

ULTRASONIC IRRADIATION OF AQUEOUS KMnO_4 SOLUTION

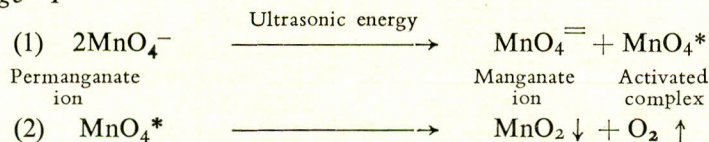
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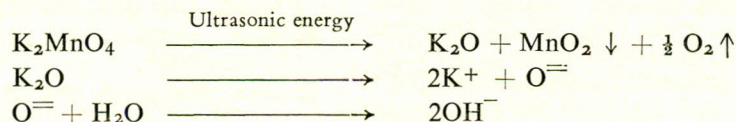
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Abstract. The study of the ultrasonic decomposition of 25.5 p.p.m. aqueous solution of KMnO_4 has been carried out at 2 MHz frequency and with an average energy intensity of 5.8 W/cm^2 at 32°C . The spectrophotometric measurements of optical density of the ultrasonic treated solutions have been performed at 580 nm and their pH values are recorded from time to time. The mechanism of decomposition of the aqueous KMnO_4 solution has been divided in two stages. The reaction proceeds as:

Stage I



Stage II



The black particles of manganese dioxide precipitated down and the remaining solution is alkaline with higher pH.

Potassium permanganate salt exists in intense purple needles appearing almost black. The crystalline geometry of the salt is bipyramidal rhombic and is stable in atmosphere after forming a thin layer of protecting film. Manganese in potassium permanganate salt is in its highest degree of oxidation state, namely +7, Mn^{VII} , and unstable particularly in the presence of reducing agents and is reduced easily to any one of the more stable oxidation state usually Mn^{II} and in doing so exhibit its powerful oxidising property.

The stability of KMnO_4 solution has been studied extensively by many workers¹⁻³ and shown to be intrinsically unstable. Nevertheless, its low cost and ease of availability enhance its usefulness as an oxidising agent in analytical chemistry. The decomposition of potassium permanganate solution depends to some extent on the concentration of the solution. Holluta¹ found that 0.004N solution is not decomposed by long boiling, more dilute solutions of the order of 0.002N are slowly decomposed by boiling, forming K_2MnO_4 and MnO_2 through intermediate formation of MnO_3 .

According to Hartley² the permanganates in dilute solution are hydrolysed and then decomposed into colloidal solution of $\text{MnO}(\text{OH})_2$ and free oxygen even in darkness. According to Skrabal and Preiss³ the reduction of KMnO_2 solution is a complex process involving a series of consecutive reactions between the

products of the reduction and between these products and permanganate itself resulting in the evolution of oxygen. The reduction in acidic solution involved a period of incubation during which a permanganate is reduced as follows in absence of reducing agent:



and the change of trivalent manganese by two side-reactions:



and



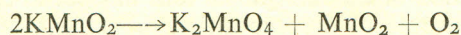
terminal period when



In the presence of reducing agent one or more stages may be accelerated. The self reduction of permanganate is very slow in neutral and feebly acidic solution in the absence of light.

The effects of irradiation of X-rays, α -rays and γ -rays on solid salt as well as in the solution state have been investigated by many workers⁴⁻⁶ and the

decomposition of the salt has been noticed in all the cases. The equation for both the thermal and radiolytic decomposition is of the type:



Ultrasonic decomposition of the aqueous potassium permanganate solution was studied by Bellarita, Leve and Cagnoli⁷ at 1 MHz with average energy intensity of 4.4 W/cm^2 . It was reported that 0.01N solution of KMnO_4 decomposed completely in 80 min. Study of the ultrasonic decomposition of the KMnO_4 solution has been carried out by the authors and the mechanism of KMnO_4 decomposition in the aqueous solution has been postulated.

