in the visible region. The absorption of the complex is also influenced by the buffer used (curves 2 and 3), i.e. higher absorption is obtained in the unbuffered solution

TABLE 4

Influence of pH on λ_{max} and Molar Absorption Coefficients, ε, of Ni–QMAP Complexes

pH	λ_{max} *(nm)*	ε *(M^{-1} cm^{-1})*
4	480	7270
6	488	16326
No buffer	488	18082
8	488	26610
10	494	35188

TABLE 5
Statistical Analysis of Calibration Graphs for Determination of Ni with QMAP at Different pH

pH	*Regression equations for determination of Ni*	r^2
4	$dA/d\lambda = (1{\cdot}39 \pm 2{\cdot}25)\,10^{-2} + (0{\cdot}12 \pm 3{\cdot}64\,10^{-3})\,\gamma$	0·9985
6	$dA/d\lambda = (-0{\cdot}57 \pm 1{\cdot}64)\,10^{-2} + (0{\cdot}28 \pm 2{\cdot}66\,10^{-3})\,\gamma$	0·9998
n.b.	$dA/d\lambda = (1{\cdot}67 \pm 6{\cdot}64)\,10^{-2} + (0{\cdot}29 \pm 1{\cdot}07\,10^{-2})\,\gamma$	0·9981
8	$dA/d\lambda = (0{\cdot}02 \pm 1{\cdot}68)\,10^{-2} + (0{\cdot}44 \pm 3{\cdot}13\,10^{-3})\,\gamma$	0·9999
10	$dA/d\lambda = (1{\cdot}42 \pm 7{\cdot}78)\,10^{-2} + (0{\cdot}57 \pm 2{\cdot}06\,10^{-2})\,\gamma$	0·9985

Abbreviations: n.b. = no buffer (pH ≅ 6); γ = mass concentration in μg/ml.

(pH ≅ 6) than in that buffered at pH 6, probably because of the formation of mixed Ni–QMAP–citrate complexes. Comparing the values of the molar absorption coefficients obtained for nickel complexes with PMAP[7] and QMAP (Table 4), which are much higher, it can be concluded that chromophoric properties are enhanced by addition of another phenyl ring to the ligand molecule. Solution stability with time of the complexes decreases with pH. The lowest Δ*A* with time was obtained between 10 and 20 min after preparation of the complexes. All the determinations were, therefore, performed after 15 min. Linear calibration diagrams show that better sensitivity can be obtained at higher pH values, but owing to the lower time stability, pH 8 can be recommended for the spectrophotometric determination of nickel. The adherence of the calibration curves to Beer's law in the range between 0 and 5 μg/ml is validated by the high value for the correlation coefficients of the regression equation (Table 5).

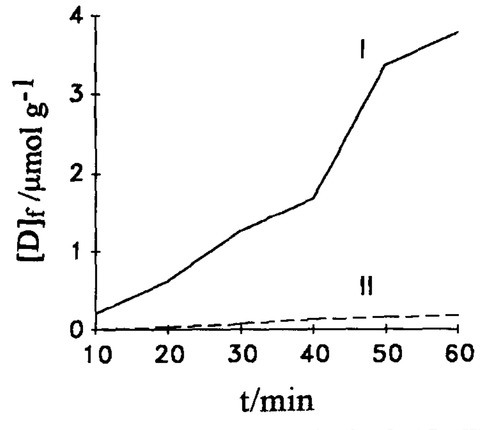

Fig. 4. Adsorption isotherms of Ni–PMAP (I) and Ni–QMAP (II) complexes at 100°C and pH 6.

TABLE 6
Exhaustion of Ni–PMAP and Ni–QMAP Dyes on Polyamide 66 Fiber at 100°C and pH 6

t (min)	*Ni–PMAP*		*Ni–QMAP*	
	n (dye)/m(fiber) (μmol/g)	*%*	*n (dye)/m(fiber) (μmol/g)*	*%*
10	0·21	2·5	0·007	1·3
20	0·63	7·5	0·035	5·5
30	1·26	15·0	0·068	6·8
40	1·68	20·0	0·131	17·5
50	3·36	40·0	0·152	20·5
60	3·78	45·0	0·166	21·0

The dyeing properties of Ni–PMAP and Ni–QMAP dyes were investigated on polyamide 66 fabrics (containing amino groups at 0·28 mol/kg) at pH 6 and 100°C. The adsorption isotherms (Fig. 4) show that Ni–PMAP satisfactory binds to polyamide 66 fabric (curve I), i.e. the concentration of dye on the fabric increases significantly with time, while the binding of Ni–QMAP is very weak (curve II). The overall percentage of dye exhaustion (Table 6 and Fig. 5) after 60 min of dyeing is 45% for Ni–PMAP and only 21% for Ni-QMAP. The equilibria dye–fiber–dye bath for Ni–QMAP is achieved after 50 min of dyeing. It can be concluded that the affinity of Ni–QMAP for polyamide, and probably also

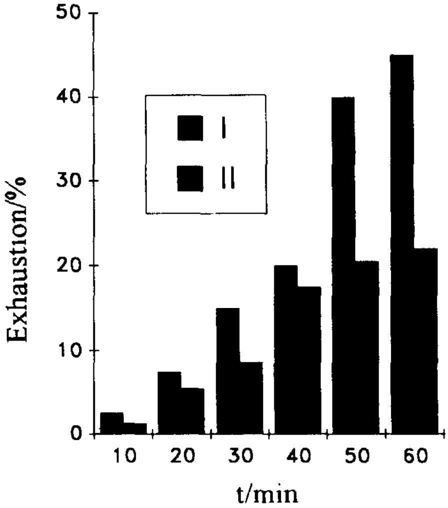

Fig. 5. Exhaustion of Ni-PMAP (I) and Ni-QMAP (II) on polyamide 66 at 100°C and pH 6.

for wool, is not satisfactory. The reason is the higher molar mass of the Ni–QMAP molecule and a sterical conformation. Ni-PMAP, as a neutral complex molecule, is bonded to the fiber with van der Waals forces. This attraction depends on the sterical conformation and dimension of the dye molecules.[15,16] High washing fastness values, between 4 and 5, were obtained for Ni–PMAP and Ni–QMAP, at 95°C, confirming that both compounds exhibit the characteristics of metal complex dyes having a hydrophilic character. The results indicate that Ni–PMAP is a satisfactory metal complex dye for polyamide 66 and, probably, for wool, also.

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