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Project Title: Ion Exchange Equilibrium and Kinetic Properties of Polyacrylate films and Applications to Chemical Analysis and Environmental Decontamination.

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One of the goals of the original proposal was to study how cross-linking affects the properties of an ion exchange material(IEM) developed at Lewis Research Center. However, prior to the start of this work, other workers at LeRC investigated the effect of cross-linking on the properties of this material.. Other than variation in the ion exchange capacity, the chemical characteristics were shown to be independent of the cross-linking agent, and the degree of cross-linking. New physical forms of the film were developed (film, supported film, various sizes of beads, and powder). All showed similar properties with respect to ion exchange equilibria but the kinetics of ion exchange depended on the surface area per unit mass; the powder form of the IEM exchanging much more rapidly than the other forms. The research performed under this grant was directed towards the application of the IEM to the analysis of metal ions at environmental concentrations.

A. Immobilization of indicators into the IEM film.

Indicators, xylenol orange and o-phenanthroline , were immobilized in the film using the following procedure.. A few drops of concentrated indicator solution were added to the initial polyvinyl alcohol/ polyacrylic acid solution. An amount of glutaraldehyde equivalent to 10% cross-linking (based on polyvinyl alcohol), was added, and a thin film cast before significant cross-linking occurred. The film was left overnight for completion of cross-linking and drying. The film was immersed in water and converted to the calcium form by addition of a calculated amount of calcium hydroxide. Some indicator leaked into the solution but most remained immobilized in the film. When the indicator films left standing in solutions containing iron(III), iron(II), lead(II), or copper(II), no indicator color changes were observed. Analysis of the solutions determined that the metal ions had been taken up by the film but no complexes were formed with the immobilized indicator. The lack of complex formation was apparent even when all exchange sites had been saturated. Research on immobilized indicators was discontinued and a different direction followed.

B. Use of metallochrome indicators to lower the detection limit in the analysis of metal ions using the IEM film.

Previous work at LeRC demonstrated that the IEM film could be employed in a simple spectrophotometric procedure for the determination of copper(II) and other colored transition metal ions at ppm levels¹. Studies supported by this grant have shown that, by use of indicators, the detection levels can be reduced to a few ppb.

Preliminary experiments indicated that the iron(II) complex of o-phenanthroline is taken up by both the acid form and the calcium form of the IEM film. This results in a colored film whose absorbance is easily measured on a spectrophotometer. If a solution of iron(III) is equilibrated with IEM film in the calcium form, the normal ion exchange procedure concentrates the iron(III) onto the film. When the film is treated with a reducing agent, hydroxylammonium chloride, and o-phenanthroline, the orange color of the iron(II) indicator complex develops on the film. The ability of the indicator to migrate into the film to form a colored complex with the bound metal ion contrasts with the inability of the immobilized indicator to form such complexes (as described in part A). Similar experiments with copper(II) and the indicators neocuproin and PAN(1-(2-pyridylazo)-2-naphthol), also demonstrated that the colored complexes could be taken up by the film. Measurements of the absorbance spectra can then be used in an analytical procedure. Using neocuproin, a selective indicator, copper solutions in the concentration range 5 ppb-100 ppb can be determined simply and reproducibly.

C. Development of a test kit for the determination of lead in drinking water .

The goal of this research was to develop a low cost, home test kit² which can be used to check if the lead in drinking water is within the EPA recommended limits, currently 15 ppb. Preliminary experiments were directed towards developing a procedure similar to that described in part B for copper and iron. Although the IEM film is very efficient in taking up lead from very dilute solutions, indicators which were sufficiently selective and sensitive, and could diffuse into

the film to detect the lead, could not be found. The indicator, 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H, 23H-porphine) showed some potential as a test kit indicator and its properties were the subject of further investigation.

In the presence of lead, this porphine indicator changes color from orange($\lambda_{\max}=425\text{nm}$) to green($\lambda_{\max}=475\text{nm}$). For this change to be observed visually, the indicator should not be in excess, and the minimum concentration of lead required was determined to be 1 ppm. When IEM film is allowed to equilibrate with a solution containing the lead-indicator complex, the lead ions and the indicator were both taken up by the film, but not the indicator complex. The spectra of the films showed the presence of the uncomplexed indicator($\lambda_{\max}=425\text{nm}$) only, and analysis of the solution determined that the lead had also been taken up by the film.

