polymer report

Stereoregularity of adsorbed poly(methyl methacrylate) on the surface of albite ore

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The aqueous polymerization of methyl methacrylate was carried out at 60°C using potassium persulphate and sodium metabisulphite as the redox pair initiation system. The viscosity average molecular weight for the prepared poly(methyl methacrylate) (PMMA) was 1.49×10^5. Adsorption of PMMA on the surface of Egyptian albite ore was carried out. The adsorption isotherm obtained was S-shaped and the monolayer surface coverage was 7×10^{-3} g g^{-1} adsorbed polymer. The stereoregularity of the prepared PMMA changed with the adsorption process. The sedimentation rate of the modified ore in the organic medium was also determined. The most stable state for the suspension of the ore was found at 4×10^{-3} g g^{-1} adsorbed polymer.

(Keywords: stereoregularity; PMMA; albite ore)

INTRODUCTION

A dispersion of particulate matter in non-aqueous media may be stabilized with respect to coagulation by adsorption of surface active agents[1] and macromolecules[2]. In the adsorption of macromolecules on the surface of inorganic particles, relatively small changes in polymer structure have been found[3,4]. The adsorption of polymers differs from that of low molecular weight species[3]. The adsorption can be very slow to reach equilibrium. The adsorption of macromolecules on solids from solutions is of interest not only from a theoretical point of view but also in practical terms.

In this paper, flocculation (sedimentation properties) of albite ore as a function of polymer adsorption, and the stereoregularity of adsorbed PMMA before and after adsorption on an albite ore surface were examined.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was obtained from BDH and was purified as described elsewhere[5].

Techniques

Egyptian albite ore ($NaAlSi_3O_8$) is a feldspar, with specific gravity of 2.62 g cm^{-3} and hardness of 6–6.5 with respect to Moh's scale.

Chemical analysis (%) of albite: SiO_2 68.2, Al_2O_3 19.6, Na_2O 11.3, K_2O 0.2, Fe_2O_3 0.1, CaO 0.3, MgO 0.16.

The aqueous polymerization of MMA was performed as described previously[6].

Molecular weight determination

The viscosity average molecular weight, $\bar{M}_v$, for PMMA was measured in chloroform at 25°C and calculated according to the following equation[7]:

$$[\eta] = 48 \times 10^{-6} \bar{M}_v^{0.8}$$

^1H n.m.r.

The ^{1}H n.m.r. spectra of the polymer samples were determined using a Varian 200 MHz spectrometer. The polymers were dissolved in deuterated chloroform (8 wt%) containing a small amount of tetramethylsilane as an internal standard. The structure was determined from the areas under the peaks obtained from the methyl ($\tau = 8.8$–9.1 ppm) resonances, which are reported in terms of the percentage of isotactic, heterotactic and syndiotactic triads in the polymer.

Adsorption isotherm measurements

The adsorption process was carried out at 25 ± 1°C for 5 days. The initial and equilibrium concentrations were determined gravimetrically. Calculations were carried out as described elsewhere[8].

The stability of the albite ore dispersion in the organic medium (sediment volume) was studied. A series of samples of known weight (4 g) albite ore were dispersed in cyclohexane (20 cm^3) using a graduated tube with a variable adsorbed amount of polymer as in the isotherm, that is in the presence of blank sample (without adsorption). The tubes were shaken carefully several times, and then the final sediment volumes were determined.

RESULTS AND DISCUSSION

Adsorption isotherm

The adsorption isotherm of PMMA on the albite ore surface was determined. The ratio of albite ore to PMMA solution was 1:10 w/v. The adsorption isotherm of PMMA on the albite ore surface is shown in *Figure 1*. The adsorption was high from the non-polar solvent at small equilibrium concentrations. The isotherm was S-shaped and a plateau region appeared at 7.0×10^{-3} g g^{-1} adsorbed polymer, followed by increasing adsorbed amount beyond this region.

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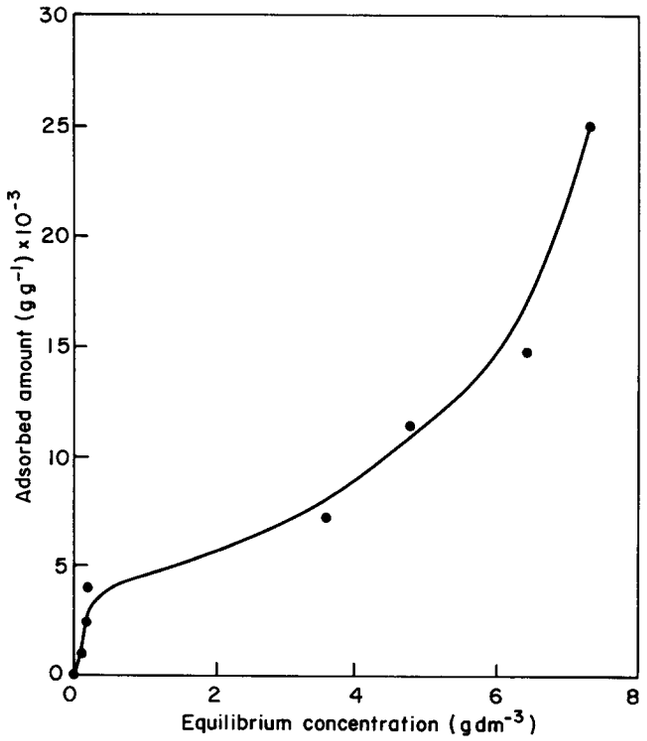

