Note

DSC dehydration peaks and solubility products of Al(OH)₃

DAVID T. Y. CHEN

*Department of Chemistry, The Chinese University of Hong Kong,
Shatin (Hong Kong)*

(Received 26 August 1974)

In a recent paper[1], it was found that the solubility products of aluminum hydroxide in systems containing different alkali metal ions were different. The solubility product was much lower in the system containing lithium ion than in systems containing other metal ions. The reason why the solubility product of aluminum hydroxide is lowered by the presence of lithium ion is still not clear. The ionization process involves breaking of all the Al–OH linkages while the dehydration process involves breaking of half of the Al–OH linkages. We would, therefore, expect a correlation between the solubility products of the aluminum hydroxide contaminated with different metal ions and their dehydration temperatures. This has been investigated in the present work.

EXPERIMENTAL

20-ml samples of 0.25 M $AlCl_3$ solution were separately mixed with solutions containing 20 mmoles of Li, Na, K, NH_4^+ and Ca chlorides. Equivalent amounts of 0.1 M solutions of the respective hydroxides were slowly added to precipitate all the aluminum ions and the mixtures were diluted to a final volume of 200 ml. The mixtures were allowed to stand for one week with occasional shaking. The aluminum hydroxide precipitates were separated from the mother liquid by centrifugation. They were dried, without further washing, in a vacuum oven at 80°C and then pulverized to pass through a 100-mesh sieve. The powdered materials thus obtained were aluminum hydroxide contaminated with different alkali metal chlorides. Approximately 20 mg of the samples were weighed out in aluminum pans and covered with lids, without being pressed. DSC curves were run using a Rigaku Desk-Top differential scanning calorimeter under normal atmosphere. α-Al_2O_3 was used as the reference sample in each case. The heating rate was 10°C min^{-1} and the DSC range was ± 8 mcal sec^{-1}. Chart speed was 4 mm min^{-1}; temperature full scale was 30 mV.

RESULTS AND DISCUSSION

The DSC curves of the five samples are shown in Figs. 1–5. In all these figures, one division in the abscissa approximately equals six min; one division in the ordinate (i.e., 3 mV) approximately equals 73°C. There are two main endothermic peaks in

