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

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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.

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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-Al_2O_3) 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, $C_6H_4(OH)COOH \uparrow$
(2) $2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
(3) $C_6H_4(OH)COOH + NaHCO_3 \rightarrow C_6H_4(OH)COONa + CO_2 + H_2O$
(4) $2\,C_6H_4(OH)COONa \rightarrow C_6H_4(ONa)COONa + C_6H_4(OH)COOH \uparrow$ (sublimation)
(5) $2\,C_6H_4(ONa)COONa \rightarrow Na_2CO_3 +$ volatile products (CO, CO_2, H_2O)
(6) $C_6H_4(ONa)COONa + C_6H_4(OH)COOH \rightarrow 2\,C_6H_4(OH)COONa$
(7) $2\,C_6H_4(OH)COOH + Na_2CO_3 \rightarrow 2\,C_6H_4(OH)COONa + CO_2 + H_2O$
(8) $C_6H_4(ONa)COONa \cdot 1.5\,H_2O \rightarrow C_6H_4(ONa)COONa \cdot 0.5\,H_2O + H_2O$
(9) $C_6H_4(ONa)COONa \cdot 0.5\,H_2O + C_6H_4(OH)COOH \rightarrow 2\,C_6H_4(OH)COONa + 0.5\,H_2O$
(10) $4\,C_6H_4(ONa)COONa \cdot 0.5\,H_2O \rightarrow 2\,C_6H_4(ONa)COONa + 2\,Na_2CO_3 + C_6H_4(OH)COOH \uparrow$ (sublimation) + volatile products (CO, CO_2, H_2O)
(11) $2\,C_6H_4(ONa)COONa + 2Na_2CO_3 \rightarrow 4\,Na_2CO_3 +$ volatile products (CO, CO_2, H_2O)

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

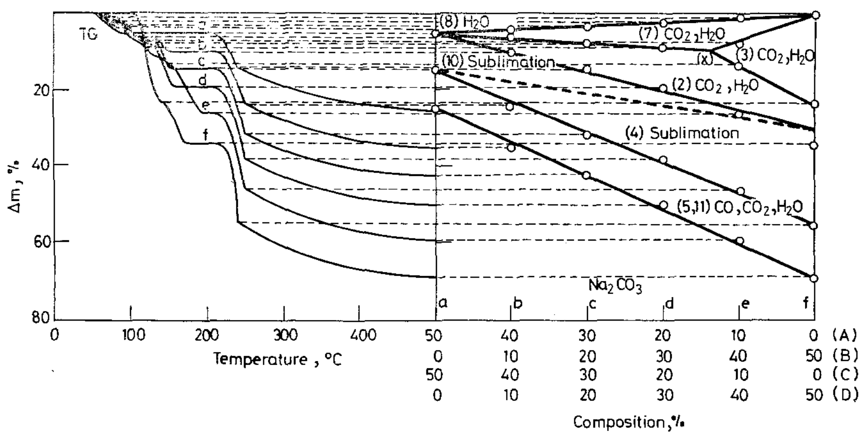

Fig. 1. Thermal decomposition of a system comprising sodium salicylate, salicylic acid, sodium carbonate and sodium hydrogen carbonate (system I). Weight loss as a function of temperature (1) and composition (2). Volatile products are liberated in reactions (7) and (3). The decomposition of sodium hydrogen carbonate, which reacted incompletely in reaction (3), occurs as shown by Eqn (2). The decomposition of sodium salicylate obeys Eqns (4) and (5). (*) a stoichiometric point of reactions (3) and (7)

