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# Friedel-Crafts Polymers. 5. Friedel-Crafts Polycondensation of p-Xylylene Dichloride with Salicylaldehyde and o-Hydroxyacetophenone

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ABSTRACT

Polymers were prepared by condensing p-xylylene dichloride (PXDC) separately with salicylaldehyde (SAL) and o-hydroxyacetophenone (OHAC) in the presence of anhydrous ferric chloride in dioxane. The polymer samples were characterized by elemental analysis, measurement of their $\overline{M}_n$ by vapor pressure osmometry, by nonaqueous conductometric titration in pyridine, by IR spectral study, by TGA in air, and by viscometric study in DMF. The ion-exchange capacities of these polymeric ligands for selected metal ions were measured by the batch equilibration method and compared. Polymeric metal chelates of PXDC-SAL and PXDC-OHAC polymer samples with $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Fe^{3+}$, and $Zn^{2+}$ were prepared and characterized by elemental analyses, by IR spectral study, and by thermal analyses.



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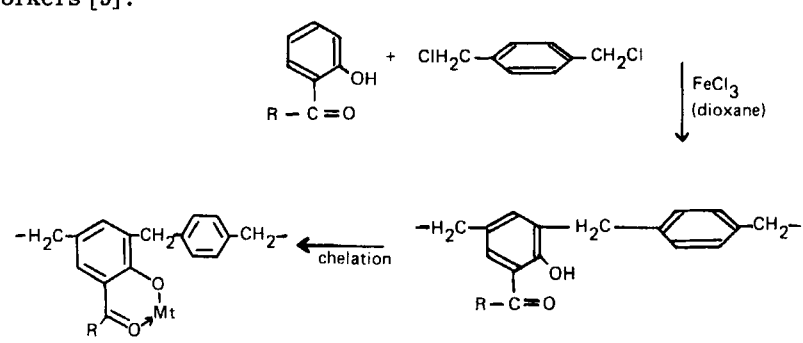
## INTRODUCTION

Friedel-Crafts polycondensation of p-xylylene dichloride (PXDC) individually with salicylaldehyde (SAL) and o-hydroxyacetophenone (OHAC) was carried out in the presence of anhydrous ferric chloride in dioxane. The polymer samples PXDC-SAL and PXDC-OHAC were characterized by IR spectral study, by estimation of number-average molecular weight ($\bar{M}_n$), both by the VPO method and nonaqueous conductometric titration against standard sodium methoxide, and by viscosity measurements of solutions in DMF. TGA of the polymer samples was carried out in air under identical conditions. The polymeric metal chelates were prepared by mixing a DMF solution of the required metal nitrates with that of a polymer sample (PXDC-SAL or PXDC-OHAC) in DMF in stoichiometric amounts. Metal:ligand (M:L) ratios and IR spectral characteristic of polymeric metal chelates were measured. The thermal properties of polymeric chelates were compared with those of the corresponding parent polymer. The main part of the study of these polymeric ligands is the measurement of their ion-exchange capacities for selected metal ions and comparison of this property with those of polymers, i.e., polymeric ligands, prepared from each of the above-mentioned 2-hydroxycarbonyl compounds with such bridges as $-CH_2-$ and $-CH_2-CH_2$ separating the ligand units in the polymer chains. The latter type of polymeric ligands were prepared by condensation of the required hydroxycarbonyl monomer with formaldehyde [1], methylene dichloride [2], or ethylene dichloride under appropriate conditions [3]. There is a report about the dependence of the ion-exchange capacity of a polymeric ligand prepared from the same ligand functioning as a monomer and the size of the bridge $-CH_2Ph-O-Ph-CH_2-$ separating the ligand units in the polymer chains [4]. In the polymeric ligand described in the present communication, both the nature of the bridge and its size have been altered. Ion-exchange capacities of these polymeric ligands were measured by the application of the batch equilibration method developed by DeGeiso et al. [1] and employed by other workers [5]:

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where R = H in PXDC-salicylaldehyde (PXDC-SAL) polymer
R = $CH_3$ in PXDC-o-hydroxyacetophenone (PXDC-OHAC) polymer
Mt = $Cu^{2+}/2$, $Zn^{2+}/2$, $Ni^{2+}/2$, $Co^{2+}/2$ and $Fe^{3+}/3$

## EXPERIMENTAL

### Materials

The monomer p-xylylene dichloride was prepared by a reported method [6, 7]. The anhydrous ferric chloride, dioxane, salicylaldehyde, o-hydroxyacetophenone, sodium acetate, metal nitrates, DMF, and the electrolytes (e.g., sodium chloride, nitrate, perchlorate, and sulfate) were laboratory-grade reagents.

