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Adsorption of Dyes, Chromate, and Metallic Ions by Poly(ethyleneimine)

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Ion exchange and chelate properties of poly(ethyleneimine) resin (PEI) were studied. Adsorption of neucoccin anions (NC^-) (maximum 1.7×10^{-4} mol/g) was greater than that of Crystal Violet cations (CV^+) (maximum 0.17×10^{-4} mol/g), indicating that PEI is an anion exchanger. CV^+ adsorption increased with the addition of sodium polyacrylate due to its bridging action between CV^+ ions and PEI. Adsorption of $CrO_4{}^{2-}$ was confirmed to be much greater than that of NC^- ions amounting to 4×10^{-3} mol/g at a sufficiently concentrated solution of $CrO_4{}^{2-}$. The acid exchange capacity of PEI was found to be about the same as the maximum amount of adsorption of $CrO_4{}^{2-}$. Kinetics of adsorption of $CrO_4{}^{2-}$ by PEI was studied at various temperatures. Adsorption followed a bimolecular reaction. Activation energy of 28.03×10^3 J/mol obtained is a right order of magnitude as an ion exchange adsorption. Chelating adsorption of Fe^{3+} and Cu^{2+} ions by PEI studied, the maximum amounts of adsorption being 3.1×10^{-3} mol/g and 3.3×10^{-3} mol/g, respectively. The values are greater than those for other synthetic polyethylene polyamine. PEI can be used as an anion and metallic cation adsorbent.

Poly(ethyleneimine) resin (PEI) is obtained in a large amount as a water insoluble by-product during the synthesis of polyethylene polyamine oligomers, causing trouble as an industrial waste. However, it is an effective anion exchanger as regards its chemical structure, and it would be worthwhile to study its behavior as both an anion exchanger and a cation chelating resin, like many synthetic polyamine reported.[1,2] It is noted that cheap anion exchangers can scarcely be found, while there exist abundant available cation exchangers such as clay minerals including bentonite and kaolinite.[3]

In the present experiment, adsorption of chromate, iron(III) and copper(II) ions as inorganic ions, and Crystal Violet and neucoccin as organic ions by PEI has been studied.

Experimental

Materials. PEI (Shunan Petroleum Co.) is a brown, fluffy, water insoluble powder. The sample for the measurement was prepared by removing impurities, washing with water and repeated decantation until the supernatant layer became clear after 10 min. The sample was then dried at 100 °C and kept in a desiccator.

Organic ions used were Crystal Violet cation (CV^+) and neucoccin anions (NC^-), inorganic ions being chromate anions ($CrO_4{}^{2-}$), iron(III) (Fe^{3+}), and copper(II) (Cu^{2+}) cations. For purification, Crystal Violet was precipitated from its ethanol solution by addition of diethyl ether. The precipitate was filtered and dried under reduced pressure. Neucoccin was recrystallized from its aqueous solution by addition of anhydrous sodium carbonate. Crystals deposited were filtered, washed with ethanol and dried under reduced pressure. Potassium chromate, iron(III) chloride, and copper(II) sulfate of guaranteed grade were used without further purification. Commercial sodium polyacrylate (NaPA) was used without further purification, the degree of polymerization being 22000—66000.

Measurement. The amounts of adsorption of CV^+ and NC^- were calculated from the difference in concentration of the solute before and after the adsorption by PEI. The concentration was determined with a spectronic colorimeter (Shimazu Spectronic 20) at wavelengths 480 nm and 580 nm for CV^+ and NC^-, respectively. The amounts of adsorption of $CrO_4{}^{2-}$, Fe^{3+}, and Cu^{2+} were calculated as in the cases of CV^+ and NC^-. The concentration was determined with a Hitachi atomic absorption spectrometer at wave lengths of 357.9, 248.5, and 324.7 nm, respectively. The experiments were carried out at room temperature, *ca.* 25 °C unless otherwise stated.

