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A fluorescence study of UO_2^{2+} ion exchange in the modified matrix: Polyethylene/poly(acrylic acid)

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Sumary

The $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow UO_2^{2+}$ ion exchange in aqueous solution was studied in the material modified by *in situ* sorption and thermal polymerization of acrylic acid in low density polyethylene films. Fluorescence spectroscopy was used to observe the percentage of UO_2^{2+} exchange. The effects of temperature and film thickness in the exchange process were analyzed. The percentage of the $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow UO_2^{2+}$ exchange was twice as that observed for Eu^{3+}. Simultaneous $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow Eu^{3+}/UO_2^{2+}$ ion exchange in LDPE-PAA matrix was investigated and from fluorescence spectra they showed no evidence of energy transfer from UO_2^{2+} to Eu^{3+}.

Introduction

The fluorescence of Eu^{3+} added to the small number and sharp fluorescence peaks of this rare earth ion make it suitable for studies of the distribution of the carboxylate groups of poly(acrylic acid), PAA, in the modified matrix low density polyethylene/poly (acrylic acid), LDPE-PAA. Previous studies dealing with Eu^{3+} ion exchange in the modified material, LDPE-PAA were made in our laboratory (1). These studies showed evidence of the ion exchange $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow Eu^{3+}$ in the modified matrix LDPE-PAA. The ion exchange is observed mainly at the surface or close to the surface and it is a temperature dependent process.

In this paper, we chose another fluorescent ion, the UO_2^{2+}, to investigate the $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow UO_2^{2+}$ ion exchange in the modified matrix, for two reasons. Firstly, the smaller hydrated UO_2^{2+} ion radius and its lower ion charge (+2) values compared to Eu^{3+} ion would make possible a better exploration of the inner layers in the LDPE-PAA. Secondly, further studies on the simultaneous exchanges $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow Eu^{3+}$ and $H^+ \leftarrow\!\!\!-\!\!-\!\!\rightarrow UO_2^{2+}$ in the matrix would predict the microstructure of the LDPE-PAA material: energy transfer from UO_2^{2+} to Eu^{3+} ions should be expected if ion exchange occurs at the ionic agregate sites (3, 4). In this way, a

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much clear picture of the carboxylic groups dispersion, in the modified material LDPE-PAA can be proposed.

Experimental

Acrylic acid (AA) was supplied by Aldrich Chem Co. and Cia. Quimica Rhodia Brasileira; it was distilled under vacuum prior to use and stored at 18°C. Hydroquinone monomethyl ether (HMME) was supplied by Cia. Quimica Rhodia Brasileira; it was purified by successive crystallizations in acetone.

Uranyl Chloride (UO_2Cl_2) from BDH Chemical Ltd Poole England was used without further purification. Low density polyethylene (LDPE) sheets (d= 0.918 g/cm^3, MI= 1.15 g/min) were supplied by Poliolefinas (São Paulo). The films were cleaned and characterized following the same procedure as described in previous paper (5).

Methods

a) Sorption and thermal polymerization of AA in LDPE.

The sorption and *in situ* thermal polymerization of AA (80% by unit volume of aqueous solution containing 350 or 500 ppm of HMME) in LDPE films followed the method described in previous work (6). The thickness of the films used were 90, 200, 250, 270 and 300 µm.

b) $H^+ \longleftrightarrow UO_2^{2+}$ ion exchange in LDPE-PAA matrix.

The fuorescence measurements of the $H^+ \longleftrightarrow UO_2^{2+}$ exchange in the LDPE-PAA matrix followed the procedure described previously (4). The work temperatures were 35°C and 45°C. The fluorescence spectra from homogenized cell solution (3.6 ml) were taken at room temperature keeping the sample out from the optical pathway. The excitation was done at 420 nm and the fluorescence spectra observed in the range of 440-660 nm. The area of the complex band (440-660 nm) in the fluorescence spectra of UO_2^{2+} in the solution showed a linear behavior with the ion concentration. Thus, the relative areas were used to calculate the $H^+ \longleftrightarrow UO_2^{2+}$ exchange percentage in LDPE-PAA matrix. The area of the complex band of the spectrum of a 10 mM UO_2Cl_2 solution was assumed to be 100%. After each thermal treatment the percent of UO_2^{2+} in the solution was calculated as follows:

$$\% \text{ of } UO_2^{2+} = A_f/A_i \times 10^2$$

and in the matrix,

$$\% \text{ of } UO_2^{2+} = 100 - A_f/A_i \times 10^2$$

were,

A_f = complex band area (440-660 nm) of the UO_2Cl_2 solution after thermal treatment;

A_1 = complex band area (440-660 nm) of 10mM UO_2Cl_2 solution.

