Heats of Immersion of Uranium Oxides in \textit{n}-Nitropropane III.\textsuperscript{*}

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Heats of wetting of uranium oxides with different O/U ratios were measured in \textit{n}-nitropropane and these heats were found to decrease with increasing oxygen content of the oxides. This behaviour was compared with the opposite tendency in water. It was concluded that a definite amount of $\text{UO}_3$ is relatively easily formed on the surface of $\text{UO}_2$ at lower temperatures.

INTRODUCTION

Recently reported results on the heats of wetting uranium oxides in water\textsuperscript{1,2} showed an increase of immersion heats with increasing O/U ratio of uranium oxides. It was further observed that annealed samples gave generally lower values and that the increase of heat values of annealed samples when approaching $\text{U}_3\text{O}_8$ composition was much less marked\textsuperscript{2}. Two possible explanations for the above observation were proposed: (a) increasing strain in the surface layers of the oxides due to the difference in density and (b) the presence of small amounts of uranium trioxide on the surface of the oxidized samples. It was the aim of our further investigations to check the last assumption.

EXPERIMENTAL

The immersion heats of both uranium oxide samples as prepared (unannealed) and annealed, were measured calorimetrically in \textit{n}-nitropropane at 25°C. The uranium oxide samples were carefully oxidized at low temperature to cover the whole range of O/U ratios from 2.00 to 2.67. The methods of preparation of the samples and the results of X-ray analysis were the same as described in reference\textsuperscript{2}.

The X-ray structures were in line with known data for uranium oxides\textsuperscript{3}. The samples were examined for infrared spectra in the 2 to 15 \textmu{} region, where the characteristic spectra of $\text{UO}_3$ and $\text{U}_3\text{O}_8$ were expected\textsuperscript{4}. Whereas the presence of $\text{U}_3\text{O}_8$ was easily detected in the samples with higher O/U ratio, the evidence for the presence of $\text{UO}_3$ was not conclusive.

The calorimeter and the methods of surface area and O/U ratio determinations were described in reference 1. The \textit{n}-nitropropane was supplied by L. Light Co., Cornbrook, England. Since the stoichiometric $\text{UO}_2$ (i.e. the $\text{UO}_2$ powder which was not exposed to air after the preparation from ADU in a stream of hydrogen gas and had a composition of $\text{UO}_2 (0.00\pm 0.01)$) was oxidized rapidly by the oxygen dissolved in organic liquid, the nitropropane had to be distilled in an argon atmosphere before the measurements were carried out. The tendency towards oxidation was much higher than in water and the argon atmosphere had to be maintained in the calorimeter during the measurements.

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RESULTS

The measured heat effects were expressed on the specific area basis and plotted vs. O/U ratio in Fig. 1. A single straight line obtained by the least squares method was drawn through the experimental points. However, the points might also be connected by two lines with a kink at UO$_2$. Our choice is based on the lowest standard deviation. The curve from previous investigations relating to heat effects in water was added for comparison. In addition, the heat values of UO$_3$ were determined in n-nitropropane and water. The measured values were 553 erg/cm$^2$ and 2470 erg/cm$^2$, respectively. The value in water is felt to be still low since the effect was not merely wetting, but hydration. The thermal equilibration was slow, probably due to the formation of a surface shell of hydrate which impeded further reaction.

DISCUSSION

As shown in Fig. 1, the heat of wetting effect of uranium dioxide in n-nitropropane is considerably higher than in water, which is a consequence of the higher dipole moment of the organic liquid (n-nitropropane 3.57 D, water 1.87 D).

It is further seen in Fig. 1 that the heat of wetting values in the organic liquid are slightly decreasing with increasing oxygen content of the uranium oxides. The effect is in accordance with De Boer's explanation of the influence of the density of substrate structure on the heat of wetting since the densities of uranium oxides are decreasing from 10.96 g/ccm for UO$_2$ to 8.3 g/ccm for U$_3$O$_8$. The similarity of the heats of wetting of U$_3$O$_8$ and UO$_3$ is again in accordance with this explanation, as the densities are nearly equal. The same explanation was proposed in connection with the observed heat of wetting effects of SiO$_2$.

The bond type of the substrate structure is another factor which could influence the wetting results. On the basis of available information it has been concluded that the lattice forces in uranium dioxide are largely ionic in
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character, whereas the higher oxides of uranium, U₃O₈ and UO₃, show a much greater tendency towards covalent bonding⁸. Since the heat effects due to ion dipole interaction are generally found to be higher than the effects based on residual Van der Waals forces, this may constitute another cause of the lower heat values obtained when wetting the oxides with higher oxygen content.

Accepting the above offered explanation for the decreasing tendency of the heat of wetting as a general one, the question arises why the effects in water show the opposite character. The increasing immersional heats with increasing oxygen content must be ascribed to some specific interaction of uranium oxides with water. Since neither UO₂ nor U₃O₈ react with water under normal conditions we ascribe the effect to UO₃. The presence of some UO₃ on the surface of the uranium oxide samples with higher oxygen content would not influence significantly the wetting heats in nitropropane since the values of U₃O₈ and UO₃ are comparable (648 and 553 erg/cm² resp.). The opposite is true for the experiments with water as wetting agent. The effect of hydration (2470 erg/cm² for UO₃) is several times larger than the effect of normal wetting, and even so small amounts of UO₃ in the outermost surface layer that they are undetectable by X-ray or infrared technique can greatly influence the results. The fact that essentially the same results were obtained with annealed and with unannealed samples in nitropropane while widely different results were obtained with these two samples in water, are also evidence in favour of the invoked role of UO₃.

It is generally agreed that the oxidation of UO₂ proceeds until the composition U₃O₈ is reached. UO₃ is not obtained easily from the lower oxides and the successful preparation requires increased oxygen pressure⁴. Up to some 700°C the formation of UO₃ is thermodynamically preferable and the general observation that the oxidation of UO₂ leads only to the formation of U₃O₈ was explained by kinetic reasons⁹. Lebau, as quoted by Katz¹⁰ concluded in his early work that U₃O₈ prepared below red heat might contain some UO₃. Boulle and coworkers¹¹ prepared crystalline UO₂ which can be oxidized directly to UO₃ at low temperature. On one of the active oxide samples with a specific area of 30 m²/g and an equilibrium composition approaching UO₂·⁵ Hoekstra found an infrared spectrum characteristic of amorphous UO₃. Belbeoch and coworkers¹² and Jakeš and Sedlakova¹³ also observed that UO₃ is formed at low temperature by oxidation of UO₂ having a large surface area. The self-consistency in our interpretation of the presented experimental evidence here and earlier¹ may be taken as strongly suggestive of UO₃ formation in the outermost layers of UO₂ at low temperature. Indeed, it would be the first evidence of UO₃ formation on a surface of medium active UO₂, since the increase of heat effects was observed even on powders with specific surfaces of 2 m²/g. This would imply that UO₃ can form relatively easily on the surface of oxidized UO₂ particles.

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IZVLEČEK

Omakalne toplote uranovih oksidov v n-nitropropanu (III)

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Omakalne toplote uranovih oksidov z različno vsebnostjo kisika so bile izerjene v n-nitropropanu. Vrednosti padajo z narastejo vsebnosti kisika. Na podlagi primerjave z nasprotno tendenco pri omakanju v vodi zaključujemo, da na površini uranovega dioksida pri oksidaciji pri nizki temperaturi nastane določena množina uranovega trioksida.

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