Experimental

KMnO_4 solution of 50 p.p.m. was prepared by accurately weighing 0.05 g KMnO_4 (A.R. grade) and dissolving it in 1 litre of conductivity water. From this solution, 10 more solutions of lower dilution were prepared as recorded (Table 1). The absorbance of all these solutions were determined at wavelength 580 nm by using S.P. 600 Unicamp spectrophotometer. A calibration curve between absorbance (A) or optical density (D) and concentration (C) of the solution was drawn (Fig. 1). These plots of $A(C)$ and $D(C)$ of the experimental solutions show that in the range of dilution involved, absorbance and optical density are linear function of concentration and approximately $D=0.005A$, whilst at higher concentration this relation does not hold good. However, as the solution of KMnO_4 undergoes slow decomposition in the presence of traces of organic materials (that are likely to be present in the conductivity water), it cannot be stored for long time. The storable solution of KMnO_4 was prepared in the following way. An approximate solution of about 30 p.p.m. was prepared and boiled for about 15 min to oxidise the organic materials. The solution was then cooled to room temperature and filtered through sintered glass funnel. The concentration of the solution was then found from the calibration curve by determining the absorbance. The solution was stored in a stoppered-flask completely wrapped by carbon papers and kept in dark. The concentration was checked from time to time by the usual spectrophotometric measurements.

Ultrasonic generator (Mullard) was employed for the ultrasonic irradiation of the solutions at 2 MHz with an average energy intensity of approximately 5.8 W/cm^2 . The temperature of the sample was maintained at approximately 32°C by circulating cold water through the jacketted cylindrical copper container fitted on the transducer. The sample tube was a large size Pyrex glass test tube whose bottom had been flattened. 10 ml of 25.6 p.p.m. solution of KMnO_4 was taken each time in the sample tube for ultrasonic exposure. The sample tube was held vertical over the transducer crystal so as to make the acoustic impedance of the wave minimum. The height of the sample tube from the transducer crystal was kept constant in each treatment so that same amount of energy should always pass through the

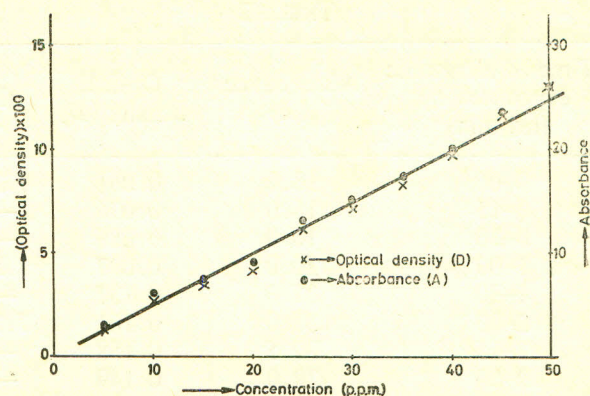


Fig. 1. The plots of $A(C)$ and $D(C)$.

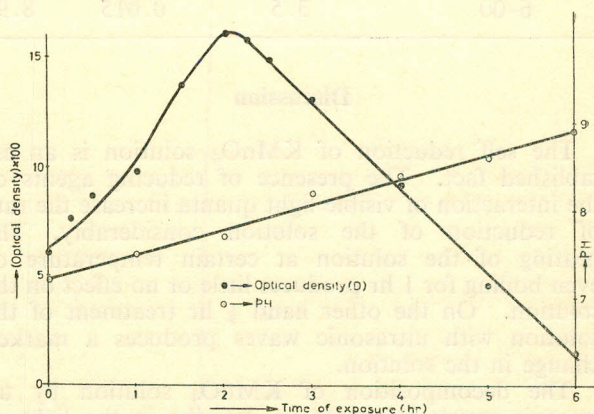


Fig. 2. The plots of $D(t)$ and $\text{pH}(t)$.

TABLE 1

Concentration (C) p.p.m.	Absorbance (A)	Optical density (D)
50	62.0	0.131
45	23.5	0.116
40	20.0	0.097
35	17.5	0.083
30	15.0	0.071
25	13.0	0.061
20	9.5	0.041
15	7.0	0.034
10	6.6	0.027
5	3.6	0.013

sample for given time of exposure. The absorbance of each of the treated sample was measured and the optical density was calculated (Table 2). The plot of the optical density against time of ultrasonic exposure $D(t)$ is shown in Fig. 2.

The pH of the ultrasonic treated solution was measured by using Cambridge pH meter, the plot of $\text{pH}(t)$ is shown in Fig. 2.