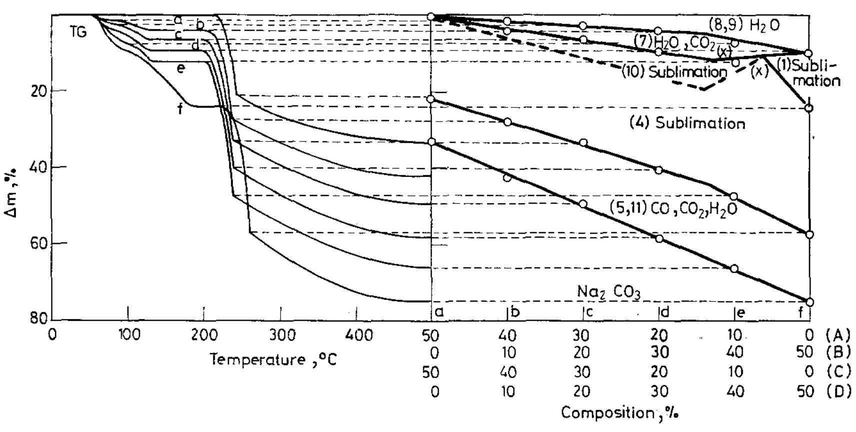

Fig. 2. Thermal decomposition of a system comprising sodium salicylate, salicylic acid, sodium carbonate and disodium salicylate sesquihydrate (system II). Weight loss as a function of temperature (1) and composition (2). Water is liberated in reaction (9), and volatile products in reaction (7). Sublimation of salicylic acid, which reacted incompletely in reactions (7) and (9), occurs as at point (1). The decomposition of disodium salicylate sesquihydrate, which reacted incompletely in reaction (9), occurs as shown by Eqns (8), (10) and (11). (*) a stoichiometric point of reactions (7) and (9). The decomposition of sodium salicylate obeys Eqns (4) and (5)

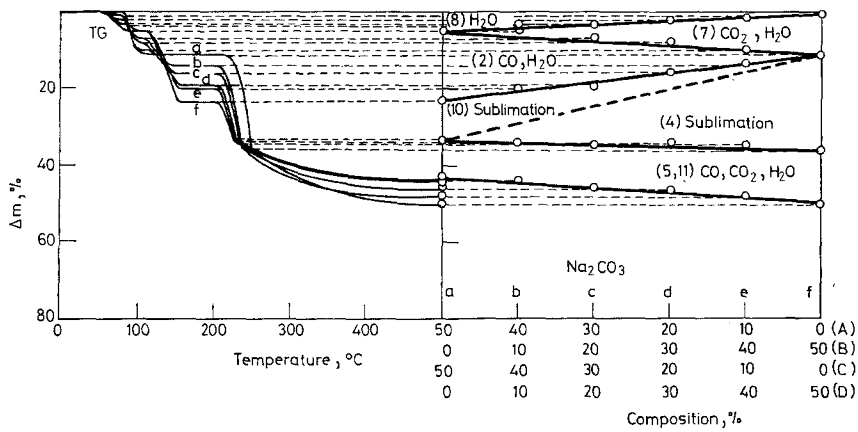

Fig. 3. Thermal decomposition of a system comprising sodium hydrogen carbonate, salicylic acid, disodium salicylate sesquihydrate and sodium carbonate (system III). Weight loss as a function of temperature (1) and composition (2). Volatile products are liberated in reaction (7). The decomposition of disodium salicylate sesquihydrate occurs as shown by Eqns (8), (10) and (11), and that of sodium hydrogen carbonate as in Eqn (2). The decomposition of sodium salicylate obeys Eqns (4) and (5)

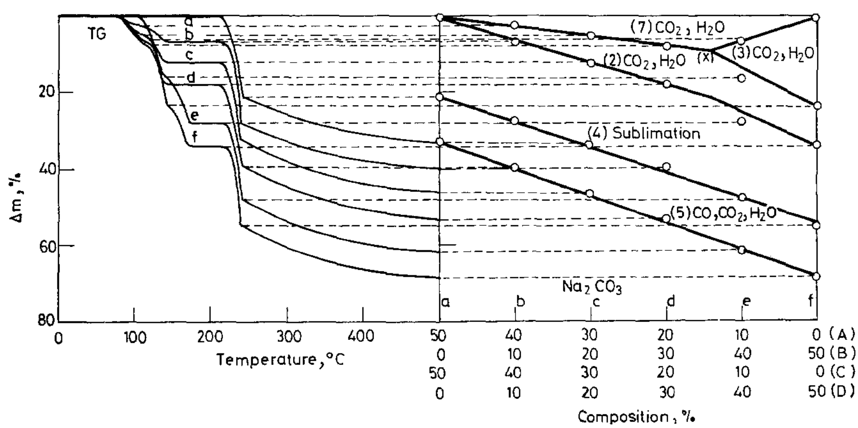

Fig. 4. Thermal decomposition of a system comprising sodium carbonate, salicylic acid, disodium salicylate sesquihydrate and sodium hydrogen carbonate (system IV). Weight loss as a function of temperature (1) and composition (2). Volatile products are liberated in reactions (7) and (3). The decomposition of sodium hydrogen carbonate, which reacted incompletely in reaction (3), occurs as shown by Eqn (2). The decomposition of disodium salicylate sesquihydrate obeys Eqns (8), (10) and (11). (*) a stoichiometric point of reactions (7) and (3). The decomposition of sodium salicylate obeys Eqns (4) and (5)

