Surface Modification of Egyptian Delta Titano Magnetite Ore and Its Effect on the Aqueous Polymerization of Methyl Methacrylate

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Synopsis

The surface modification of Egyptian delta titano magnetite ore (EDTMO) was carried out by adsorption of stearic acid molecules from benzene solution. The adsorption isotherm was found to be one-step. The modification process affected the sedimentation properties of EDTMO in organic medium. It was found that the maximum stability of EDTMO in organic medium is concerned with monolayer surface formation. The modified EDTMO was found to catalyze the aqueous polymerization of methyl methacrylate and resulted in increasing the viscosity average molecular weights.

INTRODUCTION

Sedimentation properties of the solid dispersed phase in the organic medium depend on the interaction between the surface of the particles and the medium.[1,2] This interaction can be changed by adsorption of surface active agent molecules on the surface of dispersed phase to cover it with hydrocarbon chains.[3] The adsorbed layer on the surface of dispersed phase affected the interaction between it and the medium.[4,5] There are many publications dealing with the effect of solid particles of the inorganic substances on the aqueous polymerization of methyl methacrylate.[6-8]

The aim of this work is to modify the surface of Egyptian delta titano magnatite ore (EDTMO) with stearic acid solution up to monolayer formation and to study the effect of surface modification on the aqueous polymerization of methyl methacrylate.

EXPERIMENTAL

Methyl methacrylate was from E. Merck, Schuchard, washed with sodium hydroxide solution (5%), purified and fractionated with a fractionating column of 15 theoretical plates; the fraction which boiled at 100–100.5°C was collected.

Hydroquinone and stearic acid were from E. Merck, Darmstadt. Sodium bisulfite was a product of El-Nasr Pharmaceutical Chemical Co., Egypt. Benzene and methanol were analytical grade.

Egyptian delta titano magnetite ore was a fraction of so-called black sand, which is a multimineral distributed along the Mediterranean Sea coast from

TABLE I
Analysis of the Egyptian Delta Titano Magnetite (EDTMO)

Component	(%)	Component	(%)	Component	(%)
Fe total	56.0	Cr_2O_3	0.58	Na_2O	0.31
FeO	18.6	CaO	0.36	K_2O	0.05
TiO_2	17.8	MnO	0.61	P_2O_5	0.10
SiO_2	1.5	V_2O_5	0.54	S	0.04
Fe_2O_3	58.11				
Al_2O_3	1.5				

west of Alexandria to the eastern border of the Sinai Peninsule. Complete chemical analysis of a representative sample is given in Table I.

The adsorption isotherm of stearic acid was determined using a series of experiments containing the same weight of EDTMO (4 g) in different concentrations of stearic acid solution in benzene (20 mL) $(0.1-100 \times 10^{-3}$ $mol/dm^3)$, until reaching the adsorption equilibrium (48 h). These different samples of EDTMO are filtered, dried, and used in sedimentation rates determination; then the effect of modified samples on the aqueous polymerization of methyl methacrylate was studied. The concentration of stearic acid solution was determined by titration with alcoholic botassium hydroxide solution in the presence of phenol phthalein as indicator.

The adsorbed amount n^s can be calculated using the following equation:

$$n^s = (C_0 - C_e)V/m \qquad mol/g$$

where C_0 and C_e are the concentrations of stearic acid before and after the adsorption, V represents the volume of the adsorbed solution, and m is the mass of the adsorbent EDTMO used (g).[9] Plotting of the adsorbed amount/g against the equilibrium concentration (C_e) will give the adsorption isotherm.

Samples of 1 g from EDTMO each previously modified with stearic acid are dried at 105°C for 2 h and then dispersed in graduated quick-fitted test tubes each containing 20 mL benzene. The test tubes were shake end-to-end to complete dispersion; then the change in the sediment volume with time gives the sedimentation rate of the EDTMO in benzene. The sedimentation rate is then plotted against the adsorbed amount x; also the sediment volume at equilibrium is plotted against the adsorbed amount.

