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STABILITY OF TiO_2 DISPERSIONS AT DIFFERENT pH VALUES AND IN PRESENCE OF $AlCl_3$ ELECTROLYTE

By

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The stabilities of three different rutile (Bayer) samples, denoted RKB-2, Ru-2 and RSM-2, were investigated in aqueous medium. It was found that the RKB-2 sample was unstable between pH 5 and 9.5, Ru-2 was unstable at pH < 5, and RSM-2 was stable between pH 5 and 9. The effect of $AlCl_3$ electrolyte on the stabilities of these pigments was also studied. It was found that the RKB-2 sample lost its stability at electrolyte concentrations higher than 10 mmol dm^{-3}, Ru-2 was unstable at any electrolyte concentration, and RSM-2 was stable at all electrolyte concentrations used.

Introduction

The behaviour of aqueous colloidal dispersions of metal oxides such as titanium dioxide is important in connection with industrial coatings and is an interesting field of colloid science. The existence of hydroxyl groups on the surface of titanium dioxide has been substantiated. In principle, these arise from the interaction of water vapour with the surface planes. The comprehensive experiments of Boehm [1] demonstrated the amphoteric nature of the titanium dioxide surface. There are two types of OH groups: one type is bound to one Ti^{4+} site (terminal), and the other type to two such sites (bridged OH). These would be expected to exhibit different chemical behaviour. Boehm suggested that the bridged groups should be strongly polarized by the cations and therefore they are acidic in character, while the terminal OH could be predominantly basic and exchangeable with other anions. Levine and Smith [2] found that in aqueous medium the isoelectric point (iep) is equal to the point of zero charge (pzc) when there is no specific adsorption in the inner region of the electric double layer. When adsorption occurs at the titanium dioxide/solution interface, the pzc and iep move in opposite directions as the concentration of the supporting electrolyte is increased. There is also a difference between the hydrous and dehydrated oxides as concerns the pzc values determined by Johanson and Buchanan [3].

In practice, there are two types of titanium dioxide, anatase and rutile. The main difference between them, as indicated by the energy of conversion of anatase into rutile, is that rutile has less ionic character [4]. When anatase is heated to 800 °C, its surface charge changes in sign from positive to negative, which is ascribed to the change from anatase to rutile [5,6]. All OH groups on rutile have been shown to be reasonably strongly acidic, in contrast to the anatase surface [1].

The DLVO theory can be applied to a description of the stability of titanium dioxide dispersions in aqueous medium [1-6]. The coagulation behaviour of this oxide may be examined in terms of the electrokinetic or ζ-potential, or by observation of coagulation series.

Furlong and Parfitt [7] studied the effects of surface crystallinity, dehydration and specific adsorption of anions and cations on the electrokinetic behaviour of titanium dioxide. They found that not only these factors affected the electrokinetic behaviour, but also the pretreatment of the oxide (e.g. heating, washing) before the dispersing process.

In the work of Wiese and Healy [8-11], it was found that the finite solubility of some oxides causes modification of the dissimilar surfaces. This then leads to a great difference in the rheology and stability of the suspensions.

The main purpose of our study was to investigate the stability of some rutile samples, depending on pH and $AlCl_3$ electrolyte concentration.

Materials and Methods

Rutile titanium dioxide pigments denoted Ru-2, RKB-2 and RSM-2 were prepared by Bayer in commercial grade. The BET specific areas of the samples, determined by N_2 adsorption, were 7.8, 10.4 and 5.9 m^2/g, respectively. The chemical analysis data on the RKB-2 sample are given in Table I.

Table I

Chemical analysis of RKB-2 TiO_2

Oxide	SiO_2 %	Al_2O_3 %	TiO_2 %	ZnO %	Ignition loss %
Particle composition	2.8	2.2	93.5	0.04	1.6
Surface composition	16.6	47.1	36.4	-	

All chemicals used were of AR grade. Aluminium chloride was a product of Reachin (USSR). Potassium hydroxide and calcium chloride were from Reanal (Hungary). Lanthanum chloride was a Merck product.

The sedimentation measurements on titanium dioxide dispersions in aqueous medium (5 g/dm^3) were carried out in a series of test tubes. The pH of dispersions was adjusted from 2 to 11, using dilute KOH or HNO_3. Dispersions with different electrolyte concentrations up to 50 mmol $AlCl_3/dm^3$ were made by dilution.

Results

Effect of pH

The stabilities of different types of titanium dioxide were studied at different pH values. The features of the sedimentation and the shaking number required to redisperse the settled dispersion were determined. The results observed are given in Table II.

Table II

Effect of pH on stability of different TiO_2 dispersions

pH	RKB-2		RU-2		RSM-2	
	feature of settling	number of shakings	feature of settling	number of shakings	feature of settling	number of shakings
2	diffuse	44	sharp boundary	2	sharp boundary	2
3		70		2		2
4		28		2		2
5	sharp boundary	12		2	diffuse	26
6		10	diffuse	90		37
7		5		180		41
8		13		50		30
9		17		58		26
10	diffuse	24		50	sharp boundary	17
11		116		66		18

It may be seen that the dispersions of RKB-2 TiO_2 are stable in highly acidic and basic media, but they lose their stability between pH 5.0 and 9.5. Wiese and Healy [8] found that dispersions of TiO_2 are unstable only at pH values between 5.5 and 7.0. The difference between our results and those obtained by others [8] may be due to the fact that the surface of the TiO_2 particles is modified, and for this reason it is heterogeneous. It is seen from Table I that the surface of TiO_2 particles is formed mainly from Al_2O_3 and TiO_2 but the presence of SiO_2 on the surface is not negligible.