102
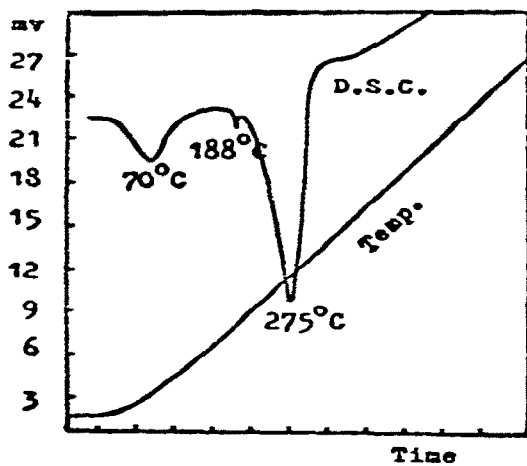
Fig. 1. DSC curve of Al(OH)₃ contaminated with NH₄Cl.
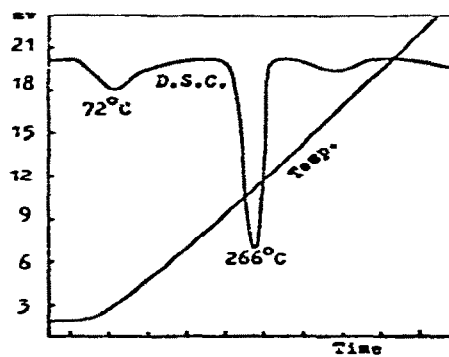
Fig. 2. DSC curve of Al(OH)₃ contaminated with NaCl.
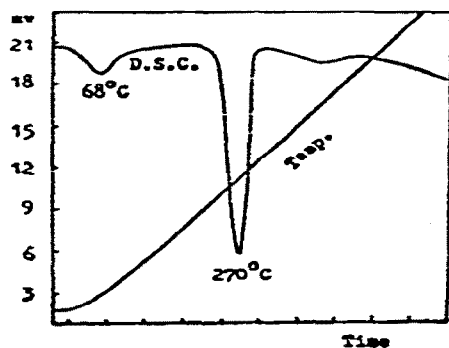
Fig. 3. DSC curve of Al(OH)₃ contaminated with KCl.
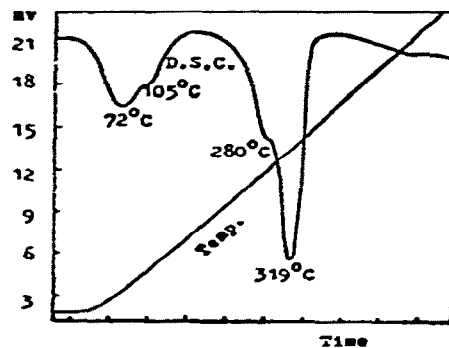
Fig. 4. DSC curve of Al(OH)₃ contaminated with LiCl.
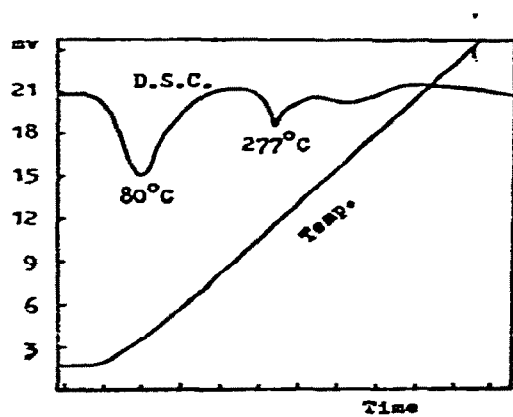
Fig. 5. DSC curve of Al(OH)₃ contaminated with CaCl₂.

each case. The first small one at about 70°C represents escape of the absorbed moisture, while the second bigger one above 250°C represents the dehydration reaction. There is a very small peak at 188°C in the $Al(OH)_3$–NH_4Cl sample. The DTA curve of NH_4Cl shows a crystalline transition peak at 191°C (ref. 2). The very small peak in the present case could therefore be attributed to the transition of NH_4Cl to its crystal form. The curve of the $Al(OH)_3$–$LiCl$ sample is somewhat different from the others; it has two humps in both the first and second peak, one at 105°C and the other at 280°C. The DTA curve of $LiCl$ shows two crystalline transition peaks at 88 and 165°C (ref. 2). The temperatures of the endothermic peaks of different samples together with the pK_{sp} values[1] are listed in Table 1. The temperature of the

TABLE 1

TEMPERATURE OF DSC PEAKS AND pK_{sp} OF $Al(OH)_3$ IN DIFFERENT SYSTEMS

System	NH_4^+	K^+	Na^+	Li^+	Ca^{2+}
t_1 (°C)	70	68	72	72	80
t_2 (°C)	275	270	266	319	277
pK_{sp}	30.55	30.36	30.75	33.15	31.00