Results and Discussion

Adsorption of CV^+ and NC^-. *Adsorption Isotherm*: 0.1 g of PEI was put in a test tube containing 20 cm^3 solution of varying CV^+ and NC^- concentrations. The solutions were shaken frequently for 1 h and the amounts of adsorption determined. The results are shown in Fig. 1. We see that maximum adsorption of NC^- of 1.7×10^{-4} mol/g PEI is greater than that

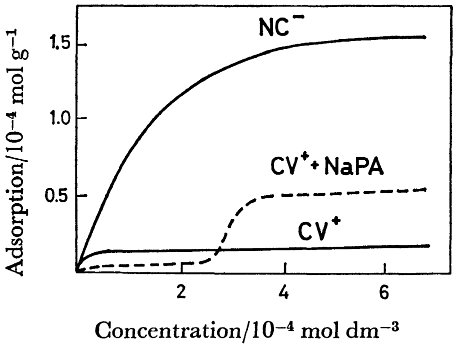


Fig. 1. Adsorption of dyes by PEI.

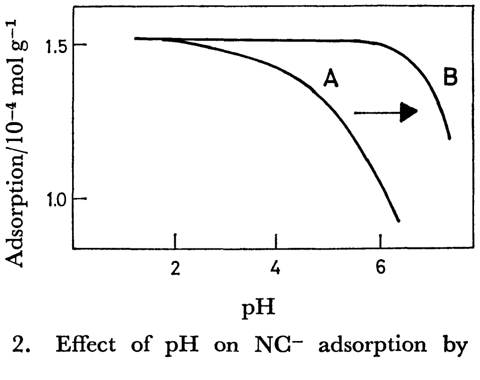


Fig. 2. Effect of pH on NC^- adsorption by PEI.

of CV^+ of 0.17×10^{-4} mol/g PEI. This confirms that PEI behaves as an anion exchanger as a whole. The slight adsorption exhibited by CV^+ might be due to the nonexchange adsorption.

Effect of pH *on* NC^- *Adsorption.* 0.1 g of PEI was added to a test tube containing 21 cm^3 of 7.88×10^{-4} mol/dm^3 NC^- solution of varying pH adjusted by the addition of HCl and NaOH, the solutions being shaken frequently for 1 h. The amount of adsorption calculated is plotted against pH before and after the adsorption in Fig. 2. The amount of adsorption increases with the decrease in pH, while pH increases with adsorption. These reactions can be explained by

$$RNH + NC^- + H^+ \longrightarrow RNH_2^+NC^-$$

where RNH denotes PEI. The equation indicates that PEI is an anion exchanger or an acid adsorbent.

Bridging Action of NaPA for the Adsorption of CV^+ *by PEI.* Because of the anion exchange property of PEI, adsorption of CV^+ was found to be small (Fig. 1). However, the adsorption of CV^+ might increase with the addition of a polymer anion such as NaPA. In the present experiment, 60 ppm of NaPA was added to the solution of CV^+ and the adsorption was measured under the same conditions as in the preceding experiments (broken line, Fig. 1). A marked increase took place in the amount of adsorption by the addition of NaPA in a higher concentration region of CV^+ as expected, but a slight decrease is seen in the lower concentration region. The increase of CV^+ adsorption by the addition of NaPA is explained by the bridging action of polyacrylate anions between PEI molecules and CV^+ cations. A similar bridging action has been reported in the case of EDTA.[4] The decrease of CV^+ adsorption at lower concentration is probably due to polyacrylate anions, not acting as a bridge but covering the sites on PEI available for the adsorption of CV^+ ions.

Adsorption of CrO_4^{2-}. *Adsorption Isotherm*: 0.2 g of PEI was added to 50 cm^3 of CrO_4^{2-} ion solutions of varying concentration in an Erlenmeyer flask, and the amount of adsorption was measured after stirring for 2 h. The result is shown in Fig. 3. The adsorption of CrO_4^{2-} ions is 4×10^{-3} mol/g PEI at 3×10^{-3} mol/dm^3 CrO_4^{2-} concentration. The amount is greater than that of NC^- ion which might be due to the smaller size of anions which can penetrate the inner surface of PEI.