Figure 1 Adsorption isotherm of PMMA on albite ore surface

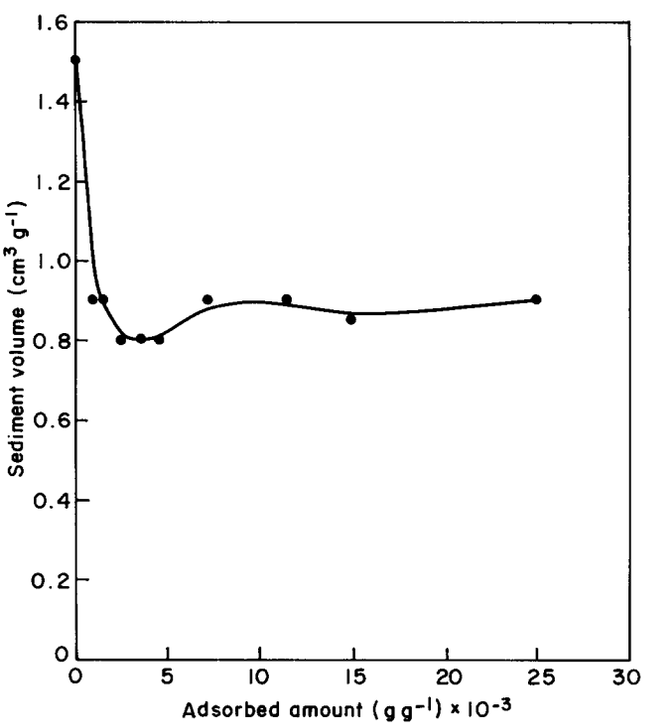

Figure 2 Effect of adsorbed amount on the sediment volume of albite

In order to obtain information on the mechanism of flocculation by polymer adsorption, it is necessary to correlate flocculation with the adsorbed amount in the isotherm.

Flocculation properties

Results obtained for the effect of polymer adsorption on flocculation response are given in *Figure 2* where the changes in the sediment volume of the albite ore for different adsorbed amounts of polymer are shown. From *Figure 2* it can be seen that the sediment volume decreased in the presence of a small amount of adsorbed polymer up to 4.0×10^{-3} g g^{-1}, followed by increasing adsorbed amount without any appreciable change in the sediment volume. The most stable suspension for the ore is formed for an adsorbed amount smaller than that of monolayer surface coverage; this is due to the long chains of the polymer molecules which restrict the particles from approaching each other.