Ie, IIe and Ve. In reaction (3), component (B) was completely consumed in systems If and IVf, whilst in reactions (3) and (7) the same component was completely consumed in systems Ie and IVe. In reaction (9) component (D) was completely consumed in systems IIf and Vf, whilst in reactions (7) and (9) component (B)

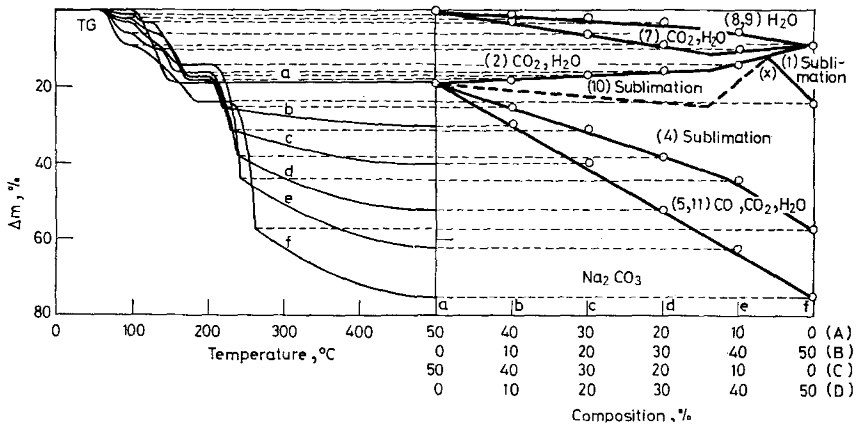

Fig. 5. Thermal decomposition of a system comprising sodium hydrogen carbonate, salicylic acid, sodium carbonate and disodium salicylate sesquihydrate (system V). Weight loss as a function of temperature (1) and composition (2). Water is liberated in reaction (9) and volatile products in reaction (7). Sublimation of salicylic acid, which reacted incompletely in reactions (7) and (9), occurs as at point (1). The decomposition of disodium salicylate sesquihydrate, which reacted incompletely in reaction (9), occurs as shown by Eqns (8), (10) and (11). The decomposition of sodium hydrogen carbonate obeys Eqn (2). (*) a stoichiometric point of reactions (7) and (9). The decomposition of sodium salicylate obeys Eqns (4) and (5)

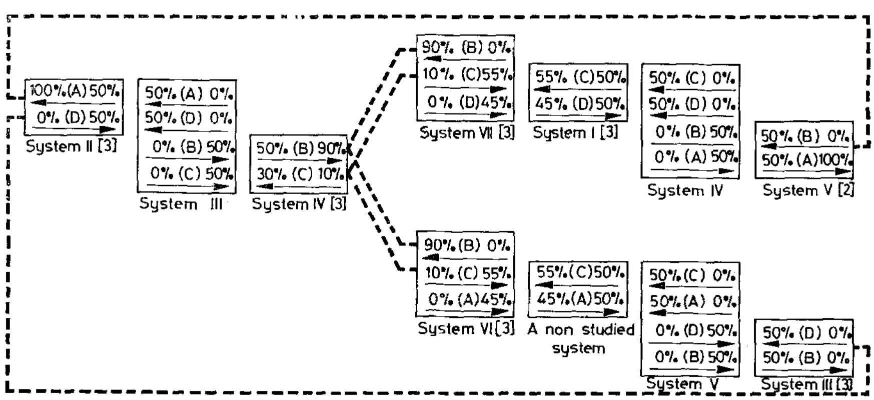

Fig. 6. A schematic diagram of binary, ternary and quaternary systems where (A), (B), (C) and (D) stand for sodium hydrogen carbonate, salicylic acid, sodium carbonate and disodium salicylate sesquihydrate, respectively