first peak does not vary much from sample to sample, although in the $Al(OH)_3$–$CaCl_2$ sample, this temperature is about 10°C higher. This can be explained as due to the higher affinity of $CaCl_2$ for free water. The temperature of the second peak seems to have some correlation with the solubility product; this is shown in Fig. 6. The correlation coefficient is calculated to be 0.95 and the student's t value is 5.27. These figures indicate that there is significant correlation between the second DSC peak
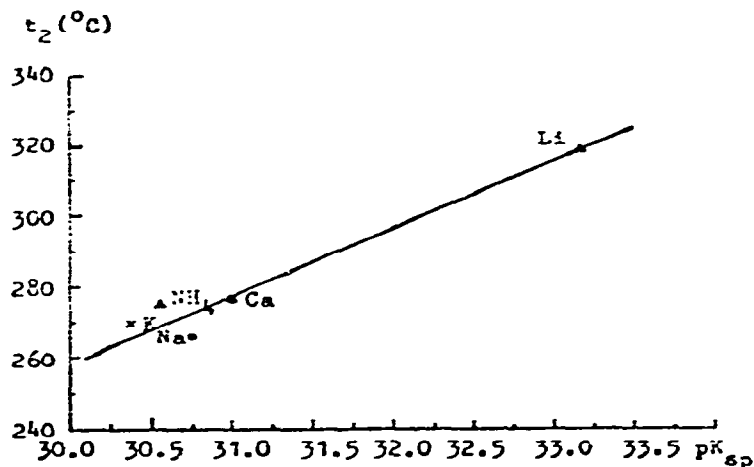

Fig. 6. Correlation between pK_{sp} and the second peak temperature of the DSC curve.

temperature and the pK_{sp} of $Al(OH)_3$ contaminated with different cations. This correlation could be explained as follows. Dehydration of a metal hydroxide involves two stages[3]. The first stage consists in a statistical rearrangement of the protons around the hydroxyl groups by a tunnelling mechanism to form water, thereby breaking the M–OH bonds. The second stage involves the diffusion and desorption of water molecules. Dissolution of an hydroxide to form metal and hydroxyl ions also involves breaking of the M–OH bond. In addition, it consists of ion hydration. Since there are several factors involved in the two processes, a correlation between solubility products and dehydration peaks for various metal hydroxides is, usually, not to be expected. The situation is simpler in the present case. There is only one kind of hydroxide, $Al(OH)_3$, which is, however, contaminated with different metal chlorides. These contaminants apparently do not affect the diffusion and desorption of water molecules, neither would they influence the hydration of the aluminum and hydroxyl ions; but they certainly affect the strength of the Al–OH bond. Judging from the electronegativities of aluminum and oxygen, the Al–OH bond has an ionic character of about sixty percent. The mechanism of how these contaminants affect the Al–OH bond is not clear. Nevertheless, it explains the parallel behavior of pK_{sp} and the dehydration peak. Assuming that in any $Al(OH)_3$ sample, the Al–OH bond is stronger, then, it will be more difficult to remove the hydroxyl ions from the aluminum ion either by ionization or by dehydration; therefore this sample would have both higher pK_{sp} and t_2 values. The dehydration temperature for the $Al(OH)_3$–LiCl sample is much higher than for other samples; this is in accord with its high pK_{sp} value. Lithium ion, in some way, strengthens the Al–OH bond; this makes both the dehydration and ionization process difficult, resulting in a low solubility and high dehydration temperature. The two humps in the DSC curve of the $Al(OH)_3$–LiCl sample are probably due to the transition of LiCl crystal forms; these transition temperatures are all higher than their original transition temperatures because of the interaction between $Al(OH)_3$ and LiCl.

The DTA curves for alumina gels have been investigated by Mackenzie et al.[4]. They found a fairly broad peak at about 400–550°C when the alumina gels were freshly prepared by adding different alkali hydroxides to solutions of $AlCl_3$. They termed it "pseudoboehmite peak". After aging, the pseudoboehmite crystallizes to α-$Al(OH)_3$, which has a sharper peak at a temperature slightly higher than 300°C. In the present case all the peaks are fairly sharp indicating that the materials are largely α-$Al(OH)_3$.

REFERENCES

1 D. T. Y. Chen, Can. J. Chem., 51 (1973) 3528.
2 The Sadtler Standard Spectra for DTA, Vol. 6, Sadtler Research Laboratories, Inc., Philadelphia, 1968.
3 F. Freund and H. Gentsch, Ber. Deut. Keram. Ges., 44 (2) (1967) 51.
4 R. C. Mackenzie, Differential Thermal Analysis, Vol. 1, Academic Press, London, 1970, pp. 284–285, and the references therein.