The fluorescence spectrum of dehydrated LDPE-PAA matrix after the ion exchange was obtained under the same conditions as described in previous work (1).

Physical Measurements

FTIR spectra were taken using a Nicolet Model 5ZDX Spectrophotometer.

Fluorescence spectra were obtained using a Spex Fluorolog-2/DM1B Spectrofluorometer.

Results

a) $H^+ \longleftrightarrow UO_2^{2+}$ exchange in LDPE-PAA matrix.

Films of the LDPE-PAA were used for the UO_2^{2+} exchange. The modified matrix films used were 90, 200, 250, 270 and 310 μm thick. The average percent of PAA in the matrix was 1.5%. Table I describes the characteristics of the samples used. A preliminary experiment of UO_2^{2+} exchange in a LDPE-PAA matrix, 200 μm thick and containing 4.5% of PAA, was done. The film was immersed in a 10mM UO_2Cl_2 solution at 60°C. After 2h of thermal treatment, no fluorescence in the solution was observed. This was explained by a total UO_2^{2+} exchange in the LDPE-PAA matrix. The evidence of a faster UO_2^{2+} exchange in the modified matrix compared to Eu^{3+} exchange (1) determined the choice of a lower ion exchange temperature (35°C and 45°C) and a lower amount of PAA in the modified matrix ($\leqslant$ 1.7%).

Table I. $H^+ \longleftrightarrow UO_2^{2+}$ exchange in LDPE-PAA matrix

Sample	Saturation Time (h)	*%PAA in LDPE-PAA Matrix	*% UO_2^{2+} in LDPE-PAA Matrix	Film Thickness (μm)	Heating Temp. (°C)
D_1	4	1.1	17.8	90	35
D_2	2	1.6	41.7	200	35
D_3	3	1.6	73.2	250	35
D_4	2	1.2	55.2	270	35
D_5	3	1.5	55.2	310	35
E_1	4	1.7	17.8	90	45
E_2	3	1.5	18.0	200	45
E_3	1	1.6	72.3	250	45
E_4	4	1.5	52.7	270	45
E_5	1	1.1	43.8	310	45

* See experimental

The FTIR spectra of LDPE-PAA and of LDPE-PAA after UO_2^{2+} exchange showed: i) a peak at 1770 cm^{-1} characteristic of C=O stretching of the PAA structure (Figs. 1a and 1b); ii) a peak at 1550 cm^{-1} identified as the stretching vibration mode of the carboxylate ion and a peak at 920 cm^{-1} identified as the stretching vibration mode of the "O-U-O" linear structure (Fig. 1b).

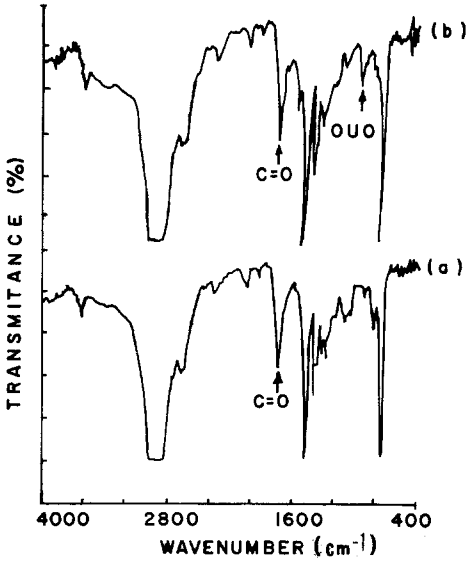

Fig. 1 FTIR spectra: (a) LDPE-PAA (90 um; 1.7% PAA); (b) LDPE-PAA matrix after $H^+ \longleftrightarrow UO_2^{2+}$ exchange (90 μm; 1.8% PAA; 18% UO_2^{2+}).

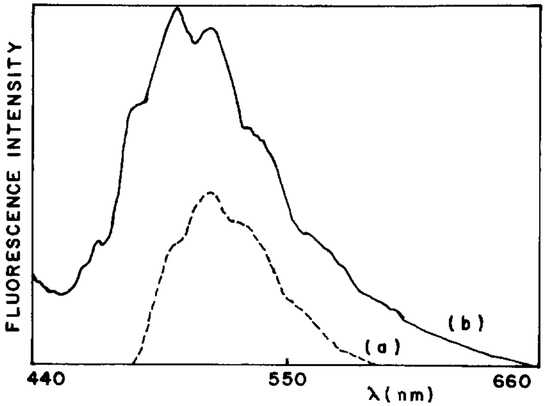

Fig. 2 Fluorescence spectra (ex. 420nm). (a) 10 mM UO_2Cl_2 solution; (b) LDPE-PAA matrix after the $H^+ \longleftrightarrow UO_2^{2+}$ exchange (200μm; 1.6% PAA; 28% UO_2^{2+}; 35°C).