## FRIEDEL-CRAFTS POLYCONDENSATION

### Polycondensation of SAL with PXDC in the Presence of Anhydrous Ferric Chloride Using Dioxane

#### Formation of PXDC-SAL

A well-powdered anhydrous ferric chloride (1.614 g, 0.01 mol) was added in small lots with stirring to a mixture of PXDC (1.74 g, 0.01 mol) and salicylaldehyde (1.22 g, 0.01 mol) in dioxane (17 mL). The reaction mass was heated at 60°C for 2 h and then at 90°C for 2 h. The cooled mixture was poured into a 1:1 water:HCl mixture (100 mL) with stirring, and a slightly sticky product separated out. It was filtered and treated with boiling 5% HCl solution (50 mL) and then twice with boiling water. The dark brown colored solid thus obtained was dried and powdered. It was refluxed with petroleum ether (60-80°C) for half an hour. The polymer sample was designated as PXDC-SAL. The yield was 1.6 g. It was soluble only in DMF.

Polycondensation of PXDC was effected with o-hydroxyacetophenone (OHAC) in a similar manner. The polymer sample was designated as PSDC-OHAC.

### Preparation of Polymeric Chelates, Preparation of the Polymeric $Cu^{2+}$ Metal Chelates of the PXDC-SAL Polymer

To a solution of $Cu(NO_3)_2.6H_2O$ (0.7375 g, 0.0025 mol) in DMF (30 mL), a solution of PXDC-SAL polymer (1.3025 g, 0.005 mol) in (50 mL)

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TABLE 1. Characterization of Polymer Samples

| Polymer sample | Elemental analysis C (%) | H (%) | Cl (%) | $\bar{M}_n \pm 30$ by conductometric titration | Intrinsic viscosity $[\eta]$ (dL/g) |
|---|---|---|---|---|---|
| PXDC-SAL | 76.65 | 4.6 | 3.5 | 850 | 0.05 |
| PXDC-OHAC | 77.56 | 5.16 | 3.65 | 910 | 0.052 |
| PXDC-SAL-$Cu^{2+}$ | 70.0 | 3.8 | - | - | - |
| PXDC-SAL-$Fe^{3+}$ | 73.5 | 3.5 | - | - | - |
| PXDC-SAL-$Co^{2+}$ | 70.9 | 4.0 | - | - | - |
| PXDC-SAL-$Ni^{2+}$ | 71.2 | 4.18 | - | - | - |
| PXDC-OHAC-$Cu^{2+}$ | 71.2 | 4.5 | - | - | - |
| PXDC-OHAC-$Fe^{3+}$ | 74.4 | 5.0 | - | - | - |
| PXDC-OHAC-$Co^{2+}$ | 71.8 | 4.55 | - | - | - |
| PXDC-OHAC-$Ni^{2+}$ | 71.6 | 4.29 | - | - | - |

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DMF was added dropwise with constant stirring. The polymeric chelate was precipitated by adding a saturated solution of sodium acetate (10 mL). A greenish yellow chelate separated out. The mixture was digested for half an hour. It was filtered; washed with boiling DMF, boiling water, and finally with ethanol; and then air-dried. The polymeric chelate weighed 1.0 g.

Following this procedure, polymeric chelates PXDC-SAL-$Fe^{3+}$, PXDC-SAL-$Co^{2+}$, PXDC-SAL-$Ni^{2+}$, PXDC-OHAC-$Fe^{3+}$, PXDC-OHAC-$Co^{2+}$, and PXDC-OHAC-$Ni^{2+}$ were prepared. The details and results of analyses of these polymeric chelates are presented in Table 1.

