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# SALT CATALYSED HETEROGENEOUS DILUTE ACID HYDROLYSIS OF CELLULOSE: EFFECT OF NATURE OF COUNTER ION

Mark Fungayi Zaranyika and Abisha Masuka
Chemistry Department, University of Zimbabwe
P.O. Box MP 167, Mount Pleasant, Zimbabwe

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**ABSTRACT.** The effect of nature of counter ion on the rate of the heterogeneous dilute acid hydrolysis of cellulose was investigated for the $Cl^-$, $Br^-$, $NO_3^-$ and $SO_4^{2-}$ ions. For the hydrolysis of the difficultly accessible portion of cellulose, the rate of hydrolysis is found to be a linear function of the mobility of the counter ion, while for the hydrolysis of the "amorphous" regions the data presented suggests that the effect of the counter ion in these regions is also influenced by the "structure making" and "structure breaking" properties of the counter ion.

## INTRODUCTION

A positive salt effect on the heterogeneous dilute acid hydrolysis of cellulose has been demonstrated for both "amorphous" and "crystalline" regions of cellulose [1]. The effect is explained on the basis of a kinetic model based on Donnan's theory of membrane equilibria. For a monobasic acid HX, in the presence of an electrolyte MX, the rate, $V_c$, of the heterogeneous dilute acid hydrolysis of the difficultly accessible region of cellulose was shown to follow equation 1.

$$V_c = \left(\frac{dp}{dt}\right)_c = K_c'' D [H^+]_s [X^-]_s \qquad 1$$

where D is the diffusion coefficient of the added salt MX in dilute aqueous solution, $K_c''$ is a "form" factor relating D to $D^1$, the diffusion coefficient of the added electrolyte in the cellulose phase of the heterogeneous system, p denotes products and the subscripts c and s denote the crystalline region of cellulose and solution phase of the system respectively. The relationship between D and $D_o$, the Nernst limiting value of the diffusion coefficient, has been described previously [2-4]. $D_o$ is a function of the absolute mobilities of the electrolyte ions. These ionic mobilities are determined by the effective sizes of, and charges on, the ions. The value of $V_c$ in eqn 1 will therefore depend on the nature of the electrolyte ions. The dependence of $V_c$ on the nature of the metal co-ion was investigated previously [5]. The aim of the present work was to investigate the effect of nature of counter ion, X, on $V_c$.

The counter ions investigated include $Cl^-$, $Br^-$, $NO_3^-$ and $SO_4^{2-}$. In all cases the same metal co-ion, $Na^+$, was used. $V_c$ was determined for each counter ion and plotted as a function of the mobility of the ion.

## EXPERIMENTAL

*Materials.* The following were used: Cellulose - microcrystalline, for column chromatography, A.R. grade, average particle size 10μ (Macherey Nagel and

Co. 300); sodium bromide, sodium nitrate, sodium sulphate, hydrochloric acid, hydrogen bromide, nitric acid and sulphuric acid, - A.R. Grade; 95% ethanol, diethyl ether - C.P. Grade.

*Equipment.* Waterbath, model 420 SE (Precise Instruments, Zimbabwe); Oven, model MLW WS 100 type 117-0100 (VEB MLW MEDIZINISCHE) and water driven magnetic stirrers were used.

*Procedure.* The experimental procedures followed were described previously [1]. The experiments were run in duplicate and the average percentage loss-in-weight figures obtained are plotted against time in Fig. 1. The rate of hydrolysis of the difficultly accessible portion, represented by $V_c$, the slope of the linear (or latter) of the hydrolysis curve (Table 1), is plotted against the mobility of the counter ion in Fig. 2.

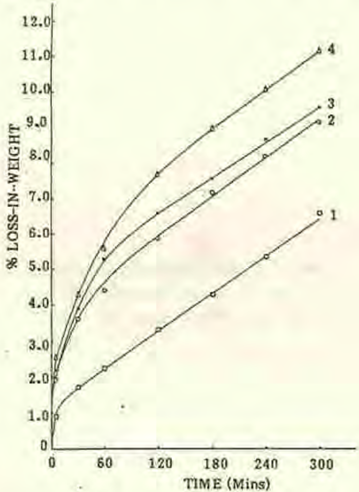

Fig. 1. Percentage loss-in-weight as a function of time for different counter ions as follows: (1) $SO_4^{2-}$, (2) $Cl^-$ (3) $NO_3^-$ and (4) $Br^-$ (present as the Na salt at 0.09M and the acid at 1.3M (HBr, HCl, $HNO_3$) and 0.65M ($H_2SO_4$)).