These are evidences of the UO_2^{2+} exchange in the modified matrix LDPE-PAA.

Fig. 2 shows the fluorescence spectra of 10 mM UO_2Cl_2 solution (Fig.2a) and of the dehydrated LDPE-PAA modified matrix after UO_2^{2+} exchange (excitation at 420 nm and emission in the range of 440-660 nm), Fig. 2b. The spectra pattern were very similar. They showed several superimposed bands. However, the fluorescence emission spectrum of the LDPE-PAA-UO_2^{2+} matrix showed the ratio between the intensities of the bands (in the range of 550-500 nm) slightly higher. This data confirms the interaction between UO_2^{2+} and the carboxylic groups in LDPE-PAA matrix.

b) Effect of the temperature in the $H^+ \leftarrow\rightarrow UO_2^{2+}$ exchange in LDPE-PAA matrix.

A film of LDPE-PAA (sample D_2) was immersed into a cell containing 3.6 ml of a 10mM UO_2Cl_2 aqueous solution. The fluorescence spectra of the solution after the thermal treatment (35°C) of the sample for 0 and 2h are shown in Fig. 3. It was observed a decrease of the fluorescence intensity in the region at 440-660nm as lowering the UO_2^{2+} solution concentration due to the $H^+ \leftarrow\rightarrow UO_2^{2+}$ exchange in the modified matrix.

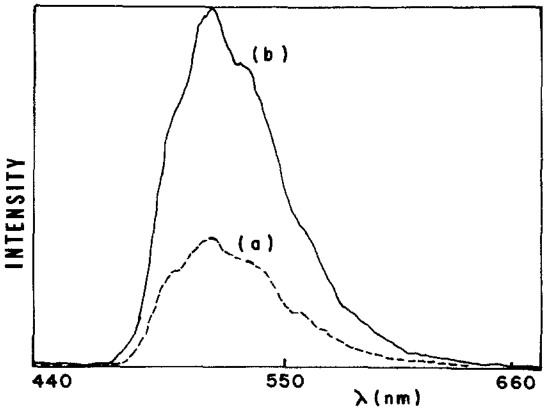

Fig. 3 Fluorescence spectra of the UO_2Cl_2 solution (ex. 420 nm). (a) after 2 h of the thermal treatment of sample D_2 at 35°C. (b) before the thermal treatment of the sample (10 mM UO_2Cl_2).

Fig. 4 shows the percent of UO_2^{2+} in the matrix with time at the temperatures of 35°C and 45°C (film thickness of 90 µm). There was not observed any significant change in the apparent rate of exchange at both temperatures. The saturation time was reached after 4 hours of thermal treatment. An amount of aproximately 18% of UO_2^{2+} ions was exchanged in the LDPE-PAA matrix.

Figs. 5 and 6 show the percent of UO_2^{2+} exchange in LDPE-PAA matrix with time at the temperatures of 35°C and 45°C using the thickness of the films of 90, 200, 250, 270 and 310µm. Saturation times in the range of 1 to 4 hours were observed.

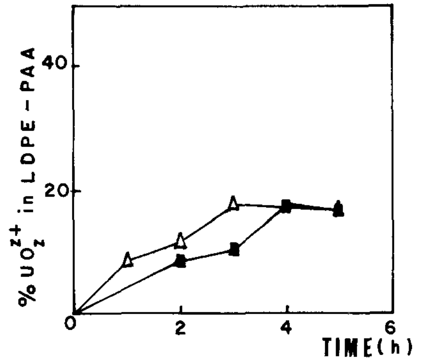

Fig.4 H^+<--->UO_2^{2+} exchange in LDPE-PAA vs time. Sample D_1: 35°C (Δ); sample E_1: 45°C (■).

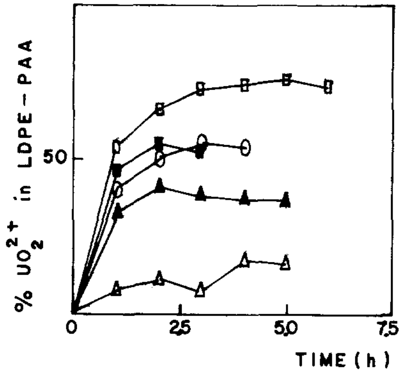

Fig.5 H^+<--->UO_2^{2+} exchange in LDPE-PAA vs time. Film thickness:90 µm (Δ); 200 µm (▲);250 µm (□) 270 µm (■); 310 µm (○). Temperature: 35°C.

c) Effect of the film thickness in the UO_2^{2+} exchange in LDPE-PAA matrix.