## Apparatus and Methods of Characterization

Elemental analyses of the polymer samples and polymeric metal chelates were carried out on a Coleman Analyzer. The chlorine content of the polymer samples was estimated by the Parr-bomb method in triplicate. The analyses of metal ions in the polymeric chelates were carried out by decomposition of a known amount of chelate by concentrated mineral acid followed by dilution with distilled water, filtration, and estimation of metal ions in solution by standard methods [8].

and Their Polymeric Metal Chelates

| Thermogravimetric analysis in air at a heating rate of 10°C/min | | | |
|---|---|---|---|
| Temperature at which rapid degradation started (±20°C) | Temperature beyond which the rate of weight loss is very low (±20°C) | Temperature at which 50% weight loss occurred (°C) | % weight loss at 700 ± 3°C |
| 350 | 600 | 485 | 95 |
| 400 | 610 | 480 | 80 |
| 240 | 400 | 250 | - |
| 230 | 550 | 250 | - |
| 250 | 500 | 265 | - |
| 150 | 580 | 300 | - |
| 320 | 600 | 460 | - |
| 300 | 600 | 325 | - |
| 300 | 600 | 335 | - |
| 300 | 590 | 345 | - |

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IR spectra of the polymer samples and polymeric metal chelates were taken in KBr on a UR-10 IR spectrophotometer.

The number-average molecular weights ($\bar{M}_n$) of the polymer samples were measured with a Hewlett-Packard vapor pressure osmometer using DMF as the solvent at 70°C; benzil was used as the calibrant.

Conductometric titration of all the polymer samples was carried out in pyridine against standard sodium methoxide in pyridine, using a Metrohm Herisan Konductoskop E 365, following the details described by Patel et al. [9].

The viscosities of polymer samples PXDC-SAL and PXDC-OHAC in DMF were measured at 35 ± 0.1°C with an Ubbelohde-type dilution viscometer. The solvent and solution were passed through a sintered glass crucible (G-4) to free them of any dust particles. The measurements were carried out in the concentration range from 0.769 to 2.0%. The intrinsic viscosity $[\eta]$ was measured from a linear plot of $\eta_{sp}/c$ vs concentration.

Thermogravimetry of all the polymer samples and polymeric metal chelates was carried out on a Linseis (Germany) thermogravimetric analyzer in air at a heating rate of 10°C/min. The results are presented in Table 1.

## Ion-Exchange Properties

The batch equilibration method was adopted for the ion-exchange properties [1, 10]. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions, and the distribution of various metal ions at different pH values were carried out following the details of the procedures described earlier [2, 4].

# RESULTS AND DISCUSSION

The polymer samples PXDC-SAL and PXDC-OHAC are brown-colored powders. These polymer samples are soluble only in DMF and insoluble in other organic solvents and also in aqueous alkali solution. Examination of the molecular weights of the polymer samples presented in Table 1 reveals that the molecular weight values of each polymer sample estimated by the conductometric titration method and by the VPO method are comparable within the limits of experimental error. The observed values of Cl % of these polymer samples agree well with the values of Cl % calculated on the basis of $\bar{M}_n$ and assuming a linear structure with $CH_2Cl$ as an endgroup. The important features of the IR spectrum (Fig. 1) of these polymer samples are a broad band extending from 3000 to 3500 $cm^{-1}$ and the inflections in this broad band around 2850 and 2920 $cm^{-1}$. These inflections are attributed to symmetric and asymmetric stretching of CH of $-CH_2-$ bridges. The carbonyl bands at 1670 and 1650 $cm^{-1}$ in the IR spectra of PXDC-SAL and PXDC-OHAC are assigned to $-CHO$ and $-\underset{\underset{O}{\|}}{C}-CH_3$, respectively, the bands around 920 and 825 $cm^{-1}$ are assigned to systems of isolated and two adjacent aromatic hydrogen atoms, respectively. The band at 670 $cm^{-1}$ can be attributed to C–Cl of the $CH_2Cl$ endgroup.

The intrinsic viscosities $[\eta]$ of PXDC-SAL and PXDC-OHAC polymer samples in DMF at 35 ± 0.1°C were found to be 0.05 and 0.052 dL/g, respectively. Examination of the TGA data of two polymers, viz. PXDC-SAL and PXDC-OHAC, reveals that both polymers degrade in air in a single step. The order of degradation of both polymer samples is around one. The energy of activation of the degradation reaction was found to be around 30 ± 10 kcal/mol. Of the two polymers, PXDC-OHAC seems to be more stable.

## Characterization of Polymeric Chelates

The polymeric chelates are found to be insoluble in common organic solvents and seem to be unaffected when they are heated up to 300°C.