Table 1

Results of thermogravimetric investigations of quaternary systems I and II

No.	System	Decomp. stage	Temp. range, °C	Residue in the crucible
I	(A) Sodium salicylate	1.	80–110 80–120*	$C_6H_4(OH)COOH$ $[C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
	(B) Salicylic acid	2.	110–140	$[C_6H_4(OH)COO]Na$ $NaCO_3$, $NaHCO_3$
		3.	120–140 140–170**	$[C_6H_4(OH)COO]Na$ Na_2CO_3
	(C) Na_2CO_3 (D) $NaHCO_3$	4.	220–240	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
		5.	240–460	Na_2CO_3
II	(A) Sodium salicylate	1.	60– 90	$C_6H_4(OH)COOH$ $[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(B) Salicylic acid	2.	90–130	$C_6H_4(OH)COOH$ $[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
		3.	100–180	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(C) Na_2CO_3 (D) Disodium salicylate $\cdot 1.5H_2O$	4.	210–240 220–240* 230–260**	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
		5.	240–450	Na_2CO_3

* decomposition point of systems Id and IIa

** decomposition point of systems Ie, f and IIf

was completely consumed in systems IIe and Ve. These reactions have been shown to eliminate completely one or two components, mostly salicylic acid, sodium carbonate and disodium salicylate sesquihydrate. In place of the eliminated component sodium salicylate appeared. Its decomposition, depicted by Eqns (4) and (5), affected the decomposition pattern of the systems studied.

comprising three interacting components

Composition of the systems											
a		b		c		d		e		f	
(A) 50		40		30		20		10		0	
(B) 0		10		20		30		40		50	
(C) 50		40		30		20		10		0	
(D) 0		10		20		30		40		50	
Percentage weight loss of the crucible content											
F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
0.0	0.0	2.3	2.3	5.0	4.5	7.5	6.7	6.5	5.9	0.0	0.0
0.0	0.0	2.3	2.3	5.0	4.5	7.5	6.7	16.5	12.1	23.5	22.5
0.0	0.0	6.5	5.9	12.0	11.9	18.0	17.8	28.0	23.3	34.0	29.7
21.0	21.6	28.0	28.2	33.0	34.8	39.5	41.5	48.0	48.1	55.0	54.7
33.0	33.5	40.0	40.5	46.5	47.5	53.0	54.5	61.5	61.5	68.5	68.5
0.0	0.0	1.0	0.9	2.0	1.7	4.5	2.6	7.0	4.4	9.0	6.5
0.0	0.0	3.5	3.1	6.0	6.2	9.0	9.3	12.0	10.2	9.0	6.5
0.0	0.0	3.5	3.1	6.0	6.2	9.0	9.3	12.0	10.2	23.5	23.4
21.0	21.6	27.5	27.7	33.0	33.7	40.0	39.9	46.0	45.6	57.0	56.5
33.0	33.5	42.0	41.7	49.0	49.9	58.0	58.2	66.0	66.4	75.0	74.7

F. — found, C. — calculated

Conclusion

1. Results of investigation of the thermal decompositions of quaternary systems (I–V) comprising salicylic acid, sodium salicylate, disodium salicylate sesquihydrate, sodium carbonate and sodium hydrogen carbonate, support conclusions drawn in preceding works [2, 3].

Table 2

Results of thermogravimetric investigations of quaternary systems III – V

No.	System	Decomp. stage	Temp. range, °C	Residue in the crucible
III	(A) $NaHCO_3$	1.	60 – 80 60 – 90*	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ Na_2CO_3, $NaHCO_3$
	(B) Salicylic acid	2.	80 – 100	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
	(C) Disodium salicylate $\cdot 1.5H_2O$	3.	110 – 150	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
		4.	220 – 250 210 – 240*	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
	(D) Na_2CO_3	5.	250 – 440 240 – 440* 250 – 470**	Na_2CO_3
IV	(A) Na_2CO_3	1.	60 – 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ Na_2CO_3, $NaHCO_3$
		2.	90 – 130 90 – 140*	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ $C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
	(B) Salicylic acid	3.	140 – 170 110 – 140**	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
		4.	140 – 160 170 – 200 140 – 170**	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(C) Disodium salicylate $\cdot 1.5H_2O$	5.	220 – 250 220 – 240** 210 – 240***	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
	(D) $NaHCO_3$	6.	250 – 420 240 – 460** 240 – 420***	Na_2CO_3