TABLE 2

Time of ultrasonic exposure (<i>t</i>) (hr, min)	Absorbance (<i>A</i>)	Optical density (<i>D</i>)	pH
0-00	13.0	0.061	7.2
0-15	16.0	0.076	—
0-30	18.0	0.086	—
1-00	20.0	0.097	7.5
1-30	27.0	0.137	—
2-00	31.0	0.161	7.7
2-15	30.5	0.158	—
2-30	29.0	0.149	—
3-00	26.0	0.131	8.2
4.00	19.0	0.092	8.4
5-00	10.0	0.052	8.6
6-00	3.5	0.015	8.9

Discussion

The self reduction of KMnO_4 solution is an established fact. The presence of reducing agents or the interaction of visible light quanta increase the rate of reduction of the solution considerably. The heating of the solution at certain temperature or even boiling for 1 hr produces little or no effect on the solution. On the other hand $\frac{1}{2}$ hr treatment of the solution with ultrasonic waves produces a marked change in the solution.

The decomposition of KMnO_4 solution by ultrasonic waves is sought to describe in the light of colour change and the variation of pH of the solution. Figure 2 shows that with the time of exposure the optical density of the solution increases first and reaches maximum at about 2 hr of treatment and then it begins to decrease with progressive decolorization of the solution. After 6 hr treatment the solution is practically colourless. The change of colour and the total decomposition of the salt in aqueous solution may be described in two stages: In the first stage purple permanganate ion reduces to green manganate ion, the process involves the transfer of an electron between the anions. The reaction proceeds:

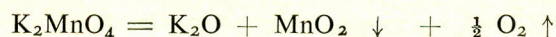


MnO_4^* may be considered as the activated complex containing manganese in the unusual oxidation state of Mn(VIII). The activation energy needed for the transition is provided by the ultrasonics. This complex then breaks



The increase in the optical density can be explained in the light of the ionic theory of colour; the potassium ions are colourless whilst the permanganate ions are purple and the manganate ions are green. The overall colour of the solution is the joint effect of the colours of the latter two ions. As the optical density increases first, it is inferred that the manganate ions absorb greater percentage of the light. The maximum value of the optical density of the solution thus points

out the maximum concentration of the manganate ions in the solution. In the stage II, the optical density starts decreasing which shows that the concentration of the manganate ions has been decreasing and the rate of decomposition of manganate ions is greater than that by which they are forming from the permanganate ions. The decomposition of the manganate ions may be taking place according to the equation:



The plot of pH of the exposed solution and the time of exposure in Fig. 2 shows that the pH value of the solution increases from the start to the end of the ultrasonic treatment. The hydrolysis of the salt is thus taking place from the first stage and our categorisation of the whole process in two stages is thus contradicted. However, the main difference between the two stages can well be explained in term of the rate of change of concentration of the manganate ion irrespective of its decomposition. In the first stage the rate of formation of manganate ion is high but the rate of decomposition is slow, resulting the detected rise of concentration, and the reverse is true for the second stage.

At the peak of the optical density the manganate ions are thus at highest concentrations and then their concentration falls due to higher rate of decomposition as compared to the rate of their formation. The solution is gradually decolourised due to the decrease in the concentration of manganate ions, causing the decrease in the optical density of the solution. Equilibrium is never attained due to the constant removal of manganate ions and more and more of the permanganate ions are being decomposed until the end of the 6 hr treatment; when the whole of the permanganate ions as well as the manganate ions have been decomposed. The overall reaction may be postulated:



The potential diagram for the reduction-oxidation of manganese in acid or neutral solution:



The diagram shows that the green manganates ion $\text{MnO}_4^{=}$ disproportionates into the permanganate ion, MnO_4^- and MnO_2 :



The preceding equation indicates that as the H^+ ions drive the reaction to the right (disproportionation), the OH^- ions drive the reaction to the left (reduction). The manganates ions are, therefore, stable in the basic solution having no tendency to disproportionate, giving back the permanganate ions. It is the ultrasonic energy which brings about the further reduction of the manganate ions in the basic solution. The course of the reaction may follow the process postulated by Skrabal and Preiss.³

Oxygen is given off, black particles of manganese dioxide precipitate down and the remaining colourless solution contains only the K^+ and OH^- ions. The increased concentration of OH^- ions is the sole cause of the alkaline characteristic of the ultrasonic treated solution.

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