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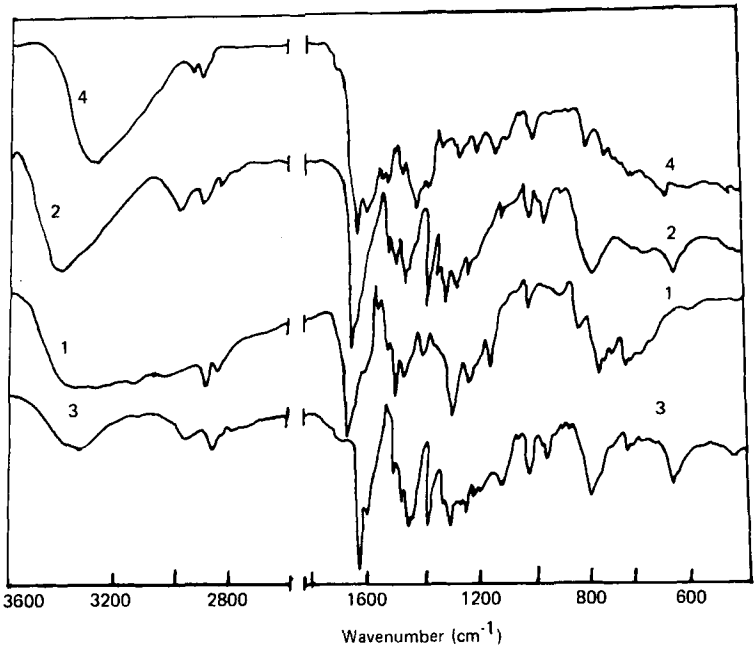


FIG. 1. IR spectra of polymers: (1) PXDC-SAL, (2) PXDC-OHAC, (3) PXDC-OHAC-$Cu^{2+}$ chelate, (4) PXDC-SAL $Fe^{3+}$ chelate.

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The results of the metal composition suggest that the metal:ligand (M:L) ratio is 1:2 for divalent metal ions and 1:3 for trivalent metal ions. The IR spectra of the polymeric chelates resemble each other in general shape and relative intensity of bands. A comparison of the IR spectrum of the polymeric chelate with that of its parent polymer reveals that in the OH-stretching region the band in the spectrum of the chelate is much less broad than that of the parent polymeric ligand, as expected. This indicates the absence of H bonding, which is also in agreement with the observation of DeGeiso et al. [11]. A sharp band at 1670 and 1650 $cm^{-1}$ in the IR spectra of the polymeric ligands PXDC-SAL and PXDC-OHAC, assigned to C=O stretching, is shifted to around 1630 and 1640 $cm^{-1}$ in the IR spectra of the polymeric chelates due to complexation. Because of very low intensity of the bands in the region of interest, it was not possible to observe the band due to the metal-carbon bond with any certainty. This region was rendered complex due to the presence of C–H out-of-plane bending vibrations. The above properties can be explained on the basis of the expected structure of the polymeric chelate shown earlier.

The typical TG thermograms of the PXDC-SAL-$Cu^{2+}$ chelate and

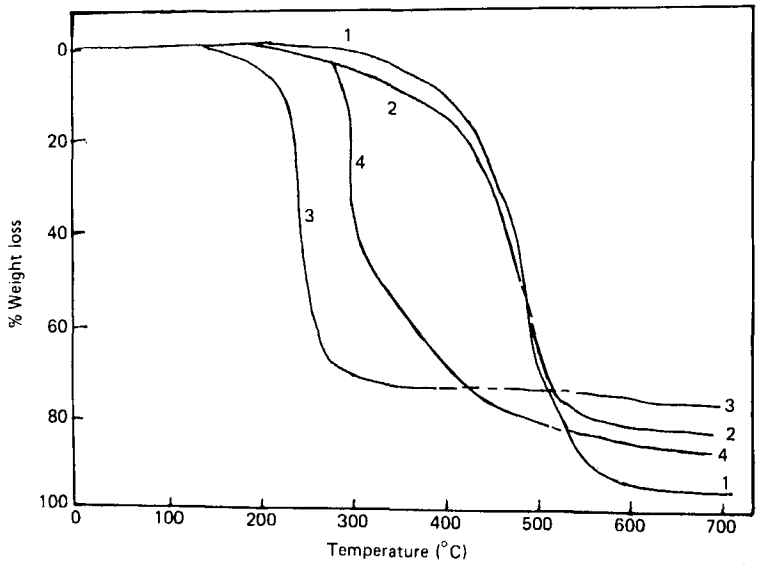


FIG. 2. TGA thermograms of polymers: (1) PXDC-SAL, (2) PXDC-OHAC, (3) PXDC-SAL-$Cu^{2+}$ chelate, (4) PXDC-OHAC-$Fe^{3+}$ chelate.

