

Synthesis of polyvinyl alcohol condensed 2,4-dihydroxy-5-antipyrinylazo phenylaldehyde and liquid-solid extraction of cadmium(II), copper(II), cobalt(II) and nickel(II)

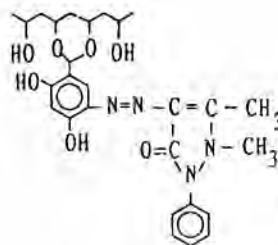
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A polymeric chromogenic reagent, polyvinyl alcohol condensed 2,4-dihydroxy-5-antipyrinylazo phenylaldehyde (PV-DHAPA), has been synthesized for the first time by condensing 2,4-dihydroxy-5-antipyrinylazo-phenylaldehyde with polyvinyl alcohol. PV-DHAPA has been used to study the liquid-solid extraction behaviour of the complexes of cadmium(II), copper(II), cobalt(II) and nickel(II) in water soluble polymer Tween 80-inorganic salt-water system under different experimental conditions.

Solvent extraction is a highly convenient method of separation and analytical estimation but is limited normally to transfer of neutral species from hydrophilic to hydrophobic phase. Another disadvantage is that the organic solvents used sometimes are toxic. Watanabe and Tanaka¹ put forward the concept of non-organic solvent extraction. In order to obtain high extraction efficiencies, they used an uncommon non-ionic surfactant (PONPE-7.5) having the cloud point temperature (T_c) near the room temperature. Schott and Royge² studied the effect of salting-out on T_c for water-soluble polymer used for non-organic solvent extraction system. Zarora³, Chen Xingguo⁴ and Li Buhai⁵ applied this property of water-soluble polymer for the efficient extraction of metal chelates without the use of any conventional organic solvents. But the extraction rate and separation efficiency were not ideal. Furthermore, only the charged complexes of metal ions with small molecule of chromogenic agent could be extracted^{6,7}. Hence, a new type of polymeric chromogenic agent polyvinyl alcohol condensed 2,4-dihydroxy-5-antipyrinylazo phenylaldehyde (PV-DHAPA) have been synthesized for the



first time and used as extractant to separate quantitatively Cd(II)-Ni(II), Cu(II)-Co(II) in Tween-80-(NH₄)₂SO₄-H₂O system. A possible mechanism responsible for the efficient extraction of the complex into the surfactant-rich phase is proposed. This method is used to separate and determine successfully Ni(II) and Cd(II) in the environmental water samples.

Experimental

Synthesis of polymeric chromogenic reagent PV-DHAPA

Preparation of DHAPA: 4-Aminoantipyrine (4.06g) was dissolved in 1.5 M hydrochloric acid (40ml) and NaNO₂ (1.44g) dissolved in 10 ml H₂O, cooled to 0°C, was added to diazotize 4-aminoantipyrine. To this diazonium salt solution was added 2,4-dihydroxy phenylaldehyde (2.76g) in 11% Na₂CO₃ (70 ml) and cooled to 0°C. The solution was kept below 5°C with stirring for 1 h and in ice box for a day. Conc. HCl was added to the resulting solution until a red precipitate appeared. The precipitate was filtered off and washed with 0.05% NaOH and dissolved in warm dimethylformamide (DMF) and to this was added conc. HCl. The precipitate was filtered and washed with 0.05% NaOH and water respectively. The red product (DHAPA) was dried at 50°C, yield: 3.6 g. [Found: C, 60.36%; H, 4.55%; N, 15.79%. C₁₈H₁₆N₄O₄ required: C, 61.36%; H, 4.58%; N, 15.90%].

Synthesis of PV-DHAPA: Polyvinyl alcohol (PVA, $n=1750\pm 50$, 2.5g, lab. reagent) was dissolved in DMF (25 ml). To this solution, purified DHAPA (1.72 g) in sufficient DMF and conc. perchloric acid (1.3 ml) were added. The mixture was kept at 50°C with stirring for 2 h and at room tem-

perature for a day, after which 4 M NaOH (10 ml) was added with stirring. The solution was transferred into a 1-l beaker and dioxane (200 ml) was added. The precipitate (PV-DHAPA) was filtered and dissolved in NaOH warm solution (100 ml) and dioxane was added to the solution until a precipitate was formed. The precipitate was filtered and washed with DMF and water respectively and dried at 50°C, yield: 1.5 g. The melting point was between 182°C and 190°C. The product is soluble in DMF, DMSO and dioxane, but not in ethanol. It contains 4.86% N (through elemental microanalysis), which shows that 10.5% of the hydroxyl groups on the PVA chain have been substituted by DHAPA and PV-DHAPA contains 30.5% DHAPA.

A Shannon model WFZ-25 UV-Vis spectrophotometer was used for photometric measurements. A Shanghai model pH S-3C pH-meter and a shaking machine were used.