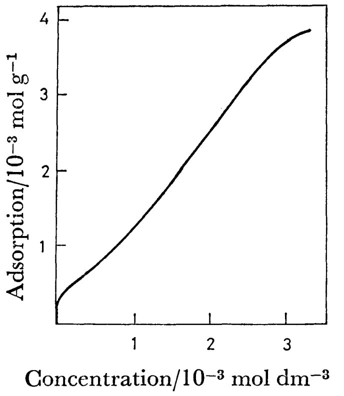


Fig. 3. Adsorption of CrO_4^{2-} by PEI.

Effect of pH *on* CrO_4^{2-} *Adsorption.* The effect of pH on CrO_4^{2-} adsorption was studied as in the case of NC^- adsorption. 0.2 g of PEI was added to 200 cm^3 of 0.84×10^{-3} mol/dm^3 CrO_4^{2-} solution, the pH of the solution being adjusted by addition of HCl. The amount of adsorption was measured after stirring at 25 °C for 1 h. The result is plotted against pH at equilibrium in Fig. 4. Adsorption of CrO_4^{2-} exhibits a maximum at pH 3, the behavior differing from the effect of pH on NC^- (Fig. 2). The increase of adsorption with the decrease of pH down to 3 can be explained by

$$2RNH + CrO_4^{2-} + 2H^+ \longrightarrow (RNH_2^+)_2CrO_4^{2-}$$

as in the case of NC^-. However, the decrease of adsorption of CrO_4^{2-} below pH 3 may be due to the following reaction:

$$(RNH_2^+)_2CrO_4^{2-} + 2HCl \longrightarrow 2RNH_2^+Cl^- + H_2CrO_4$$

The ion exchange of CrO_4^{2-} ions with Cl^- ions as well as the formation of weak acid H_2CrO_4 seem to favor the desorption of CrO_4^{2-} ions.

Rate of CrO_4^{2-} *Adsorption.* To 500 cm^3 of 0.85×10^{-3} mol/dm^3 K_2CrO_4 solution was added 0.5 g of PEI and the concentration of CrO_4^{2-} ions was measured at various intervals with stirring at constant temperatures in the range 9.5 °C—40.2 °C. Figure 5 shows plot of concentration C in 10^{-3} mol/dm^3 *vs.* time t in min at 19.8 °C. In most cases a rapid decrease in CrO_4^{2-} ion concentration took place during the first 10 or 20 min, equilibrium being attained after *ca.* 1 h.

A linear plot was obtained between $1/(C-C_\infty)$ and t (Fig. 6), which can be expressed as

$$1/(C-C_\infty) = Kt + L \qquad (1)$$

where C_∞, K, and L are constants, C_∞ being the equilibrium concentration after a sufficiently long time. Differentiating Eq. 1, we get

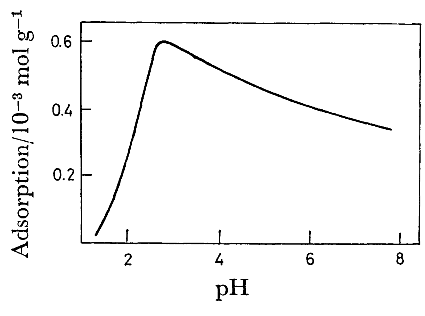


Fig. 4. Effect of pH on CrO_4^{2-} adsorption by PEI.

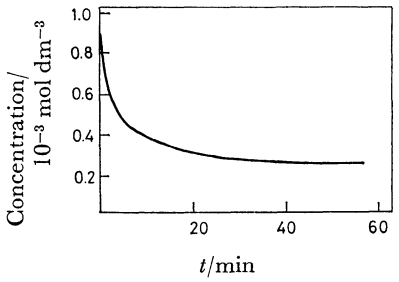


Fig. 5. Rate of CrO_4^{2-} adsorption by PEI.

