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K. A. K. Ebraheem[a]; S. T. Hamdi[b]; J. A. Al-Duhan[c]
[a] Department of Chemistry Faculty of Science, University of Jordan, Amman, Jordan [b] Department of Applied Chemistry Faculty of Science, Applied Science University, Amman, Jordan [c] Department of Chemistry Faculty of Science, University of Basrah, Basrah, Iraq

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SYNTHESIS AND PROPERTIES OF A CHELATING RESIN CONTAINING A SALICYLALDIMINE GROUP

K. A. K. Ebraheem*
Department of Chemistry
Faculty of Science
University of Jordan
Amman 11942, Jordan

S. T. Hamdi
Department of Applied Chemistry
Faculty of Science
Applied Science University
Amman 11931, Jordan

J. A. Al-Duhan
Department of Chemistry
Faculty of Science
University of Basrah
Basrah, Iraq

ABSTRACT

A phenol-formaldehyde polymer, poly(salicylaldehyde 3,5-diylmethylene) was synthesized and characterized. A chelating ion-exchange resin was obtained by reacting the polymer with *n*-butylamine. The chelation characteristics of the chelate-forming resin was studied by a batch equilibration technique. The resin showed fast rates of metal ion uptake and was found to selectively chelate Cu^{2+} and Cd^{2+} ions with capacities up to 3.56 mmol/g over a pH range of 5-8.

INTRODUCTION

Metal chelating polymers [1,2] constitute an important class of versatile polymeric materials which have found widespread applications for the separation and monitoring of trace heavy metal ions from aqueous solutions [2-12]. Several investigations have been reported in the literature [7-12] on the sorption of various heavy metal ions by phenol-formaldehyde (PF) chelate-forming polymers containing a variety of active chelating groups. However, with the exception of reports [12,13] on the chelate-forming phenol-formaldehyde polymers derived from salicylic acids (*o*- and *p*-hydroxybenzoic acids), no work seems to have been reported on the synthesis, characterization and chelation properties of chelating PF polymers derived from salicylaldehyde. This is due to the low reactivity of salicylaldehyde in the PF condensation reaction. Thus, attempts to synthesize a PF polymer by a base-catalyzed condensation of salicylaldehyde with formaldehyde using published methods [9,10] produced low molar mass oligomers. In this paper, we describe a modified procedure for the synthesis of poly(salicylaldehyde 3,5 - diylmethylene) (polymer **I**). The direct condensation of the derived Schiff's base ligand, N-butyl-salicylaldimine with formaldehyde was not particularly successful. Alternatively, polymer **I** was converted to a chelate-forming resin by reaction with *n*-butylamine to give poly(N-butyl-salicylaldimine 3,5-diylmethylene) (polymer **II**). Polymers **I** and **II**, with idealized structures depicted in Scheme 1, have been characterized and their number-average molar masses determined by conductometric titration [10].

We also report here the chelation properties of polymer **II** towards various metal ions (Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) in aqueous solutions. The rate of metal ion uptake and the pH-binding capacity profiles were investigated with the view to determine the efficiency and selectivity of the chelate-forming resin.

EXPERIMENTAL

Polymer Preparation

Polymer **I** was prepared by dissolving 12.2g (0.1 mol) of salicylaldehyde and 16.2g (0.2 mol) of 37% aq. formaldehyde in 65 mL of 50% aq. ethanol and enough NaOH to raise the pH to about 9. The mixture was refluxed for 6 hours after which the reaction mixture was evaporated and the resulting resin was cured at 120°C for 24 hours. The resin was then washed with aq. ethanol and water until neutral. After soxhlet extraction by benzene for 24 hours, the brown resin was dried at 90°C for 24 hours in vacuum, crushed and sieved (35-60 mesh). Satisfactory elemental analyses were obtained.