An aqueous solution of Tween-80 (polyoxyethylene sorbitan mono-oleate) was prepared by dissolving Tween80 (60 ml) in 200 ml of distilled water, 0.1% PV-DHAPA was prepared by dissolving PV-DHAPA (0.25 g) in 250 ml of DMF. Standard 1.0 mg/mL solution of Cd(II), Cu(II), Co(II) and Ni(II) in 0.15 M nitric acid or perchloric acid were prepared using pure cadmium, copper, cobalt and nickel salts respectively. More dilute solutions were prepared by appropriate dilution as required. All other reagents were of analytical reagent grade.

Procedure

To an aliquot of HAc-NaAc buffer solution (pH=4.56 (3.0 mL), 2% Triton X-100 (5.0 mL), 40 µg metal ion, 0.1% PV-DHAPA (1.5 mL) and 0.25% hexadecyltrimethylammonium bromide (CTMAB) (0.5 mL) were added in a 25 mL test tube. To this solution 5.0 mL of 3.0% Tween80 and 2.0 g of (NH₄)₂SO₄ were added. The mixture was shaken for 3 min, the solution separated into two liquid-solid phases. The liquid was poured out directly from the tube. The solid was washed 2 or 3 times with the saturated solution of sodium sulphate, and the washings were combined with the separated liquid phase. The washed solid was dissolved in distilled water, and added to 3.0 mL of HAc-NaAc buffer solution (pH=4.56). The liquid phase was added to 1.5 mL of 0.1% PV-DHAPA solution. The concentration of the PV-DHAPA and complexes in the dissolved solid or liquid phase was determined spectrophotometrically. The per-

centage of extraction (E%) was calculated as a ratio of the amount of the extracted species in the solid phase to the original amount in the solution. The spectrophotometric analysis of cadmium is given in reference⁸.

Results and discussion

The absorption spectra of DHAPA and PV-DHAPA at pH-4.56 have a maximum at 392 and 398 nm respectively. IR spectra and NMR of DHAPA: 3400 cm⁻¹ (ν_{-OH}, a sharp band); 1680 cm⁻¹ (ν_{C=O}); 1600, 1490, 1580, 1450 cm⁻¹ (ν_{C=C}); 1200 cm⁻¹ (ν_{C-O}). The ¹³C NMR spectrum in deuterated chloroform showed 12 bands in the range δ 112-220 ppm (-C=O, -C=C-) and 4 bands in the range δ 20.6-41.2 ppm (-C-C-, -C-N-). IR spectra and NMR of PV-DHAPA: 3450 cm⁻¹ (ν_{-OH}); 2830, 2720 cm⁻¹ (ν_{-CH}); 1600 m 1500 cm⁻¹ (ν_{C=C}); 1360 cm⁻¹ (ν_{C-O}); 780 cm⁻¹ (ν_{C-O-C}). The ¹³C NMR showed 2 groups resonance bands in the range δ 46-72 ppm (-C-C-, -C-O) for the main chain of PV-DHAPA, 12 bands in the range δ 86-193 ppm (-C-O-C-, -C-C=, -C-C-) and 4 bands in the range δ 21.2-42.2 ppm (-C-C-, -C-N-) for the chromogenic functional groups.

In accordance with above-mentioned and elemental analysis experimental results, the PV-DHAPA structure is proposed to be:

It is known that many water-soluble polymers separate into two phases in the presence of certain inorganic salts. There are obviously differences in the results of phase separation when various polymers and salts are used. Tween80, Tween60 and TritonX-100 aqueous solutions lead to easy separation liquid-solid phases in the presence of Na₂SO₄, (NH₄)₂SO₄ and Na₂CO₃, and into liquid-liquid phases in the presence of NaCl, NH₄Cl and NaNO₃. In the presence of Na₂SO₄ and (NH₄)₂SO₄, it is difficult for PEG (polyethylene glycol) to be separated into liquid-solid phases. As extractive solvents. Tween80 leads to easy phase separation as also in the presence of (NH₄)₂SO₄ as inorganic salt. The necessary salt concentration increase as the Tween80 concentration decreases.

The extraction behaviour of Mⁿ⁺-PV-DHAPA and Mⁿ⁺-PV-DHAPA in Tween80-(NH₄)₂SO₄-H₂O system has been examined at different pH. The results showed that the metal ions were not extracted, PV-DHAPA and Mⁿ⁺-PV-DHAPA could be extracted easily.

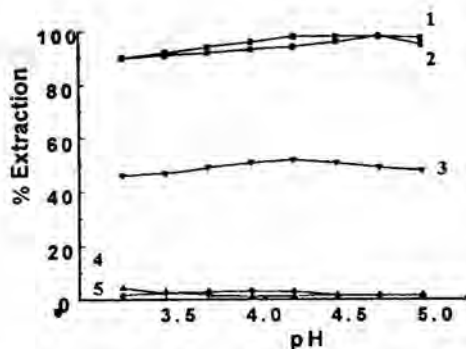


Fig. 1—Relationship between E% of metals and pH. $C_{\text{Tween80}}=15\%$, $C_{(\text{NH}_4)_2\text{SO}_4}=1.2 \text{ M}$, $C_{\text{PV}\cdot\text{DHAPA}}=0.10\%$, $C_{\text{CTMAB}}=0.10\%$ 1: Ni(II)-R(PV·DHAPA-CTMAB); 2: Co(II)-R; 3: Cu(II)-R; 4: Cd(II)-R; 5: Cu(II)-R-sulphourea, Cd(II), Co(II), Cu(II), Ni(II), 40 μg .

