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Adsorption of the Chromate Ion on Cured Diphenyl Phosphonate–Aldehyde Resins

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The adsorption of the chromate ion on cured diphenyl phosphonate–aldehyde resins has been investigated. Phosphorus-containing novolak type resins, obtained from the reaction of diphenyl phosphonate with aldehydes have been cured with additional hexamethylenetetramine. The adsorption of the chromate ion on the cured resins decreased in the order: propionaldehyde ≈ acrylaldehyde > butyraldehyde > crotonaldehyde > acetaldehyde > furfural > formaldehyde. The optimum pH for the adsorption of the chromate ion was in the range 3.0 to 4.0. In the case of the cured diphenyl phosphonate–propionaldehyde resin, the amount of the adsorption of the chromate ion was 20.5 mg Cr/g resin. Under the same conditions, the amounts of the adsorption of molybdate and tungstate ions were 40.5 mg Mo/g resin and 80.0 mg W/g resin, respectively. The adsorbed chromate ion was recovered at approximately 80 wt% as chromium by elution with 1.0 mol/l aqueous HCl solution. The adsorbed molybdate and tungstate ions were desorbed with 2.0 and 3.0 mol/l aqueous H_2SO_4 solutions, respectively. The recovery rate for Mo and W was 100 wt%. The mechanism of adsorption of the chromate ion on the cured resins having phosphinylden groups, >P(O)H, has been discussed.

In a previous paper,[1] diphenyl phosphonate (abbreviated to DPP) was reported to react with several aldehydes, *e.g.*, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acrylaldehyde, crotonaldehyde and furfural to produce phosphorus-containing novolak type resins (abbreviated to DPP resin). The DPP resins were cured with additional hexamethylenetetramine at 120 to 180 °C to give insoluble resins containing phosphinylden groups, >P(O)H. In the present paper, it has been observed that the cured DPP resins selectively adsorbed Group VIB oxide ions, *e.g.*, chromate, dichromate, molybdate and tungstate ions.

The literature is extensive concerning ion exchange resins based upon organophosphorus polymers.[2–6] Organophosphorus resins have been prepared by the treatment of three-dimensional unsaturated aromatic hydrocarbon polymers with phosphorus trichloride in the presence of aluminum chloride, or by the treatment of polymers containing halogenated methyl groups with trialkyl phosphates, followed by oxidation and hydrolysis of the reaction products.[3] The phosphorus-containing ion exchange resins based on phenolic resins have also been prepared by condensing the product obtained from the reaction of *m*-hydroxyphenyl dihydrogenphosphate with formaldehyde.[4] In addition, the ion exchange resins prepared from styrene–divinylbenzene copolymers and phosphorus trichloride[6] are commercially available under the names of Duolite-62 and 63. The phosphorus-containing resins are three-dimensional high molecular weight compounds which contain free phosphonic acid [–P(O)(OH)$_2$] and phosphinic acid [>P(O)(OH)] groups. The active centers for ion exchange are the P–OH bonds and consequently the phosphorus-containing resins adsorb mainly metallic ions, behaving as cation exchangers. To date there are very few reports on phosphorus-containing anion exchangers.[7]

In this paper, the adsorption of chromate, molybdate and tungstate ions on cured DPP resins has been studied. The effect of pH on the adsorption of Group VIB oxide ions, the rate of adsorption, the amount of adsorption and elution of adsorbed Group VIB oxide ions have been examined. Furthermore, the mechanism of the adsorption of the chromate ion on the cured DPP resins has been discussed.

Experimental

Materials. All chemicals used for the preparation of the cured DPP resins were extra-pure grade reagents. Potassium chromate(GR) and dichromate(GR), potassium molybdate(GR) and potassium tungstate(GR) were used without further purification. Other chemicals used for colorimetric determination and preparation of buffer solutions were of analytical reagent-grade.

Preparation of the Cured DPP Resins. The cured DPP resins used for the adsorption were phosphorus-containing resins cured with additional hexamethylenetetramine.