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PXDC-OHAC $Fe^{3+}$ chelate are shown in Fig. 2. Examination of the TG thermograms of all polymeric chelates and their parent polymer samples PXDC-SAL and PXDC-OHAC reveals that the polymeric chelates appear to be less stable than the parent polymeric ligands. This is revealed by the data furnished in Table 1. The rate of decomposition of the chelate is higher than that of the parent polymer. It seems that metal ions accelerate decomposition of the polymeric chelate [12].

## Results of Ion-Exchange Capacity

Examination of the data presented in Table 2 for polymer sample PXDC-SAL reveals that the amount of $Cu^{2+}$ and $Fe^{3+}$ ions taken up by the polymer sample decreases with a decrease in the concentration of nitrate and chloride ions, and increases with a decrease in the concentration of sulfate and perchlorate ions, whereas amount of $Co^{2+}$ ion taken up by the polymer sample increases with a decrease in the concentration of nitrate, sulfate, chloride, and perchlorate ions. The amount of $Zn^{2+}$ ion taken up by the polymer sample decreases with a decrease in the concentration of sulfate ion and increases with a de-

TABLE 2. Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions ($[Mt(NO_3)_2]$ = 0.1 mol/L)[a]

| Metal ion | pH | Electrolyte (mol/L) | Adsorption of meq × $10^1$ of the metal ion on PXDC-SAL polymer[b] | | | |
|---|---|---|---|---|---|---|
| | | | NaCl | $NaNO_3$ | $NaClO_4$ | $Na_2SO_4$ |
| $Fe^{3+}$ | 2.5 | 0.01 | 0.70 | 0.69 | 1.07 | 1.33 |
| | | 0.05 | 0.95 | 0.93 | 0.94 | 1.26 |
| | | 0.1 | 1.14 | 0.96 | 0.90 | 1.21 |
| | | 0.5 | 1.17 | 1.08 | 0.86 | 1.13 |
| | | 1.0 | 1.21 | 1.1 | 0.67 | 1.06 |
| $Cu^{2+}$ | 4.5 | 0.01 | 0.18 | 0.09 | 0.25 | 0.38 |
| | | 0.05 | 0.11 | 0.12 | 0.23 | 0.35 |
| | | 0.1 | 0.30 | 0.14 | 0.19 | 0.29 |
| | | 0.5 | 0.66 | 0.17 | 0.17 | 0.20 |
| | | 1.0 | 0.71 | 0.19 | 0.11 | 0.08 |
| $Co^{2+}$ | 4.5 | 0.01 | 0.09 | 0.23 | 0.12 | 0.18 |
| | | 0.05 | 0.08 | 0.19 | 0.07 | 0.15 |
| | | 0.1 | 0.06 | 0.13 | 0.05 | 0.13 |
| | | 0.5 | 0.04 | 0.12 | 0.03 | 0.12 |
| | | 1.0 | 0.02 | 0.11 | 0.01 | 0.04 |
| $Zn^{2+}$ | 4.5 | 0.01 | 0.03 | 0.35 | 0.27 | 0.01 |
| | | 0.05 | 0.06 | 0.28 | 0.21 | 0.03 |
| | | 0.1 | 0.10 | 0.20 | 0.10 | 0.14 |
| | | 0.5 | 0.13 | 0.15 | 0.06 | 0.19 |
| | | 1.0 | 0.15 | 0.14 | 0.03 | 0.21 |
| $Ni^{2+}$ | 4.5 | 0.01 | 0.07 | 0.05 | 0.20 | 0.14 |
| | | 0.05 | 0.13 | 0.09 | 0.18 | 0.10 |
| | | 0.1 | 0.18 | 0.12 | 0.16 | 0.09 |
| | | 0.5 | 0.20 | 0.15 | 0.14 | 0.07 |
| | | 1.0 | 0.41 | 0.18 | 0.09 | 0.01 |

[a]Volume of electrolyte solution, 40 mL, time, 24 h; volume of metal ion solution, 2 mL; temperature, 30°C.
[b]Weight of polymer, 25 mg.