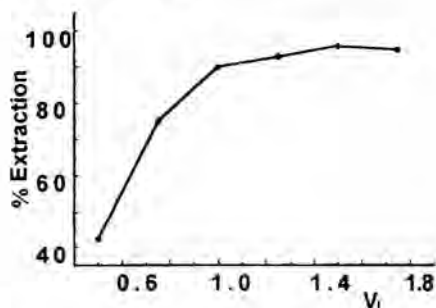


Fig. 2—Relationship between % E of metals and concentration of PV·DHAPA. Ni(II) 40 μg , other conditions as in Fig. 1. V_1 represents the volume of 0.1% PV·DHAPA

Results on extraction of metal ions in the presence of PV·DHAPA shows that E% of Cd(II), Cu(II), Co(II) and Ni(II) is dependent on the pH value (Fig. 1). The stability of the complexes of Cd(II), Cu(II), Co(II) and Ni(II) can be increased by raising the pH. So the E% is correspondingly increased. The E% of the complexes of Co(II) and Ni(II) becomes nearly 100% in the pH range 4.56-5.00, but the Cu(II) complex can be partly ex-

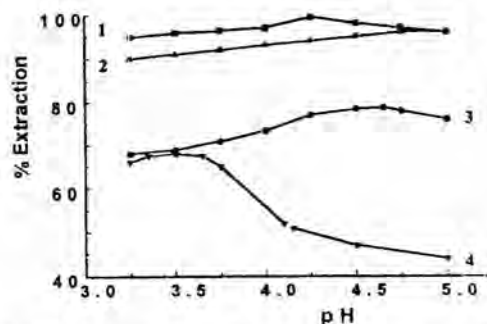


Fig. 3—Comparison of the extractive properties of PV·DHAPA and DHAPA. Other conditions as in Fig. 1. 1: Ni(II)-PV·DHAPA-CTMAB; 2: Ni(II)-PV·DHAPA, 3: Ni(II)-DHAPA; 4: Ni(II)-DHAPA-CTMAB

tracted under these conditions, Cd(II) complex can not be extracted. Moreover, Cu(II) can not be extracted in the presence of sulphourea. At a fixed pH, the E% values of metal complexes increase with increase in the PV·DHAPA concentrated up to a certain value, beyond which the E% remains constant (Fig. 2). As the salt concentration increase the Tween80 is salted out and therefore the E% is increased. After the Tween80 is completely salted out, the salt-effect of the excess salt decreases the stability of the complex, and the E% also decreases. The temperature between 10° and 60°C has not effect on the E% of complexes, but effects the equilibrium time of phase separation.

The extraction rate is higher using PV·DHAPA as an extractant than that using DHAPA. Moreover, the extraction rate of M^{n+} -PV·DHAPA is not affected by various concentrations of cationic surface active agent added into the solution of extraction system. It shows that the unchanged or hydrophobic species can also be extracted into the solid phase. The structural characteristics and physico-

Table 1—Separation and determination of Cd(II), Ni(II) in environmental water samples*

No.	Cd(II) measured (ppm)	Cd(II) standard (ppm)	Relative standard deviation (%)	Cd(II) added (ppm)	Cd(II) found (ppm)	Recovery (%)
GSBZ 5009-88						
0113	0.163	0.160	2.3	2.00	2.05	96~103
0115	0.206	0.201	4.2	2.00	2.11	95~105
	Ni(II) measured (ppm)	Ni(II) standard (ppm)		Ni(II) added (ppm)	Ni(II) found (ppm)	
0113	0.612	0.601	2.1	2.00	2.05	96~102
0115	0.786	0.797	2.5	2.00	1.96	93~100

*The average from 9 determinations.

chemical properties of PV·DHAPA and water-soluble polymers are similar. Extraction can be completed by hydrogen bonding between PV·DHAPA and water-soluble polymer. But the % extraction of DHAPA is decreased by increasing the cationic surfactant CTMAB (Fig. 3). In other words, only charged complexes can be extracted into the solid phase using DHAPA as an extractant.

Separation and determination of Cd(II) and Ni(II) in environmental water samples

HAc–NaAc buffer solution (3.0 mL, pH=4.56), 2% TritonX-100 (5.0 mL) were added to a 10.00 mL of water sample, following the noted steps as in the procedure. The Co(II) and Ni(II) were quantitatively extracted into solid phase, but Cd(II) and Cu(II) remained in the liquid phase. The results are shown in Table 1.

Acknowledgement

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