DPP Resins: The phosphorus-containing novolak type resins have been prepared by a method described previously;[1] *i.e.*, DPP has been allowed to react with formaldehyde or acrylaldehyde in water at 80 °C for 3 h. Acetaldehyde, propionaldehyde, butyraldehyde and crotonaldehyde resins were prepared by the direct reaction of DPP with each aldehyde at 80 °C for 8 h. The furfural resin was produced at room temperature in 6 h.

Curing: The curing of the DPP resins was conducted by the method described previously;[1] *i.e.*, to the crude DPP resins, 10 to 15 wt% hexamethylenetetramine was added, and the mixture heated in an oil bath at 120—180 °C for 1 h to give the insoluble DPP resin. The optimum curing rates and temperatures are shown in Table 1. The products were washed with 3-pentanone, 1.0 mol/l aqueous HCl solution, and water to near the point of neutrality. The cured DPP resins were dried at 60 to 80 °C for 4 h, ground and milled to 100—150 mesh.

Procedure. The method for the adsorption of chromate, molybdate and tungstate ions was a batch type as follows; an amount of the cured DPP resin, 10—100 mg, and an aliquot of K_2CrO_4, K_2MoO_4, and K_2WO_4 solutions were added to a 100 cm^3 volumetric flask and diluted to 100 cm^3. The solutions were stirred at room temperature for 24 h. After removal of the resin, the concentrations of chromate, molybdate and tungstate ions were determined by colorimetric

Table 1. Properties of cured DPP-aldehydes resins

Compound R	Utmost curing rate wt%	Cured temp °C	P %	Amount of Cr to resin[a)] mg/g	Resistance to 50 vol% H_2SO_4 Residual weight wt%
H	95.0	150	2.8	1.9	97.0
CH_3	76.0	170	3.0	7.6	75.0
C_2H_5	89.0	140	2.7	10.0	70.0
C_3H_7	69.0	170	3.1	9.1	96.0
C_3H_6	89.0	170	3.1	8.4	80.0
C_2H_3	93.0	120	2.8	10.0	86.0
C_4H_3O	92.0	120	2.6	2.8	95.0

a) Value measured for 10 ppm Cr(VI) solution.

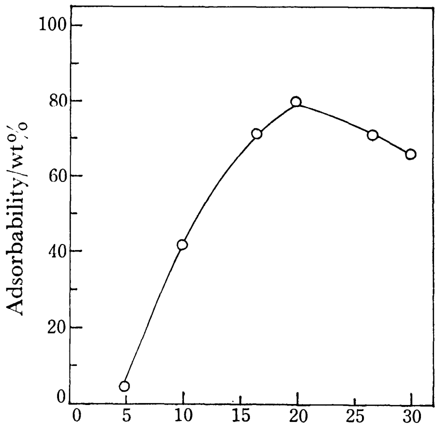

Fig. 1. Effect of amount of hexametylenetetramine in curing reaction on adsorption of chromate ion. Conditions; resin: DPP–PA, curing temp: 120 °C, curing time: 2 h.

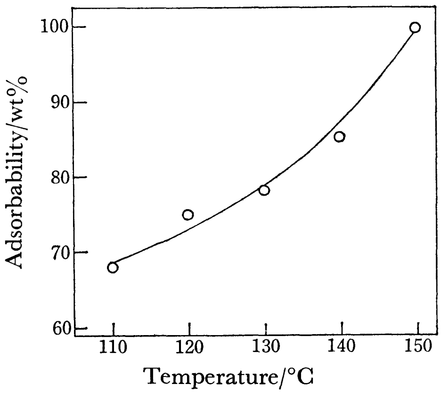

Fig. 2. Relation between adsorption of chromate ion and curing temperature. Conditions; resin: DPP–PA, curing time: 30 min, amount of hexamine: 20 wt%.