Polymer I (Found):	C%	71.42	H%	4.47
Calcd. for $[C_8H_6O_2]_n$:	C%	71.64	H%	4.51

Polymer **II** was obtained by reacting 20g (0.149 mol) of polymer **I** with 12g (0.164 mol) of n-butylamine with gradual heating to 80°C for 3 hours. The yellow product is then separated, washed with ethanol and purified by soxhlet extraction by benzene for 24 hours, the yellowish resin was dried at 90°C for 24 hours in vacuum. Polymers **I** and **II** decomposes at 150°C.

Measurements

Elemental analyses (C,H,N) were carried out at the Alfred Berhardt Analytical Laboratories, Elbach, Germany. Infrared spectra of polymers **I** and **II** were recorded as Nujol mulls between KBr plates from 4000 to 650cm^{-1}. Ultraviolet-visible spectra of $1x10^{-5}$-$1x10^{-4}$ M solutions of the polymers were measured in spectral quality dimethyl formamide (DMF). The number-average molar masses (M_n) were determined by conductometric titration as described previously [10]. Water regain of the polymers were determined using the procedure of Sugii et al. [14].

Sorption of Metal Ions on the Resin

A dry 0.5g sample of polymer **II** was suspended in 70 mL of 0.25M sodium acetate - 0.10M hydrochloric acid solution adjusted to the required pH (5-8) and left to equilibrate. The mixture was charged with 5mL aqueous metal ion solution containing 40.0 mg of the metal ions and shaken at 25°C. After being shaken for a definite contact time, the mixture was filtered and the amount of the metal ions remaining in the filtrate was determined by atomic absorption spectrometry or by chelatometric titration with EDTA. A series of experiments was undertaken in which the exposure time was varied from 1 to 24 hours at fixed pH of 7. Experiments were also carried out in which the pH was varied between 5 and 8 at fixed contact time of 3 hours.

RESULTS AND DISCUSSION

Characterization of the Polymers

The number-average molar masses (M_n) of the polymers were estimated

TABLE 1. Conductometric Titration Data and M_n Values for Polymers **I** and **II**

	Milliequivalents (MEQ) of NaOMe per 100 g polymer at each peak in the conductance plot	P_n [a]	M_{nu} [b]	M_n [c]
Polymer **I**	120 160 320 480 800 1200 6800 8000	66.7	134	8,900
Polymer **II**	120 160 360 400 440 780 1200 4400 6000 6800 8000	66.7	167	11,100

[a] Number-average degree of polymerization,
P_n = MEQ of NaOMe up to the final peak / MEQ of NaOMe up to the first peak.

[b] Molar mass of repeating unit (g/mol); for polymer **II**, the copolymer composition calculated from N% was used to calculate an average value of 167 g/mol for the molar mass of repeating units.

[c] Number-average molar mass (g/mol), $M_n = P_n \times M_{nu}$.

by conductometric titration of a dilute polymer solution in 95% DMF-methanol against a standard sodium methoxide solution in the same solvent mixture. The results are reported in Table 1. The estimated M_n values are 8900 and 11100 g/mol for polymers **I** and **II**, respectively. The nitrogen content of polymer **II** was found to be 4.98% compared with 7.4% calculated theoretically for the total conversion of the aldehyde groups in polymer **I** to the imine groups. Thus, polymer **II** may be regarded as a copolymer consisting of ~40% salicylaldehyde and ~60% N-butylsalicylaldimine repeating units. The copolymer composition was taken into account in calculating an average molar mass for the repeating unit in polymer **II** (Table 1).

Polymers **I** and **II** are readily soluble in acids, moderately soluble in N,N-dimethylformamide (DMF), slightly soluble in dimethylsulfoxide (DMSO), but are insoluble in other common solvents. Although the imine group, in general, is readily hydrolyzed by treatment with acids, it is fairly stable on polymer **II**. The nitrogen content of polymer **II** showed no significant decrease on treatment with 0.1-1.0 M HCl for 48 hours. The hydrophilic character as reflected by water regain was higher in polymer **II** (~0.85 g water/g resin) compared with polymer **I** and other chelate-forming PF polymers [10] with water regain values around ~0.4 g water/g resin [15].

