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# Volume Properties of the Hydrolyzed Aluminum Species

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**Abstract**—The composition of polynuclear aluminum hydroxo complexes, their hydrolysis constants, and the volume changes due to complex formation have been determined by CPESSP software analysis of the potentiometry and dilatometry data.

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Hydrolysis is probably the most common chemical reaction in solutions, typical of all metal ions except for alkali ones [1]. Hydrolysis determines the solution composition in terms of the concentration of various homo- and polynuclear hydroxo complexes. Aluminum is known for the extreme diversity of such species.

This work was aimed to study the forced hydrolysis in the $Al(NO_3)_3$–($H^+$)–($OH^-$)–$H_2O$ system by means of potentiometry, dilatometry, and computer processing of the obtained data in order to characterize the volume properties of the hydrolysis products.

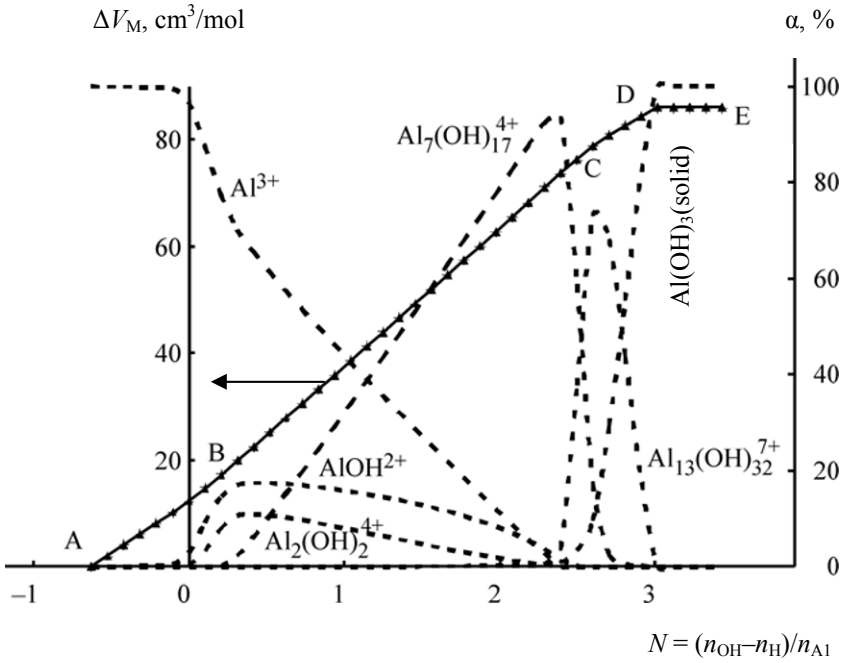
The volume properties may serve as sensitive indicator of the chemical reaction occurring in the studied system. There are two possible approaches to detection of the volume changes: indirect method, based on the recalculation of the pycnometry data, and the direct one, using the precision dilatometer. The direct dilatometry titration (see [2, 3] for details) allows monitoring continuous volume change in the course of a single experiment. As a result, the isotherm of volume changes as a function of the components concentration is obtained. So far, most of dilatometry titration experimental results have been presented without any mathematical processing. Moreover, the data on molar volume changes upon hydroxo complexes formation are absent in the literature.

In this work, the aluminum ions hydrolysis was studied by the dilatometry titration of the mixture of 0.1 mol/L of $Al(NO_3)_3$ and 0.06 mol/L of $HNO_3$ with 0.31 mol/L NaOH solution at ionic strength of 1 mol/L ($NaNO_3$) and 25.00°C. The procedure was described in detail in [3].

The experimental data were plotted as the volume change with respect to 1 mol of the substance $\Delta V_M$ as a function of the OH/Al molar ratio *N*. The so obtained isotherm consisted of several linear parts AB, BC, CD, and DE (see the Figure) characterized by a different rate of the molar volume change.

The first part of the curve, AB, reflected the molar volume change due to neutralization reaction: $H^+ + OH^- = H_2O$. This was supported by the volume change of 19.78 $cm^3$/mol, coinciding with the previously reported value in the case of ($HNO_3$–1 mol/L $NaNO_3$) + (NaOH–1 mol/L $NaNO_3$) system, $\Delta V_M$ 19.99 $cm^3$/mol [4]. The observed $\Delta V_M$ value resulted from the volume of water formed (18.07 $cm^3$/mol) and the effect of electric deelectrostriction due to the dehydration of the interacting $H^+$ and $OH^-$ ions.

In the course of further titration, at the BC range (*N* of 0–2.6) the new positive volume effect was found ($\Delta V_M$ = 25.9 $cm^3$/mol), stronger than that of neutralization reaction.




The dilatometry titration curve $\Delta V_M = f(N)$ [(triangles) experimental data; (solid line) calculated data] and the composition diagram (from potentiometric titration) [(dashed lines) molar fractions of the respective hydroxo complexes in the solution, α].

The CD linear part of the curve ($N$ = 2.6) corresponded to the start of aluminum hydroxide formation; at that stage the volume effect $\Delta V_M$ was 17.2 cm$^3$/mol).

The D point ($N$ = 3) corresponded to the completion of aluminum hydroxide formation. At $N$ > 3, no noticeable volume changes were detected, thus revealing the absence of any chemical interaction.

From the potentiometric titration data, applying the nonlinear least squares-method implemented in the CPESSP software [5], the hydroxo complexes present in the solution and the corresponding hydrolysis constants were determined: $AlOH^{2+}$ (log$K$ –4.12±0.09), $Al_2(OH)_2^{4+}$ (log$\beta_{2,2}$ –10.78±0.15), $Al_7(OH)_{17}^{4+}$ (log$\beta_{7,17}$ –57.24±0.25), $Al_{13}(OH)_{32}^{7+}$ (log$\beta_{13,32}$ –109.27±0.37), and $Al(OH)_3$ (p$K_s$ 30.34±0.15).

The constants so obtained were used in the processing dilatometry data and plotting the diagrams of the complex forms composition.

The dilatometry data were processed by the nonlinear least squares data using the CPESSP software. The best fit of the calculated data to the experimental values was achieved with the following set of parameters, $\Delta V_{calc}$ (cm$^3$/mol): 10.36 ($AlOH^{2+}$), 10.61 [$Al_2(OH)_2^{4+}$], 27.35 [$Al_7(OH)_{17}^{4+}$], 29.71 [$Al_{13}(OH)_{32}^{7+}$], and 29.54 [$Al(OH)_3$].

The analysis of the complexes composition diagram provided the understanding of the positions of the characteristic points in the dilatometry isotherm. As mentioned above, the AB line reflected the neutralization of excess acid. The appearance of the first portions of hydroxo forms $AlOH^{2+}$ and $Al_2(OH)_2^{4+}$ indicated the onset of hydrolysis reflected in the slope change at point B. The BC part of the curve corresponded to the formation of mononuclear and polynuclear complexes with $\Delta V_M$ of 25.9 cm$^3$/mol. The new polymeric complex, $Al_{13}(OH)_{32}^{7+}$, appeared in this stage, and the C point reflected the completion of the prevailing complex formation.

The D point corresponded to the completed formation of aluminum hydroxide; indeed, from the composition diagram, its fraction was 100% in the DE stage.

This analysis showed that the two methods differing in the origin and sensitivity (potentiometry

and dilatometry) led to the well consistent conclusions on the hydrolytic behavior of aluminum-containing ions in aqueous solutions.

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