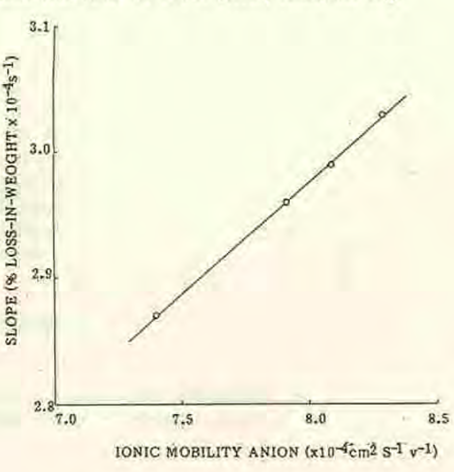

Fig. 2. Graph of the slope of the latter portion of the hydrolysis curve (from Fig. 1) versus mobility of the counter ion.

Table 1. Slope of the latter portion of the hydrolysis curve in Fig. 1 and ionic mobilities of the counter ion*.

| | $NO_3^-$ | $Cl^-$ | $Br^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|
| Slope (% Loss-in-weight-$S^{-1}$ x $10^{-4}$) | 2.87 | 2.96 | 2.99 | 3.03 |
| Ionic Mobility of counter ion (x $10^4$ $cm^2$ $S^{-1}$ $v^{-1}$) | 7.40 | 7.91 | 8.08 | 8.29 |

*Source* CRC Handbook of Chemistry and Physics, 60th Ed. (1979-1980) CRC Pres, page F51.

## RESULTS AND DISCUSSION

For the counter ions investigated it is apparent from Fig. 2 that $V_c$ is a linear function of the mobility of the counter ion thus confirming the validity of equation 1 and the kinetic model proposed in reference 1.

From Fig. 1 it is apparent that the $SO_4^{2-}$ ion had the lowest effect on the overall yield of hydrolysis, especially the "amorphous" portion of the cellulose. This is attributed in part to protonation of the sulphate ion with the resultant reduction in the concentration of the hydroxonium ion which is the hydrolysing reagent:

$$H_3O^+ + SO_4^{2-} = H_2O + HSO_4^- \quad (pKa = 1.92)$$

However as this would only result in a 6.4% reduction in $[H_3O^+]$, the much lower effect for the $SO_4^{2-}$ ion relative to the other counter ions cannot be entirely attributed to this effect.

Table 1 shows that the $SO_4^{2-}$ leads to the highest $V_c$ value, yet it has the least positive salt effect on the "amorphous" region of the cellulose. A possible explanation of this behaviour of the sulphate ion lies in its "structure making" property on water as discussed below.

The "amorphous" regions of cellulose can be pictured as regions which have sorbed water resulting in intercrystalline swelling so that H-bonds between cellulose molecules are ruptured and replaced by H-bonds between cellulose molecules and water [6]. From the crystalline region outwards the water molecules sorbed become progressively more loosely bound to the cellulose in the "amorphous" region. In spite of this fact these water molecules remain bound in the cellulosic material even in the dry state and are described as "bound" or "non-freezing" water [6]. A notable feature of these swollen regions of cellulose is that even in those regions in which the cellulose is associated with more loosely bound water molecules, the intramolecular H-bonds between the hydroxyls on C-2 and C-6 and OH-3 and the pyranose ring oxygen remain intact. This shows that the "amorphous" regions of cellulose maintain their crystalline nature, albeit in a swollen state.

Relatively small ions, e.g. $F^-$, and multivalent anions such as $SO_4^{2-}$ are known to increase the viscosity of water and are said to have net "structure making" effect on the water. This results from their high electric fields which, not only polarise, immobilise and electrostrict water molecules in the primary hydration sphere, but also induce additional order (loss of entropy) beyond the first hydration shell (secondary and long range hydration) [7]. The presence of $SO_4^{2-}$ ions during the heterogeneous dilute acid hydrolysis of cellulose will thus favour maintenance of the crystalline nature of the "amorphous" regions as described above. Large monovalent ions, on the other hand, generally exert a nett "structure breaking" effect on water because their relatively weak electrostatic fields can only immobilise water molecules of only the first hydration layer. Thus ions such as $Cl^-$, $Br^-$, $NO_3^-$ decrease the viscosity of water, and, during the heterogeneous hydrolysis of cellulose, should favour the rapid disintegration of the crystalline nature of the "amorphous" regions of cellulose.

## CONCLUSIONS

From the foregoing discussion we conclude that the effect of nature of counter ion on the rate of hydrolysis of cellulose is a function of the mobility of the counter ion, although its nett salt effect on the rate of hydrolysis of the "amorphous" regions depends on the "structure making" and "structure breaking" properties of the counter ion.

## ACKNOWLEDGEMENT

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