The stability region is wide, which may be attributed to the existence of AlOH, SiOH and TiOH amphoteric sites on the surface of this sample.

The pzc values for the different oxides [15] are as follows:

	pzc
γ-Al_2O_3	9.1
α-Al_2O_3	8.5
TiO_2	6.0
SiO_2	3.0

The charge of the amphoteric surface is positive at a pH lower than the pzc, and negative at a pH higher than the pzc. From examinations of the charge of each site which can exist on the surface of this TiO_2 sample in different pH ranges, it is found that the situation is as follows:

pH range	sign of charge		
	AlOH	TiOH	SiOH
< 3	+	+	+
3...6	+	+	-
6...9	+	-	-
> 9	-	-	-

It can be seen that both positive and negative charges exist on the surface of the particles between pH 5 and 9. Heterocoagulation between surface parts of opposite charge takes place in this pH range. The suspensions become unstable and settle with a sharp boundary. The results on the stability region were confirmed by the shaking number required to redisperse the sediment. Table II shows that this number is high at pH < 5 and higher at pH > 9, indicating the formation of caked sediments which can only form from stabilized particles. The stability behaviour is correlated with the number of shakings: the larger this number, the more stable the dispersion.

The Ru-2 TiO_2 suspensions were stable at pH ≥ 6, as can be seen in Table II, but they were unstable in acidic medium. The same results were obtained from the number of shakings for redispersion, which was small in acidic medium and large at pH ≥ 6.

The third TiO_2 sample (RSM-2) was found to be unstable in highly acidic and basic media, but it is stable for a short time at pH 5-9. This agrees with the shaking number results. The shaking number was found to be very small at pH < 5, somewhat higher at pH > 9, and large in the pH range 5-9.

These last two types of TiO_2 differ in behaviour from the first. An explanation of their behaviour is not possible, because the surface modification is unknown.

Effect of aluminium chloride

The stabilities of TiO_2 dispersions were studied in the presence of electrolyte. The results are shown in Table III.

The RKB-2 TiO_2 dispersion was unstable in aqueous medium, and the presence of a small amount of electrolyte (up to 1 mmol dm^{-3}) had no effect. The pH of the dispersion was in the instability region given in Table II. The larger the electrolyte amount added, the more stable the dispersion in the concentration region 2.5-5 mmol dm^{-3}, where the pH was in the stable region given in Table II. The dispersion was increasingly unstable with increase of the electrolyte

Table III

Effect of electrolyte on stability of TiO_2 dispersions

$AlCl_3$ mmol dm^{-3}	RKB-2			Ru-2			RSM-2		
	stability	no.of shakings	pH	stability	no.of shakings	pH	stability	no.of shakings	pH
-	unstable	5	7.0	unstable	3	6.6	stable	19	6.9
1		19	5.1		32	3.3		20	5.0
2	stable	72	4.0		32	2.8		400	4.8
5		44	3.9		32	2.7		220	4.2
10	unstable	90	3.7		30	2.7		98	4.1
15		85	3.5		30	2.6		24	4.0
20		92	3.1		20	2.4		20	3.9
50		100	2.9		20	2.2		20	3.8

concentration. This may be due to the coagulating effect of larger amounts of electrolyte.

The behaviour of the second sample (Ru-2) differed from that of the first one. It was unstable at all electrolyte concentrations. The pH of all dispersions was in the unstable pH region in Table II. This is also evident from the small number of shakings.

The last type of TiO_2 dispersion, which was made from the RSM-2 sample, was stable in the presence of all amounts of electrolyte added. The pH-s of the dispersion, 6.9-3.8, were roughly in the stability region in Table II. This may be due to the complex-forming effect of Al^{3+} ions. The abnormal behaviour of aluminium salts has likewise been reported by others [12-14].

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СТАБИЛЬНОСТЬ ДИСПЕРСИЙ TiO_2 ПРИ РАЗНЫХ pH СРЕДЫ И В ПРИСУТСТВИИ ЭЛЕКТРОЛИТА $AlCl_3$

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Изучена стабильность дисперсии трех различных образцов рутила (фирмы Bayer, RKB-2, Ru-2 и RSM-2) в водной среде. Было найдено, что дисперсии образцов RKB-2 неустойчива в интервале pH среды от 5 до 9.5, Ru-2 неустойчива при pH5, а RSM-2 стабильна между pH5 и 9. Найдено, что дисперсия образца RKB-2 теряет своего стабильность при концентрациях $AC1_3$ превышающих 10 ммоль/$см^3$, дисперсия образца Ru-2 нестабильна при любой концентрации электролита, а дисперсия образца RSM-2 стабильна при любых концентрациях $AlCl_3$.