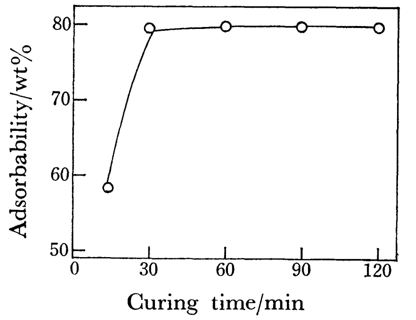

Fig. 3. Relation between adsorption of chromate ion and curing time. Conditions; resin: DPP–PA, curing temp: 120 °C, amount of hexamine: 20 wt%.

and atomic absorption. The rate of adsorption was calculated from the ratios of the concentration before and after the adsorption of each ion. The concentration of Cr(VI) was determined by the diphenylcarbazide method. The total Cr content was determined by atomic absorption. The concentrations of molybdate and tungstate ions were determined by tin(II) chloride and dithiol methods.[8)]

Buffer Solution.[9)] Sulfuric acid was added for the preparation of the solution bellow pH 2. The buffer solutions (pH 2.0—3.0) were prepared from chloroacetic acid and KOH, succinic acid and KOH (pH 3.0—7.0), and tris(hydroxymethyl)methanamine and HCl (pH 7.0—9.0).

Measurements. The resin adsorbing chromate ion was washed with water, and dried under vacuum for 24 h. The IR and ESR spectra for the treated samples were recorded on JASCO IR-G, and JEOL-3BSX-ESR spectrometers.

Results and Discussion

Adsorption Characteristics of the Cured DPP Resins. For the seven DPP resins, cured at a temperature giving maximum curing, the adsorptions were conducted as follows; the cured DPP resins (100 mg) and K_2CrO_4 solution containing 1 mg Cr(VI) were added to a 100 cm^3 volumetric flask, the pH adjusted to 3.2 and then diluted to 100 cm^3. The rates of adsorption were calculated and the results are shown in Table 1. As may be seen the chromate ion is comparatively well adsorbed on the cured DPP–propionaldehyde and DPP–acrylaldehyde resins. The adsorption of the chromate ion on seven kinds of cured DPP resins decreased in the order, propionaldehyde resin≈acrylaldehyde resin > butyraldehyde resin > crotonaldehyde resin > acetaldehyde resin > furfural resin > formaldehyde resin. Therefore, subsequent adsorption experiments were conducted using the cured DPP–propionaldehyde resin (abbreviated to cured DPP–PA resin).

The Effect of Curing Conditions on the Degree of Adsorption. The DPP–PA resins have been cured under several conditions, *e.g.*, the amount of curing agent, the curing temperature and the curing time. The effect of each of the conditions on the degree of adsorption of the chromate ion has been examined. Figure

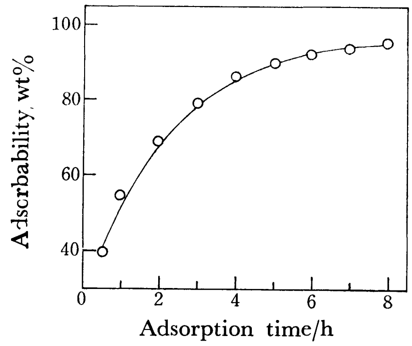

Fig. 4. Adsorption time dependence of chromate ion on cured DPP–PA resin. Conditions; amount of resin: 100 mg, pH: 3.2, concentration of CrO_4^{2-}: 1.0 mg/100 cm^3, temp: 25 °C.

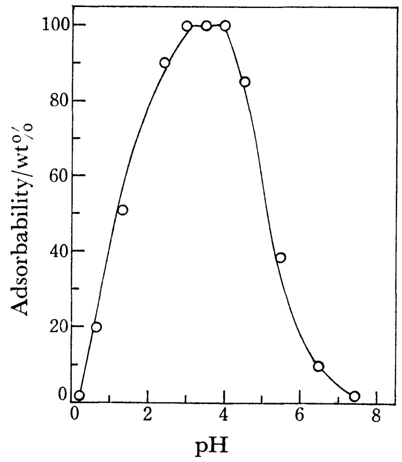

Fig. 5. Effect of pH on adsorption of chromate ion. Conditions; Amount of resin: 100 mg, Concentration of CrO_4^{2-}: 1.0 mg/100 cm^3, Shaking time: 24 h, temp: 25 °C.