The possible interference with the lead porphine indicator system by other metal ions which might be present in drinking water was studied. Sodium and calcium ions have no effect on the absorption spectrum of the indicator or the lead-indicator complex. Iron(III) and copper(II), both form complexes with the indicator but do not cause spectral changes. If present in solutions containing lead and indicator, these ions reduce the absorbance of the lead complex due to competition for the indicator. Zinc ions also form an indicator complex which absorbs at a different wavelength($\lambda_{\max}=435\text{nm}$) than the free porphine, as does cadmium($\lambda_{\max}=447\text{nm}$). For this indicator to be used in a test kit for lead in drinking water, the concentration of lead must be increased from 15 ppb to about 1 ppm, and the concentration of the interfering ions in the final solution must be low enough not to affect the absorbance values, or able to be masked. The affinity of the IEM for lead ions suggested that selective concentration of lead in drinking water might be achievable through ion exchange.

The efficiency of metal ion uptake by the IEM as a function of pH has been studied by other workers at LeRC. These investigations showed that lead ions can be removed from solutions at lower pH's than can most other metal ions. In the present study, attempts were made to find a pH at which the IEM will remove lead from drinking water while leaving behind the

interfering ions such as zinc and copper. Test solutions contained 15 ppb lead, 5.0 ppm zinc and 1.3 ppm copper. Ion exchange columns were prepared from 0.2g samples of 40-60 mesh IEM resin beads. The resin was pre-equilibrated to the pH of the experiments by addition of small volumes of calcium hydroxide solution (to which a small amount of EDTA had been added to complex any lead present as an impurity) or dilute nitric acid, to a stirred slurry of the resin in deionized water. All solutions were analyzed by graphite furnace AA to insure the absence of lead contamination.

The test solutions were also brought to the appropriate pH and buffered by HMTA (hexamethylene tetra-amine), which had been shown previously not to affect the ion exchange process. In each experiment 400mL aliquots of test solution were passed through the columns at the rate of 5mL /min. Samples of the eluant were collected at different times and analyzed for the three metals. The optimum pH for maximum uptake of lead and minimum uptake of zinc and copper was determined to be pH=4.2. At this pH, the uptakes of metal ions by the resin were found to be: lead, 90%; copper, 82%; zinc, 4%.

To improve the separation of ions, especially of copper and lead, the effect of different complexing agents was studied. These included: succinate; tartrate; imidazole; picolinate; o-phenanthroline. Most complexing agents suppressed the ion exchange of both copper and lead. Of those investigated, tartrate was found to be the most selective. By controlling the pH and adding tartrate it was possible to selectively concentrate lead from a solution which also contained copper and zinc. The lead was selectively absorbed from 400mL of test solution by an IEM column and then eluted from the column using 2.0mL of dilute nitric acid. From a test solution containing 15 ppb lead, 1.3 ppm copper, 5.0 ppm zinc, a final solution was obtained with the following concentrations: lead= 1.0 ppm, copper=5ppm, and zinc= 5 ppm). Using this procedure the concentration of zinc can be increased to a level which can be detected by the porphine indicator, while not significantly increasing the concentration of interfering ions.

The porphine indicator discussed previously must be used in the pH range 9-11. This is best achieved by adding concentrated ammonia. If the pH is greater than 10, the concentration of ammonia is sufficient to complex with the copper(II) and zinc(II) and mask any effect of these

ions on the indicator providing that their concentrations do not exceed a few ppm. Under these conditions, 1 ppm of lead can be detected by observing the color change from orange to yellow/green.

For use in a home test kit, the slight color change resulting from a change in the absorption maximum from $\lambda=425\text{nm}$ to $\lambda=475\text{nm}$ is not sufficiently distinct. If the solutions are viewed through a colored glass filter the differences are more obvious. Inclusion of a filter would, unfortunately, make the test kit more expensive and more complicated. More research must be directed towards improving the detection system.

References:

1. Hill C.M; Street, K.W.; Philipp, W.H.; Tanner, S.P. Determination of Copper in Tap Water Using Solid-Phase Spectrophotometry. *Analytical Chemistry Letters* 1994,27,2589.
2. Street,K.W., Tanner, S.P., Wan, W. Safe Drinking Water Act -Analysis of Lead. A paper presented at the Pittsburgh Conference, March 1995

Patent Disclosure

No patents have been disclosed.