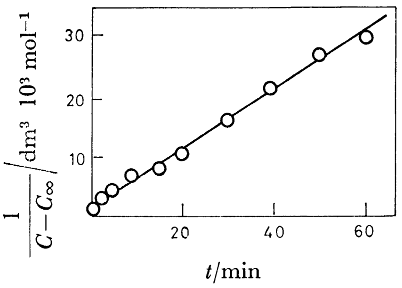


Fig. 6. $\frac{1}{C-C_\infty}$ *vs.* t plots.

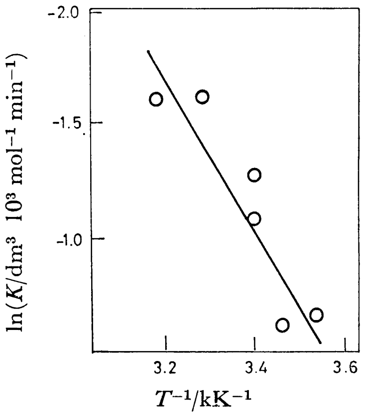


Fig. 7. Arrhenius plots.

$$-\mathrm{d}C/\mathrm{d}t = K(C-C_\infty)^2 \qquad (2)$$

The precise physical meaning of Eq. 2 expressing a bimolecular reaction is not clear. Arrhenius plot was made between ln K and the reciprocal of the absolute temperature T (Fig. 7). From the straight line we get the activation energy 28.03×10^3 J/mol. This is considered to be reasonable as a value for the ion exchange reaction in an aqueous solution.[5]

Anion Exchange Capacity of PEI. Anion exchange capacity was measured for PEI by the method of Kunin and Myers.[6] A given amount of the chloride form of PEI prepared by treatment with HCl solution and washing with ethanol was first treated with ammonia and then with aqueous Na_2SO_4 solution. The chloride contents in ammonia and aqueous Na_2SO_4 solution were then determined by titration with aqueous $AgNO_3$ solution. Weak base, strong base and total exchange capacities were calculated from the chloride contents, and found to be 1.51, 8.23, and 9.73 meq/g PEI, respectively. The strong base exchange capacity can be compared with the saturation amount, *ca.* 8 meq/g PEI, of CrO_4^{2-} adsorption, as estimated from Fig. 3. It was also confirmed that the exchange capacity obtained for PEI is larger as compared with that for the polyethylene polyamine synthesized as an ion exchanger.[2]

Adsorption of Fe^{3+} and Cu^{2+}. Although the adsorption of dye cation, CV^+, by PEI is comparatively small, the adsorption of metallic cations such as Fe^{3+} and Cu^{2+} might be large due to the amine complex formation of these ions with PEI.[1]

Rate of Fe^{3+} and Cu^{2+} Adsorption. 0.1 g of PEI was added to 200 cm^3 of 1×10^{-4} mol/dm^3 (pH=8) and Cu^{2+} (pH=7) ion solutions and the resulting solutions were stirred. 5 cm^3 each was taken at different times from these solutions and the concentration decrease due to the adsorption measured, the result being plotted against time of adsorption (Fig. 8). Adsorption is rapid and is completed within 10 min.

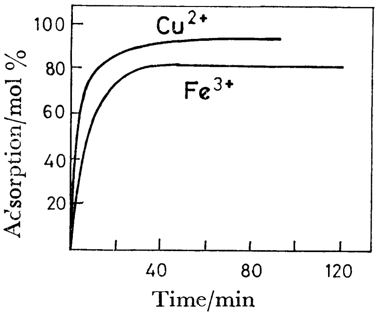


Fig. 8. Rate of adsorption of Fe^{3+} and Cu^{2+} by PEI.