comprising four interacting components

Composition of the system											
a		b		c		d		e		f	
(A) 50		40		30		20		10		0	
(B) 0		10		20		30		40		50	
(C) 50		40		30		20		10		0	
(D) 0		10		20		30		40		50	
Percentage weight loss of the crucible content											
F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
5.0	4.3	3.5	3.5	3.0	2.6	2.0	1.7	1.0	0.9	0.0	0.0
5.0	4.3	5.0	5.7	7.0	7.1	8.0	8.5	10.0	9.8	11.0	11.2
23.5	22.8	20.0	20.5	19.5	18.2	16.0	15.8	14.0	13.5	11.0	11.2
33.5	34.0	34.0	34.5	34.5	34.9	34.0	35.3	35.0	35.9	36.0	36.2
43.5	43.1	44.0	44.5	46.0	45.9	46.0	47.3	48.0	48.6	50.0	50.0
5.0	4.3	3.5	3.5	3.0	2.6	2.0	1.7	1.0	0.9	0.0	0.0
5.0	4.3	6.0	5.7	7.0	7.1	8.0	8.5	7.5	6.7	0.0	0.0
5.0	4.3	6.0	5.7	7.0	7.1	8.0	8.5	13.5	13.0	23.5	22.5
5.0	4.3	10.0	9.4	14.0	14.5	19.0	19.5	26.0	24.6	34.0	29.7
15.0	15.6	23.5	23.4	31.5	31.3	38.0	39.0	46.0	46.9	55.0	54.7
25.0	24.7	34.5	33.4	42.0	42.2	49.5	50.9	59.0	59.7	68.5	68.5

Table 2

No.	System	De-comp. stage	Temp. range, °C	Residue in the crucible
	(A) $NaHCO_3$	1.	60– 90	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ $[C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
	(B) Salicylic acid	2.	90–130	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ $[C_6H_4(OH)COO]Na$ Na_2CO_3, $NaHCO_3$
V	(C) Na_2CO_3	3.	140–180 140–160* 100–150***	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $C_6H_4(OH)COOH$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
	(D) Disodium salicylate $\cdot 1.5H_2O$	4.	100–180	$[C_6H_4(O)COO]Na_2 \cdot 0.5H_2O$ $[C_6H_4(OH)COO]Na$ Na_2CO_3
		5.	210–240 230–260**	$[C_6H_4(O)COO]Na_2$ Na_2CO_3
		6.	240–450 260–460**	Na_2CO_3

* decomposition point of systems IIIa, IVd, e and Vd, e
** decomposition point of systems IIIf, IVf and Vf
*** decomposition point of systems IVa and Va

2. TG traces of quaternary systems comprising three or four interacting components show that reactions (3) and (7) and (7) and (9) occur simultaneously at elevated temperatures in systems Ie, IIe, IVe and Ve, thereby making impossible quantitative assessment of four components in one sample.

3. Sodium salicylate formed by elimination of salicylic acid in reactions (3), (7) and (9) increases the percentage of this compound present in systems I and II, thus forming a system of three non-interacting components. Moreover, elimination of sodium carbonate in reaction (7) in systems Ie and IIe reduces the numbers of components to two non-interacting ones.

4. Similar processes are observed in systems III, IV and V, comprising four interacting components. Sodium salicylate, which is being formed, produces a system comprising four non-interacting components, whilst elimination of sodium carbonate in systems IVe and Ve converts them to ternary ones.

(Continued)

Composition of the system											
a		b		c		d		e		f	
(A) 50		40		30		20		10		0	
(B) 0		10		20		30		40		50	
(C) 50		40		30		20		10		0	
(D) 0		10		20		30		40		50	
Percentage weight loss of the crucible content											
F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.
0.0	0.0	1.0	0.9	2.0	1.7	3.0	2.6	6.0	4.4	9.0	6.5
0.0	0.0	3.0	3.1	6.0	6.2	9.0	9.3	10.0	10.2	9.0	6.5
18.5	18.5	18.0	17.9	17.0	17.3	16.0	16.7	14.0	13.9	9.6	6.5
18.5	18.5	18.0	17.9	17.0	17.3	16.0	16.7	14.0	13.9	23.5	23.4
18.5	18.5	25.0	25.2	31.0	31.8	38.0	38.5	44.0	45.2	57.0	56.5
18.5	18.5	30.0	29.7	40.0	40.9	52.0	52.2	62.0	63.4	75.0	74.7

F. — found, C. — calculated

5. Under the conditions studied, sodium carbonate has been found to react most readily with salicylic acid (systems I–V). When a system involves salicylic acid, sodium hydrogen carbonate and disodium salicylate sesquihydrate, a component occurring in a large excess reacts most readily with salicylic acid (system IV and V).