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TABLE 3. Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions ($[Mt(NO_3)_2]$ = 0.1 mol/L)[a]

| Metal ion | pH | Electrolyte (mol/L) | Adsorption of meq × $10^1$ of the metal ion on PXDC-OHAC polymer[b] | | | |
|---|---|---|---|---|---|---|
| | | | NaCl | $NaNO_3$ | $NaClO_4$ | $Na_2SO_4$ |
| $Fe^{3+}$ | 2.5 | 0.01 | 1.28 | 1.36 | 1.11 | 0.86 |
| | | 0.05 | 1.23 | 1.27 | 1.07 | 0.81 |
| | | 0.1 | 1.20 | 1.19 | 0.97 | 0.74 |
| | | 0.5 | 1.07 | 1.08 | 0.94 | 0.68 |
| | | 1.0 | 0.92 | 0.98 | 0.88 | 0.64 |
| $Cu^{2+}$ | 4.5 | 0.01 | 1.48 | 1.60 | 0.98 | 0.80 |
| | | 0.05 | 1.40 | 1.50 | 0.92 | 0.75 |
| | | 0.1 | 1.30 | 1.40 | 0.82 | 0.55 |
| | | 0.5 | 1.15 | 0.95 | 0.63 | 0.36 |
| | | 1.0 | 1.10 | 0.25 | 0.55 | 0.26 |
| $Co^{2+}$ | 4.5 | 0.01 | 0.38 | 0.43 | 0.34 | 0.13 |
| | | 0.05 | 0.35 | 0.33 | 0.31 | 0.28 |
| | | 0.1 | 0.33 | 0.25 | 0.29 | 0.26 |
| | | 0.5 | 0.29 | 0.14 | 0.26 | 0.10 |
| | | 1.0 | 0.21 | 0.12 | 0.06 | 0.03 |
| $Zn^{2+}$ | 4.5 | 0.01 | 0.20 | 0.30 | 0.28 | 0.16 |
| | | 0.05 | 0.17 | 0.25 | 0.15 | 0.12 |
| | | 0.1 | 0.15 | 0.21 | 0.12 | 0.08 |
| | | 0.5 | 0.12 | 0.19 | 0.05 | 0.05 |
| | | 1.0 | 0.05 | 0.16 | 0.02 | 0.03 |
| $Ni^{2+}$ | 4.5 | 0.01 | 0.16 | 0.44 | 0.41 | 0.31 |
| | | 0.05 | 0.12 | 0.36 | 0.26 | 0.27 |
| | | 0.1 | 0.09 | 0.26 | 0.14 | 0.10 |
| | | 0.5 | 0.06 | 0.21 | 0.03 | 0.07 |
| | | 1.0 | 0.02 | 0.14 | 0.01 | 0.04 |

[a]Volume of electrolyte solution, 40 mL; time, 24 h; volume of metal ion solution, 2 mL; temperature, 30°C.
[b]Weight of polymer, 25 mg.

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crease in the concentration of perchlorate and nitrate ions and with an increase in the concentration of the chloride ions.

For polymer sample PXDC-OHAC, examination of the data presented in Table 3 reveals that the amounts of $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Fe^{3+}$, and $Ni^{2+}$ ions taken up by the polymer sample increase with a decrease in the concentration of nitrate, chloride, perchlorate, and sulfate ions.

## Rate of Metal Uptake

The rates of metal absorption by the PXDC-SAL polymer were measured for $Fe^{3+}$, $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ ions in the presence of 1 M $NaNO_3$ to determine the time required to reach the equilibrium stage. All experiments were carried out at pH $< 4.5$. Examination of the results presented in Table 4 shows that the $Fe^{3+}$ ion required slightly more than 4 h for the establishment of equilibrium, while $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ required about 6 h. In experiments with solution containing more than 70% $Fe^{3+}$ ions equilibrium was established in 3 h. The results show that the rate of uptake of $Fe^{3+}$ ions is more than those of the other four metal ions. In the case of PXDC-OHAC polymer, a similar behavior was observed.

## Distribution Ratios of Metal Ions at Different pH Values

Examination of the results (Table 5) of the effect of pH on the amount of metal ions distributed between two phases indicates that the relative amount of metal ions taken up by the polymeric material increases with an increase in the pH of the medium, and the manner in which this happens depends on both the nature of the polymeric ligand and that of the metal ions under study. The trend in the values of the distribution ratio of a given metal ion under the given experimental conditions for different polymeric ligands is the same as the trend in the values of the stability constants of the same metal ion for the respective ligands forming repeat units in the polymeric ligands [13]. The selectivity of the polymer samples (PXDC-SAL and PXDC-OHAC) for $Fe^{3+}$ ions is higher than for the remaining metal ions. In the case of $Fe^{3+}$ ions, the distribution ratio is higher than for the other metal ions. Among the remaining metal ions, the distribution ratio for $Cu^{2+}$ and $Ni^{2+}$ ions is higher at pH = 6.0; for the other two metals ($Co^{2+}$ and $Zn^{2+}$ ions) the distribution ratio is lower in the pH range from 4 to 6. This can be attributed to the low stability constants of the metal complexes [14, 15].