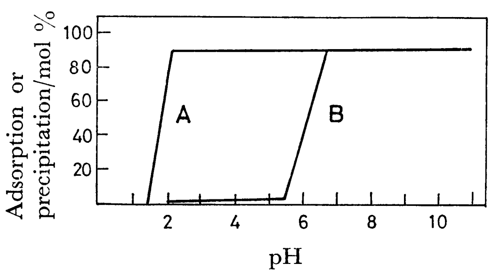


Fig. 9. Effect of pH of Fe^{3+} adsorption by PEI. A; Amount of adsorption, B; amount of precipitation.

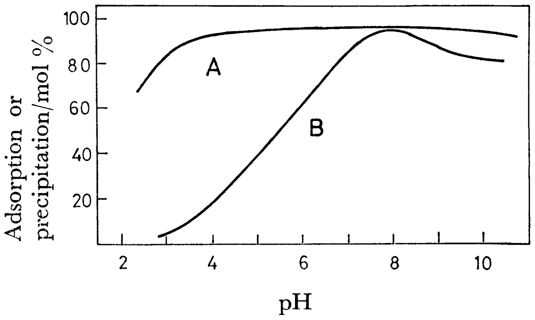
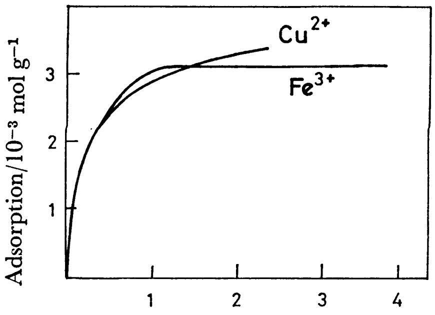


Fig. 10. Effect of pH on Cu^{2+} adsorption by PEI. A; Amount of adsorption, B; amount of precipitation.

Effect of pH on Fe^{3+} and Cu^{2+} Adsorption. The pH of 1×10^{-4} mol/dm^3 Fe^{3+} and Cu^{2+} ion solutions was adjusted by the addition of HCl and NaOH. To 50 cm^3 of these solutions was added 0.1 g of PEI and the amount of adsorption was calculated from the concentration decrease of the solution due to adsorption after stirring for 1 h. The amount of adsorption expressed in terms of the percentage of the initial amount of solute is plotted against the pH in Figs. 9 and 10; the amount of removed Fe^{3+} and Cu^{2+} ions due to precipitation by the addition of NaOH without PEI was measured and the results are also plotted against pH for comparison. We see a distinct adsorption effect of Fe^{3+} and Cu^{2+} by PEI below pH 7. However, the amount of adsorption and precipitation became equal for the systems with and without PEI above pH 7. Thus, from this graph alone we cannot



Concentration/10^{-3} mol dm^{-3}

Fig. 11. Adsorption isotherm of Fe^{3+} and Cu^{2+} by PEI.

confirm whether adsorption or precipitation takes place above pH 7. However, we believe that the adsorption of Fe^{3+} and Cu^{2+} on PEI takes place even in this pH region, since these ions can be floated with PEI by shaking the suspension with the addition of polyacrylamide and cationic surfactant, while iron and copper hydroxides without PEI cannot be floated from its suspension by a similar treatment.

Adsorption Isotherms of Fe^{3+} and Cu^{2+}. To 50 cm^3 of Fe^{3+} and Cu^{2+} ion solutions of varying concentration was added 0.1 g of PEI at pH 5 and the solutions were continuously stirred. After 1 h the amount of adsorption was measured; the result is plotted against equilibrium concentration in Fig. 11. The maximum amounts of adsorption were found to be about 3.1×10^{-3} mol/g and 3.3×10^{-3} mol/g PEI for Fe^{3+} and Cu^{2+}, respectively. The maximum amount of adsorption for Cu^{2+} is larger in the order of magnitude than the amount of adsorption reported for synthetic polyethylene polyamine,[5] but smaller than the simple ion exchange adsorption of CrO_4^{2-} ions by PEI.

Conclusion. From the results obtained, PEI is considered as a good anion exchange adsorbent as well as a chelating agent for metallic cations. Such properties are conveniently and effectively utilized further in the operation of ion flotation.

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