The aqueous polymerization of methyl methacrylate (4.7 g) in water (45 mL) was carried out using sodium bisulfite (0.05 mol/dm^3) as initiator at 40°C in the absence and presence of both unmodified and modified EDTMO substances. After a definite period of time, the polymerization reaction was stopped by cooling and addition of hydroquinone and then filtered, washed, and finally dried at 105°C. The viscosity average molecular weights $(\overline{M}_v)$ for the obtained poly(methyl methacrylate) were calculated according to the equation

$$[\eta] = 0.94 \times 10^{-4} \overline{M}_v^{0.76} \, dL/g$$

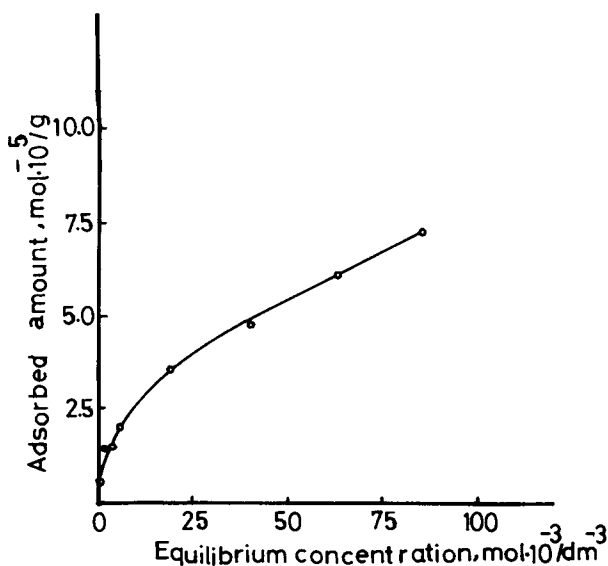in benzene solution at 25°C,[10] where $[\eta]$ is the intrinsic viscosity for each polymer.

Fig. 1.   Adsorption isotherm of stearic acid on EDTMO surface.

RESULTS AND DISCUSSION

Adsorption Isotherm

The adsorption isotherm of stearic acid solution in benzene on the surface of EDTMO at 25°C and their results are shown in Figure 1. From Figure 1, the adsorbed amount of stearic acid increased largely with a small increase in the equilibrium concentration, followed by a slow increase in the adsorbed amount. The surface of the EDTMO was modified by adsorption of stearic acid molecules to a different extent up to the region where there is a slow change in the adsorbed amount, which represents the formation of monolayer surface coverage,[11] 3.4×10^{-5} mol/g, on EDTMO surface.

Sedimentation Rate

The sedimentation rates for the samples which were modified to a different extent were determined from the slope of the relation between the sediment volume and the time.

Figure 2 represents the changes taking place in the sedimentation rate with the adsorbed amount of stearic acid on the EDTMO surface. From the figure it is shown that the sedimentation rate decreases with the adsorbed amount up to a certain value, which represents the inflection point, followed by an increase in its value with the adsorbed amount. This inflection starts at 3.6×10^{-5} mol/g adsorbed amount, which is near to the formation of monolayer surface coverage in the adsorption isotherm.

Sediment Volume

The sediment volume formed at equilibrium state were determined and the results were plotted against the adsorbed amount (Fig. 3). From the figure, the
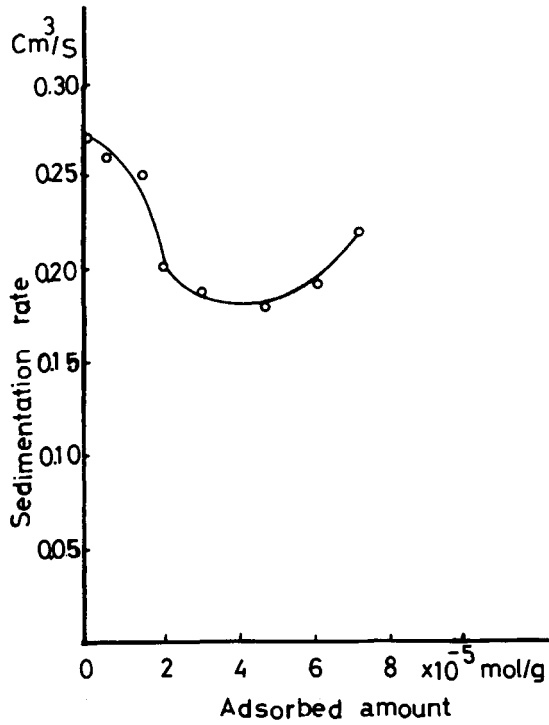
Fig. 2.   Change in sedimentation rate with adsorbed amount.

sediment volume was found to decrease with the adsorbed amount till about 3.4×10^{-5} mol/g adsorbed amount, which is near to the formation of mono-layer surface coverage in the adsorption isotherm.