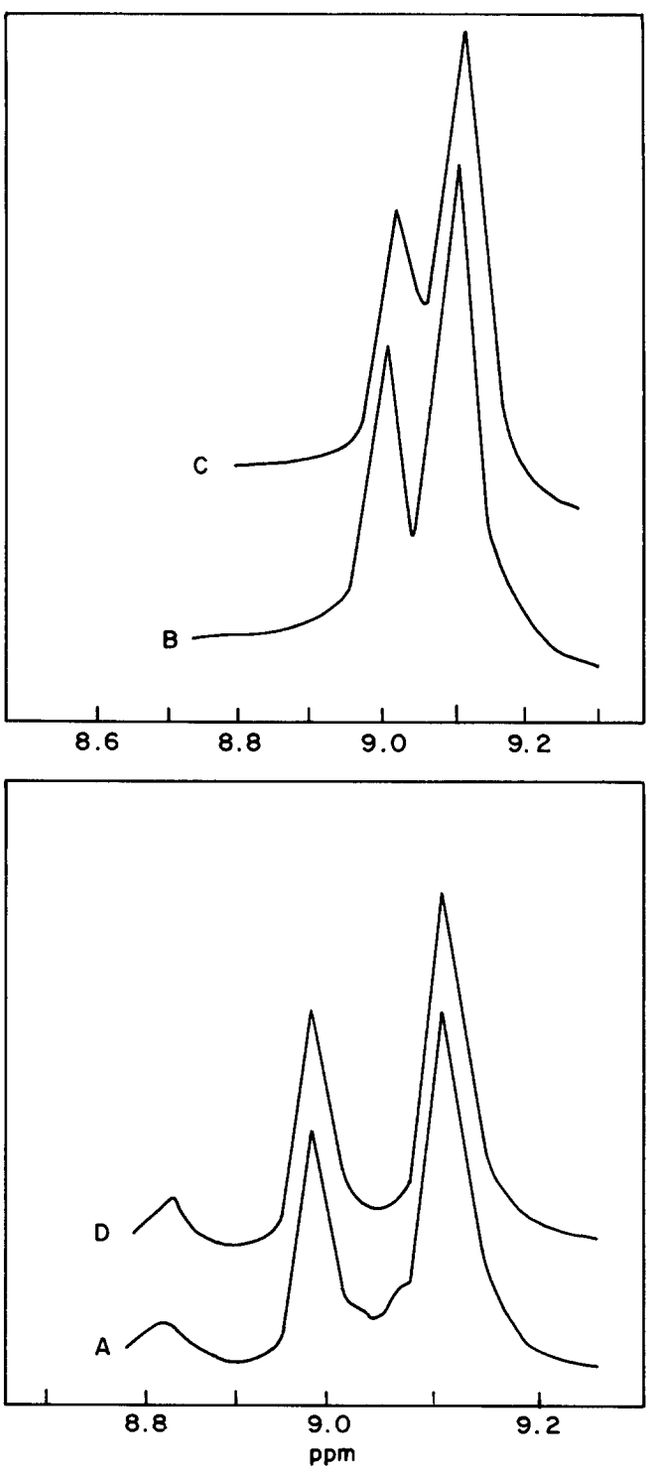

Figure 3 α-Methyl peaks of ^{1}H n.m.r. spectra of PMMA: (A) before adsorption as blank sample; (B) 0.1, (C) 0.25 and (D) 0.4 g dm^{-3} as initial concentrations after adsorption

Table 1 Triad fractions obtained from ^{1}H n.m.r. spectra

Concentration ($g\,dm^{-3}$)	Sequence fraction (%)[a]		
	Isotactic	Heterotactic	Syndiotactic
0.02	–	10.00	90.00
0.06	–	34.56	65.44
0.10	–	28.41	71.59
0.25	–	33.68	66.32
0.40	1.02	32.71	66.28
Blank	3.00	32.00	65.00

[a] Probable error ±2%

Also, from the sedimentation properties the untreated albite was found to be unstable in the non-polar medium; stability with respect to flocculation was improved when polymer adsorption was increased.

Stereoregularity of the PMMA obtained

The configuration triad fractions obtained from ^{1}H n.m.r. spectra are presented in *Table 1*. From *Table 1* it can be seen that the PMMA sample prepared by radical polymerization had a slightly syndiotactic-rich microstructure. The spectra were found to be very similar to that for a radical PMMA first analysed by Inoue *et al.*[9]. The ratios of isotactic (*mm*) to heterotactic (*mr* and *rm*) to syndiotactic (*rr*) triads were found to be close to 3:32:65. This result is approximately the same as that previously obtained for PMMA[10–12]. It can be concluded from the ^{1}H n.m.r. spectra that the propagation steps in this polymerization are of conventional radical type, and are uninfluenced from the steric point of view by the nature of the polymerization medium in the presence of various additives.

For the study of adsorption and change in the tacticity of PMMA from solution on the surface of Egyptian albite ore, it is necessary for the albite ore to be in contact with the polymer for a long time. ^{1}H n.m.r. was used to detect the change in tacticity of the polymer after adsorption. The changes in tacticity (triad fractions) of the PMMA remaining in solution after adsorption are given in *Table 1* and shown in *Figure 3*. From *Figure 3*, it is clear that the isotactic fraction (*mm*) disappears at low PMMA concentrations. This indicates that the albite ore adsorbs the isotactic form first, i.e. there is a selective adsorption process.

REFERENCES

1 Abd El-Hakim, A. A., Balazs, J. and Szanto, F. *Acta Phys. Chem. Szeged* 1980, **26**, 197
2 Howard, G. J. and Ma, C. *J. Coatings Technol.* 1979, **51**, 47
3 Rickert, S. E., Balik, C. M. and Hopfinger, G. A. J. *Adv. Colloid Interface Sci.* 1979, **11**, 149
4 Howard, G. J. and Barron, M. J. *J. Polym. Sci. A* 1974, **12**, 1269
5 Moustafa, A. B., Badran, A. S. and Abd El-Maboud Sakr, M. *Acta Polym.* 1986, **37**, 317
6 Moustafa, A. B., Badran, A. S. and Abd El-Hakim, A. A. *J. Appl. Polym. Sci.* 1985, **30**, 1963
7 Bischoff, J. and Desreux, V. *Bull. Soc. Chem. Belg.* 1952, **61**, 10
8 Voytsky, S. 'Colloid Chemistry', Mir, Moscow, 1978, p. 151
9 Inoue, Y., Nishioka, A. and Chujo, R. *Polym. J. Jpn* 1971, **4**, 535
10 Moustafa, A. B., Badran, A. S., Ebdon, J. R. and Hunt, B. J. *J. Polym. Sci.* 1982, **20**, 2903
11 Moustafa, A. B., Ebdon, J. R. and Hunt, J. *J. Appl. Polym. Sci.* 1978, **22**, 2471
12 Moustafa, A. B., Nosseir, M. H. and Nashed, N. E. *Angew. Makromol. Chem.* 1976, **52**, 71