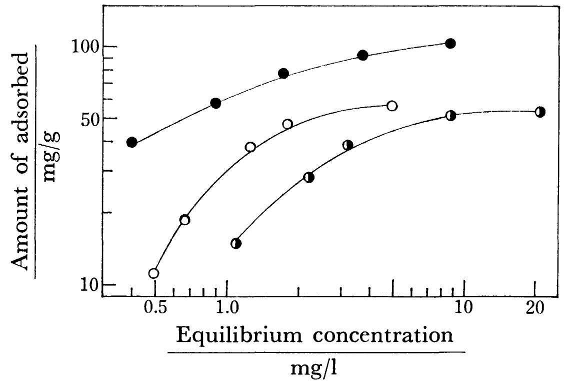

Fig. 6. Adsorption isotherm of Cr(VI), Mo(VI), and W(VI) on cured DPP–PA resin. Conditions; pH: 3.2, shaking time: 24 h, temp: 25 °C, ○: Cr(VI), ◑: Mo(VI), ●: W(VI).

Table 2. Desorption of chromium, molybdenum and tungsten from cured DPP–PA resin by aqueous HCl, H_2SO_4, and NaOH solution

Elute mol/l	Recovery of metal ion		
	Chromium	Molybdenum	Tungsten
	wt%	wt%	wt%
HCl			
0.05	46.4	0	0
0.1	60.0	10.6	2.1
0.5	63.0	21.2	10.2
1.0	80.0	26.5	25.0
4.0	81.0	42.5	40.0
H_2SO_4			
1.0	56.7	64.7	10.5
2.0	56.0	100	50.1
3.0	55.0		100
4.0	55.0		
NaOH			
0.1	100	100	100

1 illustrates the relationship between the amount of curing agent, Fig. 2, the curing temperature and Fig. 3, the curing time and the degree of adsorption chromate ion. From these results, it has been found that the chromate ion is heavily adsorbed on the cured DPP–PA resin cured with an additional 20 wt% hexamethylenetetramine at 150 °C for up to 30 min.

The Rate of Adsorption. The rate of adsorption of the chromate ion on the cured DPP–PA resin has been examined, the results of which are shown in Fig. 4. It may be seen that the degree of adsorption of the chromate ion increases up to over 90 wt% in approximately 5 h. Subsequent adsorption proceeded slowly reaching 100 wt% after 16 h. The results of the adsorption of molybdate and tungstate ions were approximately the same.

Influence of pH. The effect of pH on the adsorption of the chromate ion has been examined by varying pH between 0 and 8.5, and the results are illustrated in Fig. 5. The residual Cr observed below pH 2.5 was Cr(III), Cr(VI) being absent. The residual Cr up to pH 4.5 was completely Cr(VI). It may be seen that the optimum pH range for the adsorption of the chromate ion 3.0—4.0. Similarly, the optimum pH range for the adsorption of molybdate and tungstate ions was 3.0—4.0, consistent with the results for the chromate ion.

Degree of Adsorption. The degree of the adsorption of chromate ion on the cured DPP–PA resin was measured as follows; a series of K_2CrO_4 solutions containing 1.5—6.0 mg as Cr were added to the cured DPP–PA resin (100 mg). Each solution was adjusted to pH 3.2 and diluted with water to 100 cm^3. Each adsorption was calculated and plotted against the equilibrium concentration of total Cr, the results of which are shown in Fig. 6. The degree of adsorption of each Cr unit to resin (1 g) was 20.5 mg. The degree of adsorption of molybdate and tungstate ions on the cured DPP–PA resin were measured in the same manner. The degree of adsorption of the Mo and W units to resin (1 g) were 40.5 and 80.0 mg, respectively.

