THERMOGRAVIMETRIC STUDIES OF QUATERNARY SYSTEMS INVOLVING SALICYLIC ACID, SODIUM SALICYLATE, SODIUM CARBONATE AND SODIUM HYDROGEN CARBONATE, PART III*

A. Radecki and M. Wesolowski

Institute of Chemistry and Analytics, Medical Academy, 80-416 Gdansk, Poland

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The thermal decompositions of quaternary systems comprising salicylic acid, sodium salicylate, disodium salicylate sesquihydrate, sodium carbonate and sodium hydrogen carbonate were investigated using thermogravimetry and differential thermal analysis. A possibility was shown of analyzing quaternary systems comprising three or four interacting components. Use can be made of the results of these investigations in the control of the course and degree of conversion of reagents in commercial-scale production of sodium salicylate as well as in checking the declared compositions, hydration degrees and contamination with starting reagents of multicomponent salicylate mixtures.

This work comprises a continuation of our studies on the control of the course and degree of conversion reagents in the commercial-scale production of sodium salicylate [1], as well as in checking the declared compositions of multicomponent salicylate mixtures, their hydration degrees and contamination with starting reagents.

Results of the preceding studies revealed the possibility of employing the thermogravimetric method for studying binary systems composed of non-interacting components or interacting ones. Further, it has been found that there is a possibility of analyzing ternary systems comprising two interacting components by eliminating one of them owing to reactions occurring at elevated temperature, thereby leaving a binary system [2]. A possibility of analyzing ternary systems comprising three interacting components has been suggested as well. In these systems a new component is formed, which replaces one of the components to form a system of three non-interacting ones. Ternary systems involving components which do not react with each other at elevated temperature have also been considered [3].

In the present work quaternary systems have been investigated comprising three or four interacting components.


Experimental

Reagents

The results used were the same as in the preceding works [2, 3].

Apparatus

The thermal analysis of the quaternary systems was performed on an OD-130 Paulik – Paulik – Erdey (MOM, Budapest) derivatograph [4] in air, using platinum crucibles. Powdered components were intimately mixed together in the ratios specified in Tables 1–3, and the sample weight was 200 mg. The heating rate was 5°/min up to the final temperature of 500°. Alumina (α-Al₂O₃) was employed as reference material.

Results and discussion

The results are listed in Tables 1 and 2 and presented in Figs 1–5. The thermal decompositions of the quaternary systems studied can be characterized by the following equations:

1. Sublimation of salicylic acid, \( C_6H_4(OH)COOH \) →
2. \( 2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \)
3. \( C_6H_4(OH)COOH + \text{NaHCO}_3 \rightarrow C_6H_4(OH)\text{COONa} + \text{CO}_2 + \text{H}_2\text{O} \)
4. \( 2 C_6H_4(OH)\text{COONa} \rightarrow C_6H_4(\text{ONa})\text{COONa} + C_6H_4(OH)\text{COOH} \) (sublimation)
5. \( 2 C_6H_4(\text{ONa})\text{COONa} \rightarrow \text{Na}_2\text{CO}_3 + \text{volatile products (CO, CO}_2, \text{H}_2\text{O}) \)
6. \( C_6H_4(\text{ONa})\text{COONa} + C_6H_4(OH)\text{COOH} \rightarrow 2 C_6H_4(\text{OH})\text{COONa} \)
7. \( 2 C_6H_4(\text{OH})\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2 C_6H_4(\text{OH})\text{COONa} + \text{CO}_2 + \text{H}_2\text{O} \)
8. \( C_6H_4(\text{ONa})\text{COONa} \cdot 1.5 \text{H}_2\text{O} \rightarrow C_6H_4(\text{ONa})\text{COONa} \cdot 0.5 \text{H}_2\text{O} + \text{H}_2\text{O} \)
9. \( C_6H_4(\text{ONa})\text{COONa} \cdot 0.5 \text{H}_2\text{O} + C_6H_4(\text{OH})\text{COOH} \rightarrow \)
10. \( 2 C_6H_4(\text{OH})\text{COONa} + 0.5 \text{H}_2\text{O} \rightarrow 2 C_6H_4(\text{ONa})\text{COONa} + 2 \text{Na}_2\text{CO}_3 + C_6H_3(\text{OH})\text{COOH} \) (sublimation) + volatile products (CO, CO₂, H₂O)
11. \( 2 C_6H_4(\text{ONa})\text{COONa} + 2\text{Na}_2\text{CO}_3 \rightarrow 4 \text{Na}_2\text{CO}_3 + \text{volatile products (CO, CO}_2, \text{H}_2\text{O}) \)

The above reactions were interpreted in the preceding works [2, 3]. The experimental evidence presented in Tables 1 and 2 and in Figs 1–5 reveals a correlation between the content of a component in a quaternary system and the course of its thermal decomposition. The decomposition has been shown to be largely affected by reactions (3), (7) and (9). For example, owing to reaction (7), component (A) was completely consumed in system IVe, component (B) in systems Ib, c, d, IIb, c, d, IIIb, c, d, e, f, IVb, c, d, and Vb, c, d, and component (C) in systems