TABLE 2. The Rate of Metal Ion Uptake by Polymer **II**.

	Milligrammes of metal ions taken up by the resin[a]			
Metal ion	1 hour	5 hours	9 hours	24 hours [b]
Cu^{2+}	22.36	25.07	28.47	31.86 (587.1)
Cd^{2+}	16.30	18.67	22.22	28.15 (356.3)
Ni^{2+}	12.09	15.19	16.43	19.54 (143.3)
Zn^{2+}	5.76	11.16	13.66	18.27 (126.1)
Ca^{2+}	10.42	11.25	11.67	12.08 (64.9)
Mg^{2+}	1.03	1.28	1.54	2.05 (8.1)

[a] Initially 75 mL solution containing 40 mg metal ion and 0.5 g resin.

[b] Values between backets are for distribution coefficients K_d, defined as $K_d = [M]_{resin} / [M]_{solution}$ where $[M]_{resin}$ is the amount (in mg) of metal ions taken up by 1g of resin and $[M]_{solution}$ is the amount (in mg) of metal ions remaining in 1 mL of solution.

The IR spectra of the present polymers reflect the characteristic features of the phenolic repeating units. The broad band observed in the 3250-3600 cm^{-1} region is due to the intramolecularly hydrogen bonded O-H stretching vibration [10,16]. The aromatic C-H stretching vibration was observed as a weak band in the region 3030-3058 cm^{-1}. In polymer **I**, the C-H stretching bands at 2850 and 2926 cm^{-1} are due to the $-CH_2-$ groups connecting the aromatic units. Such bands were obscured in polymer **II** due to the presence of $-CH_2-$ and $-CH_3$ groups of the *n*-butyl moiety which absorb at 2850-2960 cm^{-1} [16]. The C=O and C=N stretching vibrations were observed at 1660 and 1630 cm^{-1} in polymer **I** and **II**, respectively.

The UV spectra of polymers **I** and **II** in DMF exhibited two distinct $\pi^* \leftarrow \pi$ bands characteristic of the phenolic repeating units. These bands are observed at 268nm (ε=408.1 m^2/mol) and 326nm (ε=432.4 m^2/mol) for polymer **I** and at 268nm (ε=879.4 m^2/mol) and 340nm (ε=422.9 m^2/mol) for polymer **II**.

Sorption of Divalent Metal Ions on Polymer II

The sorption of various divalent ions (Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) on polymer **II** was investigated by a batch operation as a function of pH and contact time. The result are collected in Tables 2 and 3. The nitrogen content of

TABLE 3. The pH-dependence of Metal Ion Uptake by Polymer **II**

	Milligrammes of metal ions taken up by the resin[a)]				
Metal ion	pH = 5.5	pH = 6	pH = 6.5	pH = 7	pH = 8
Cu^{2+}	10.82	15.57	23.71	28.47	30.50
Cd^{2+}	4.90	6.67	15.56	18.89	21.11
Ni^{2+}	1.55	4.03	12.71	14.82	16.22
Zn^{2+}	1.81	2.47	3.79	12.35	15.64
Ca^{2+}	2.08	6.67	10.00	11.67	12.08
Mg^{2+}	1.03	1.28	1.54	1.85	2.05

a) Initially 75 mL solution containing 40 mg metal ion and 0.5 g resin. Contact time was 3 hours.

polymer **II** allows the calculation of the theoretical sorption capacity which is 3.56 mmol/g resin.

Table 2 shows the dependence of the metal ion uptake on contact time for various divalent metal ions. Distribution coefficients, K_d, [17] provide a more convenient parameter for comparing the activity of a given chelating resin towards various metal ions. The calculated values of K_d at equilibrium (24 hours) are also reported in Table 2. Examination of these results indicates fast rates of equilibration, particularly for Cu^{2+} and Cd^{2+} which experienced 50% uptake in less than one hour. Such fast equilibration is attributed to the relatively high hydrophilic character of polymer **II** in comparison with other PF polymers and to the absence of cross-linking.