Desorption. The desorption of chromate, molybdate and tungstate ions adsorbed on the cured DPP–PA resin were conducted using aqueous HCl, H_2SO_4 and NaOH solutions. The amounts of chromate, molybdate and tungstate ions desorbed with various concentration of acidic or basic solutions are shown in Table 2. For the desorption of Cr it is more advantageous to use aqueous HCl rather than aqueous H_2SO_4 solution. Elution with 1.0 mol/l aqueous HCl solution, gave 80.0 wt% recovery of Cr. For the desorption of Mo and W, both ions were eluted with aqueous H_2SO_4 solution. Elution with 2.0 mol/l aqueous H_2SO_4 solution, gave 100 wt% recovery of Mo and 3.0 mol/l aqueous H_2SO_4 solution, gave 100 wt% recovery of W.

The residual weight of the cured DPP–PA resin after soaking in 50 vol% H_2SO_4 for two days was approximately 70 wt% as shown in Table 1. Consequently it has been concluded that the cured DPP–PA resin is very resistant to acid. The elution of Cr, Mo, and W by 0.1 mol/l aqueous NaOH solution, gave a recovery of 100 wt%, but as the cured DPP–PA resin was completely decomposed, elution with aqueous NaOH solution is not a suitable technique.

It has been observed that Cr eluted with HCl is recovered as Cr(III) and that Cr eluted with sodium hydroxide is Cr(VI) in 70 wt% of the total Cr content. Mo and W were recovered as Mo(VI) and W(VI) because of their lower oxidizing properties in comparison with Cr.

Mechanism of Adsorption. In order to elucidate the adsorption mechanism of the chromate ion on the cured DPP–PA resin, the IR and ESR spectra of the cured DPP–PA resin adsorbing chromate ion were measured. In the IR spectrum of the DPP–PA resin, the absorption bands assigned to the P–H and P=O bonds were observed at 2450 and 1250 cm^{-1}. In the IR spectrum of the cured DPP–PA resin adsorbing chromate ion, the absorption band of the P–H bond disappeared but the remaining absorption did not change. In the ESR spectrum, a signal with a *g* value of 1.97 and H_{msl} of 20, was observed together with a broad signal, the *g* value of which could not be determined. The two signals are thought to agree with the so-called β phase proposed by O'Reilly,10) and thus it has been assumed that the former signal corresponds to Cr(V) while the latter corresponds to Cr(III). In the desorption of the chromate ion using aqueous sodium hydroxide solution, approximately 70 wt% in total Cr adsorbed on the cured DPP–PA resin was Cr(VI). This result does not agree with the ESR data which shows the presence of Cr(V) in the cured DPP–PA resin adsorbing chromate ion. The observed difference may be resolved assuming the β phase signal of Cr(V) is regarded as the signal associated with a three-chromium-atom center of mixed valency, Cr(VI)–Cr(III)–Cr(VI), as proposed by Spitz for the polymerization of olefins with a catalyst of chromium oxide.11)

It has been reported12) that the chromate ion reacts with phosphonic acid to produce the intermediate, $O_3CrO-P(OH)_2H$, and as the reaction proceeds furthermore, Cr(VI) is reduced to Cr(V) and finally to Cr(III). It is suggested that the P–H bond is broken in the rate-determining step of chromate ion reduction. It has been reported13) that the P–H bond in the reaction of DPP with Cu(II) salts breaks as follows; $>P(O)H + H_2O \rightarrow >P(O)OH + 2H^+ + 2e$. Simultaneously the Cu(II) is reduced. It is suggested that the active center for the adsorption of the chromate ion on the cured DPP–PA resin is the P=O bond. In water solution the P=O bond reacts with a water molecule to form $>P(OH)_2H$,1,13) and $>P(OH)_2H$ reacts with chromate ion as follows; $>P(OH)_2H + CrO_4^{2-} \rightarrow >P(H)-O_2CrO_2 + 2OH^-$. At the same time the chromate ion is reduced by the P–H bond. It has been concluded that the chromate ion is adsorbed on the cured DPP–PA resin in the form of a mixed valency, Cr(VI)–Cr(III)–Cr(VI).

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