After complete sedimentation of the modified surface of EDTMO, we observed that two different fractions are formed in the sedimentate. The
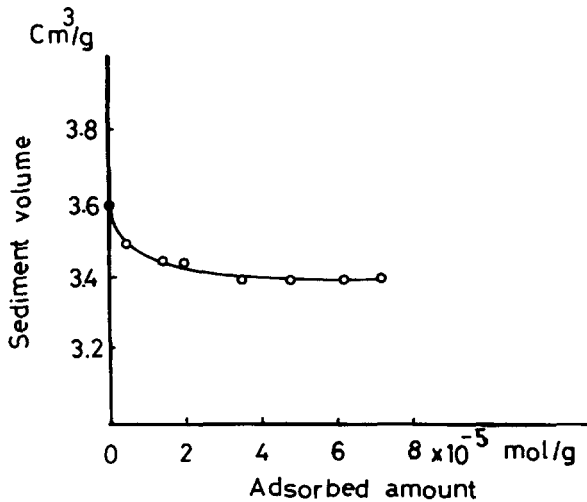

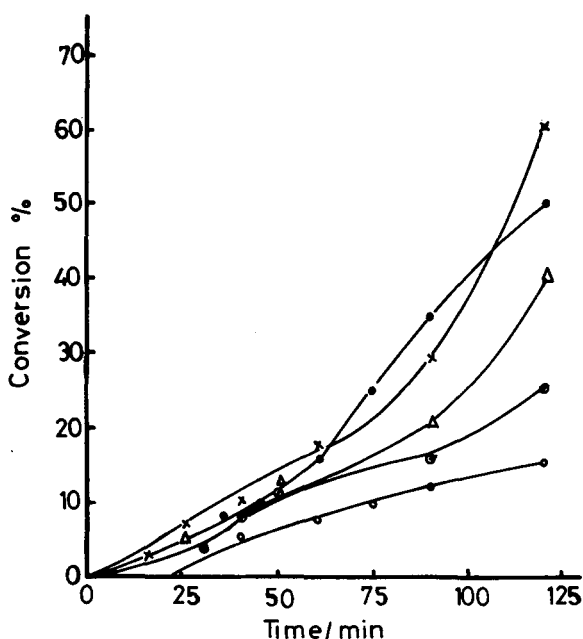Fig. 3.   Change in sediment volume with adsorbed amount.

Fig. 4. Conversion–time curves: (O) in the absence of EDTMO; (⊙) in the presence of EDTMO; (●) in the presence of modified EDTMO; (×) in the presence of upper fraction; (△) in the presence of lower fraction.

brown upper fraction represents 20% of the weight of the sedimentate and the lower black fraction represents the rest, i.e., 80% of the sedimentate.

POLYMERIZATION OF MMA

The polymerization of methyl methacrylate (4.7 g) in water (45 mL) was carried out using sodium bisulfite (0.05 mol/L) as initiator at 40°C in the absence and presence of 0.2 g[12] from lower fraction, upper fraction, unmodified, and modified EDTMO substances. The conversion–time data are represented in Figure 4, and the initial rate values are present in Table II, from which it is clear that the upper fraction, the lower one, and the modified and unmodified EDTMO catalyze the aqueous polymerization of methyl methacrylate. It is also seen that the very fine powdered upper fraction increases the rate of polymerization than the lower fraction. The rate of

TABLE II
Initial rates for the polymerization of methyl methacrylate.

Inorganic substance	Initial rate $\times 10^5$ (mol L^{-1} S^{-1})
In the absence of	2.09
Unmodified EDTMO	3.41
Modified EDTMO	3.82
Upper fraction	4.48
Lower fraction	4.12

TABLE III
Viscosity Average Molecular Weights
of Obtained Poly(methyl Methacrylate)s

Inorganic substance	Conversion (%)	$[\eta]$ (dL/g)	$\overline{M}_v$
In the absence of	15.5	1.25	265,000
Unmodified EDTMO	25.0	1.60	370,000
Modified EDTMO	50.0	2.37	620,000
Upper fraction	60.0	2.42	636,000
Lower fraction	40.0	1.83	440,000

polymerization in the case of modified EDTMO substance is higher than that in the case of unmodified substance; this may be due to the increase in the wettability of modified EDTMO with the monomer in the reaction medium.

Viscosity Average Molecular Weights

The viscosity average molecular weight values of the obtained poly(methyl methacrylate)s are presented in Table III, from which it is seen that the viscosity average molecular weight of poly(methyl methacrylate) obtained in the presence of EDTMO substance is higher than that obtained in the absence of it, but that obtained in the presence of the modified EDTMO was found to be the highest. It is also clear that the viscosity average molecular weight of the polymer obtained in the presence of the upper fraction is higher than that obtained in the presence of the lower one.

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