The effect of the film thickness upon the percentage of UO_2^{2+} exchange on the saturation time at 35°C and 45°C is shown in Fig. 7. The percentage of ion exchange at the saturation time increased with the film thickness (90 to 250 µm thick) reaching a value of 72 % of UO_2^{2+} exchange. This was followed by a decrease using films of higher thicknesses (270 and 310 µm).

d) Simultaneous H^+<--->Eu^{3+}/UO_2^{2+} ion exchange in the LDPE-PAA matrix.

Simultaneous H^+<--->Eu^{3+}/UO_2^{2+} ion exchange in LDPE-PAA matrix (250 µm thick and 4.5% of PAA) was investigated. The ion exchange was carried out using a 1:1 of 10mM of both $EuCl_3$ and UO_2Cl_2 solutions. After the thermal treatment at 60°C for 4 hours, the matrix was dehydrated. Preliminary fluorescence studies showed no evidence of energy transfer from UO_2^{2+} to Eu^{3+} into LDPE-PAA matrix. The spectral data showed flourescence peaks due to Eu^{3+} and UO_2^{2+} transitions only (excitation at 392nm or 420nm). In other words, if the modified matrix after the simultaneous ion exchange is excited at 420 nm (UO_2^{2+} excitation) no fluorescence peak is observed at the Eu^{3+} fluorescence region (550-620 nm).

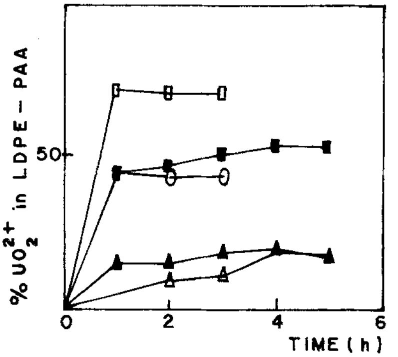

Fig. 6 H^+<--->UO_2^{2+} exchange in LDPE-PAA vs time. Film thick.: 90 µm (Δ); 200 µm (▲); 250 µm (□); 270 µm (■); 310 µm (o). Temperature: 45°C.

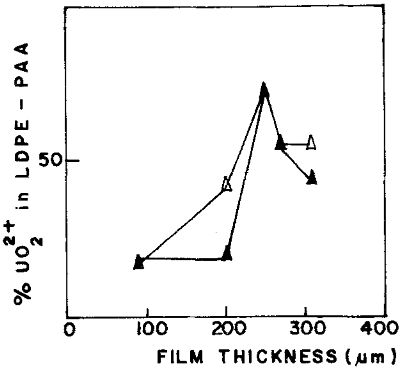

Fig.7 Effect of the film thick. in the H^+<---> UO_2^{2+} exchange in LDPE-PAA; 35°C (Δ); 45°C (▲).

Discussion

The UO_2^{2+} exchange in the LDPE-PAA matrix is evidenced by: the formation of carboxylate groups; the presence in the IR spectrum of a peak at 920 cm^{-1} characteristic of the stretching mode of the O-U-O linear structure; the increase of the ratio between the fluorescence intensity bands at 550-500 nm in the matrix as compared to the same bands in the UO_2^{2+} solution.

A faster ion exchange in the matrix is observed using UO_2^{2+} compared to that using Eu^{3+} (1). In this way, the temperature is not a limiting factor for the UO_2^{2+} exchange in the matrix. At lower temperatures (35°C and 45°C) than the ones used for the Eu^{3+} exchange (60°C and 80°C) it is observed shorter periods of saturation times and a two folds percentage of UO_2^{2+} exchange in LDPE-PAA matrix. This is explained by the effects of the charge and of the hydrated ion size, probably. The hydration of the UO_2^{2+} might be lower than that of the Eu^{3+} ion (2) and so, a higher apparent rate of UO_2^{2+} exchange would be expected.

The effect of the film thickness on the UO_2^{2+} exchange showed a different behavior as compared to Eu^{3+} exchange for thickness superior to 250 µm. The decrease of the UO_2^{2+} percentage at saturation on the films thicknesses of 270 and

310 µm was not observed in the Eu^{3+} exchange (1). However, this behavior was similar to that previously observed for the thermal polymerization of AA in the LDPE matrix (6). The increase of the percentage of ion exchange at saturation with the film thickness suggests a diffusion free of UO_2^{2+} ion into LDPE-PAA matrix. The decrease of the percentage of ion exchange at saturation observed in the film thickness higher than 250 µm is explained as a diffusion controlled process. According to our previous results (6) and the literature data (7) the thickness of 125 µm is proposed as the limit between diffusion free and diffusion controlled exchange process of UO_2^{2+}. .

The simultaneous ion exchange did not show the existence of ionomer agregates. These studies are under investigation.

Acknowledgments

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