The pH dependence of metal ion uptake by polymer II was studied in the pH range 5.5-8 for a fixed contact time of 3 hours. The results are given in Table 3. At higher pH values, hydrolysis of the metal ions investigated becomes appreciable and may compete with polymer chelate formation. The pH-binding capacity profiles are shown in Figure 1. In general, the binding affinity of polymer **II** towards various metal ions increases as the pH is increased. It is evident from these pH profiles that polymer **II** is highly selective towards Cu^{2+} and Cd^{2+}. The observed order of metal ion uptake at pH >7 follows the order:

$$Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Ca^{2+} > Mg^{2+}$$

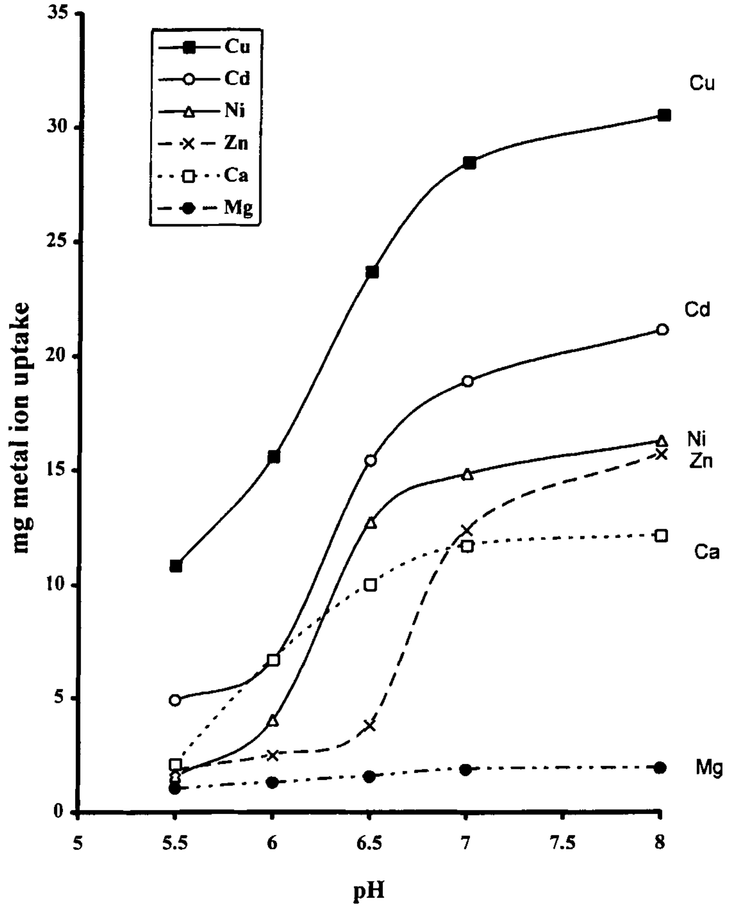

Figure 1. pH-binding capacity profiles for metal ion uptake by polymer **II**.

This order reflects only partial agreement with the stability constants of divalent metal complexes with N,O ligands [10], but agrees with that found for other chelating polymers with N,O binding sites [9,10]. Comparison with the stabilities of metal complexes of the parent monomer is probably unrealistic due to differences in stoichiometry and steric restrictions imposed by the polymer structure. Steric limitations and the distribution of binding sites within the polymer may result in the formation of a predominantly 1:1 metal complexes with the salicylaldimine repeating units. This proposal is supported by ESR measurements on copper complexes of poly(8-hydroxyquinoline 3,5-diylmethylene) [10] and salicylaldimine Schiff's bases covalently anchored to silica [18].

Preliminary desorption experiments carried out on copper(II) chelates of polymer **II** have revealed that the copper(II) can be recovered with HCl and HNO_3 of concentrations higher than 1 *M*.

CONCLUSION

The observed variations in the relative selectivity and capacity of chelating polymers towards various metal ions are influenced to a larger extent by the hydrophilic character of the polymer and the absence of cross-linking and steric restrictions on the availability of metal binding sites.

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