6. Sodium carbonate, providing one of the components of the quaternary systems, greatly simplifies their thermal decompositions, since it does not decompose over the temperature range studied.

7. Systems III–V, comprising four identical components, show different thermogravimetric behaviours owing to differences in their percentage compositions (a–f).

8. The overlapping temperature ranges of reactions (4), 220–260°, and (10), 210–240°, the formation of identical stable compounds and similar volatile products in reactions (4) and (10), as well as the endothermic effects of both reac-

tions, mean that it is not possible to distinguish between the weight losses occurring in reactions (4) and (10). The weight losses in reactions (4) and (10) were summed as for one decomposition stage (systems I–II and IV–V) and decomposition stages 4 and 5, respectively.

9. The presence of four components in the systems studied reduces their contents in the samples taken, as compared with ternary and binary systems. This results in reduction of the DTG and DTA peak areas owing to the weaker thermal effects of the reactions.

10. The results obtained in this work suggest that there is a possibility of employing the quaternary systems for the control of the course and degree of conversion in the commercial-scale production of sodium salicylate, and for checking the declared compositions, hydration degrees and contamination of mixtures comprising salicylates. Each of the quaternary systems can be employed in chemical analysis alone or in combination with any other binary or ternary systems. One of such possibility has been shown in Fig. 6.

References

1. S. ROLSKI, Chemia środkiw leczniczych (Chemistry of drugs), PZWL, Warsaw 1964.
2. A. RADECKI and M. WESOŁOWSKI, J. Thermal Anal., 9 (1976), 357.
3. A. RADECKI and M. WESOŁOWSKI, J. Thermal Anal., 10 (1976) 233.
4. F. PAULIK, J. PAULIK and L. ERDEY, Z. Anal. Chem., 160 (1958) 241.

RÉSUMÉ — Etude de la décomposition de systèmes quaternaires contenant de l'acide salicylique, du salicylate de sodium, du salicylate disodique sesquihydraté, du carbonate de sodium et de l'hydrogénocarbonate de sodium, par thermogravimétrie et par analyse thermique différentielle. On montre qu'il est possible d'analyser des systèmes quaternaires dans lesquels trois ou quatre composants réagissent entre eux. Les résultats de la présente étude peuvent servir pour contrôler l'avancement de la réaction dans la production à l'échelle commerciale du salicylate de sodium et pour vérifier la composition déclarée, le degré d'hydratation et la contamination éventuelle par les réactifs initiaux dans les mélanges de salicylate à composants multiples.

ZUSAMMENFASSUNG — Die thermische Zersetzung Salicylsäure, Natriumsalicylat, Dinatriumsalicylat Sesquihydrat, Natriumkarbonat und Natriumbikarbonat enthaltender quaternärer Systeme wurde mittels Thermogravimetrie und Differentialthermoanalyse untersucht. Die Möglichkeit der Analyse quaternärer Systeme mit drei oder vier aufeinander einwirkenden Komponenten wurde gezeigt. Die Ergebnisse dieser Untersuchungen können bei der Kontrolle des Verlaufs und des Konversionsgrades der Reagentien, bei der Herstellung von Natriumsalicylat im Handelsmaßstab sowie bei der Prüfung der deklarierten Zusammensetzung des Hydratierungsgrades und der Verunreinigung mit Ausgangsreagentien von Salicylatgemischen mit einer Vielzahl von Komponenten eingesetzt werden.

Резюме — Используя термогравиметрию и дифференциальный термический анализ, исследовано термическое разложение четвертичных систем, включающих салициловую кислоту, салицилат натрия, полуторный гидрат динатрий салицилата, карбонат — и гидрокарбонат натрия. Показана возможность анализа четвертичных систем, включающих в себя три или четыре реагирующих компоненты. Результаты исследований были и использованы для контроля и степени превращения реагентов при производстве салицилата натрия в промышленном масштабе, а также для проверки предъявленного состава, степени гидратации и загрязнения исходными реагентами многокомпонентных салицилатных смесей.