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TABLE 4. Comparison of the Rates of Metal (Mt) Ion Uptake[a]

| Time (h) | Percentage of the relative amount of metal ion uptake[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | PXDC-SAL | | | | | PXDC-OHAC | | | | |
| | $Fe^{3+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ | $Fe^{3+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ |
| 1/2 | 42 | 10 | 18 | 14 | 16 | 36 | 12 | 16 | 12 | 14 |
| 1 | 60 | 26 | 27 | 21 | 33 | 57 | 20 | 25 | 25 | 28 |
| 2 | 69 | 31 | 37 | 42 | 44 | 62 | 28 | 33 | 37 | 50 |
| 3 | 77 | 52 | 45 | 64 | 55 | 77 | 48 | 45 | 62 | 64 |
| 4 | 87 | 74 | 64 | 78 | 66 | 82 | 64 | 62 | 75 | 71 |
| 5 | 100 | 84 | 82 | 85 | 88 | 100 | 80 | 75 | 93 | 85 |
| 6 | - | 100 | 100 | 100 | 100 | | 100 | 100 | 100 | 100 |

[a]$[Mt(NO_3)_2]$ = 0.1 mol/L, volume, 2 mL; $(NaNO_3)$ = 1 mol/L, volume, 4C mL; pH for $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ = 4.5 and for $Fe^{3+}$ = 2.5.

[b]Related to the amount of metal ions in the state of equilibrium (100%).

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TABLE 5. Distribution Ratios D of Different Metal Ions as a Function of the pH

| | Distribution ratio[a] of the metal ions[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | PXDC-SAL | | | | | PXDC-OHAC | | | | |
| pH | $Fe^{3+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ | $Fe^{3+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ |
| 1.0 | 87 | - | - | - | - | 160 | - | - | - | - |
| 1.5 | 150 | - | - | - | - | 183 | - | - | - | - |
| 2.0 | 217 | 54 | 20 | 9 | 58 | 240 | - | 9 | 18 | 78 |
| 2.5 | 540 | - | - | - | - | 671 | - | - | - | - |
| 3.0 | | 82 | 38 | 27 | 78 | - | 111 | 48 | 44 | 153 |
| 4.0 | | 111 | 54 | 56 | 142 | - | 141 | 68 | 54 | 182 |
| 5.0 | | 131 | 88 | 92 | 153 | - | 183 | 109 | 102 | 245 |
| 6.0 | | 204 | 130 | 142 | 256 | - | 295 | 141 | 162 | 289 |

[a] $D = \frac{\text{meq of metal ions taken up by 1 g of polymer}}{\text{meq of metal ions present in 2 mL of solution}}$

[b] Error ± 5%, $[Mt(NO_3)_2]$ = 0.1 mol/L, volume, 2 mL; $NaNO_3$ = 1 mol/L, volume, 40 mL; 30°C; 24 h (equilibrium state).

## Comparative Study to Bring Out the Effect of the Nature and Size of the Bridge

Comparison of the ion-exchange capacities as revealed by the values of the distribution ratios of different polymeric ligands prepared from the same ligand monomer but having different types of bridges (e.g., $-CH_2-$, $-CH_2-CH_2-$, or $-CH_2-Ph-O-Ph-CH_2-$, $-CH_2-Ph-CH_2-$) separating the ligand units reveals that selectivity for different metal ions is the same and the $K_D$ values increase with an increase in pH. The $K_D$ value for different metal ions depends upon the size of the bridge interspaced between the SAL units. The $K_D$ values decrease with an increase in the size of the bridge [1, 3, 4, 12, 16-18]. Similar trends have been observed in the behavior of polymeric ligands based on o-hydroxyacetophenone with intervening bridge such as $-CH_2-$, $-CH_2-CH_2-$, $-CH_2-Ph-CH_2-$, and $-CH_2-Ph-O-Ph-CH_2-$ [1, 3, 4, 10, 12, 16-18].

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