

INVESTIGATION OF THE ALKALINE SALTS OF SOME ACIDS IN MOLTEN PHASE*

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The study of changes taking place in organic compounds upon the effect of heat is interesting from both theoretical and practical points of view. Organic compounds are known to undergo far more complicated and uncontrollable decomposition processes upon heating than do inorganic compounds, furthermore the changes in experimental conditions influence to a greater extent the nature of the thermal process.

There are many organic compounds containing ionic bonds. But among this kind of compounds the various organic acids and their alkaline salts form model compounds more accessible to thermal analysis since a lot of them do not decompose after attaining their melting points, furthermore, because they are inclined to dissociation, consequently they dispose of a relatively well measurable electric conductivity. It is characteristic of these compounds, that in the initial period of decomposition they are homogeneous and a heterogeneous phase will be formed only stepwise with the progress of the reaction, namely when a heat stable and slightly soluble decomposition product form. A further characteristic feature of the decomposition process is that it is accompanied by a relatively small number of known side reactions.

This paper is to report on several characteristic features of the full alkaline acetate series as well as benzene sulfonic acid and its salts in molten phase.

Experimental

The test compounds were carefully purified in multiple recrystallization processes and their composition was controlled by chemical analysis. The temperature intervals of the stable molten phase of the compounds were defined by means of the Paulik—Paulik—Erdey type derivatograph manufactured by the Hungarian Optical Works, making use of the simultaneously

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recorded complex thermoanalytical curves. This examination was carried out in inert gas atmosphere at a heating rate of 1 to 2 °C per min. Results are summarized in Table 1.

For every alkaline acetate there is a period of molten stage suitable for the measurement. Melting and decomposition of lithium benzene sulfonate are processes beginning and taking place simultaneously. Also the decomposition of sodium benzene sulfonate lies very near to its melting point, but even at its melting point it delivers evaluable data. For the examination of the

Table 1

Thermal data of alkaline benzene sulfonates and acetates

Benzene sulfonates	Melting point °C	Begin of decomposition °C	Molten phase region Δ°C
Li	520	520	0
Na	415	430	15
K	375	430	45
Rb	325	480	155
Cs	232	500	268
Acetates			
Li	280	320	40
Na	330	380	50
K	302	390	88
Rb	241	380	139
Cs	197	380	183

molten salts we have constructed a melting thermostat [1] which worked up to 600 °C and ensured a temperature constancy within ± 0.05 °C. It suited to simultaneously examine several samples and permitted visual observation. For our investigations involving small quantities of the substances we have constructed a tube furnace to increase the usual isothermal working range (2 to 3 cm) by nearly one order of magnitude over a wide temperature range. For density measurements we have constructed a modified Mohr—Westphall type instrument to work at high temperatures. For measuring the viscosity at high temperatures an Oswald-viscosimeter was used. The electric conductivity has been determined in our special measuring cell which ensured gas-flushing, combined with a R.L.C. electric bridge manufactured by General Radio. By means of this equipment we have established that within the range of audio-frequency the conductivity of the melts varied as a function of frequency only to an extent within the limits of error.

Results and discussion

The changes in the density of the melts as a function of temperature were measured in order to obtain the molar volumina for various temperature values to be applied in our further calculations. It was interesting to see, that for the melts of benzene sulfonic acid and its salts the correlation between density and temperature was linear in the experimental range, while acetates exhibited deviations of both convex and concave character.

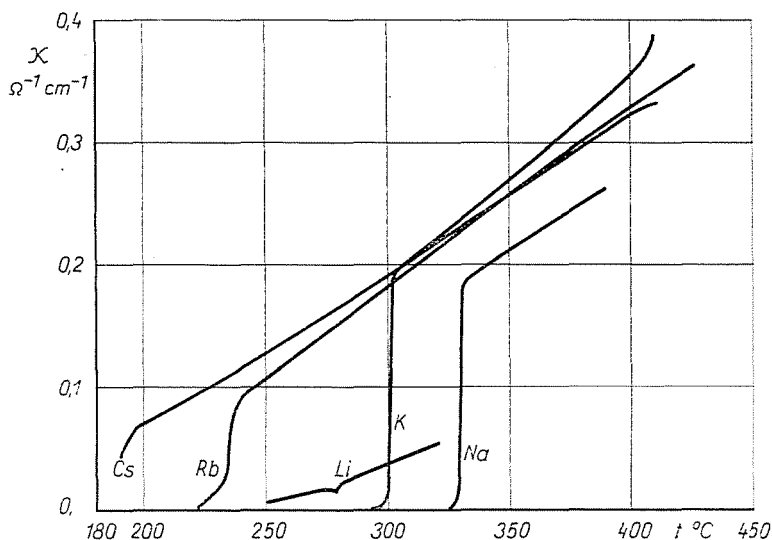


Fig. 1. Specific electric conductivity of alkaline acetates vs. temperature

The temperature dependence of the specific electric conductivity (χ) of alkaline-acetates and benzene-sulfonates is seen in Figs 1 and 2. A common feature of these graphs is an abrupt increase at the melting points, the data obtained in the course of heating and cooling coincide excepted around the melting and solidification point where showed a hysteresis 4 to 5°C wide in χ values.

The χ value of the benzene sulfonic acid is by about one order of magnitude lower than that of its salts (Fig. 2). At a temperature lower by 0.5 °C than the melting point an inflexion is seen, likely to be reproducible and ascribable to a reversible transformation process in the crystal modification. We were not able to detect this transformation so far, even with the help of the very sensitive DTA method, but we shall try to prove our assumption by the exact X-ray examinations in the near future.

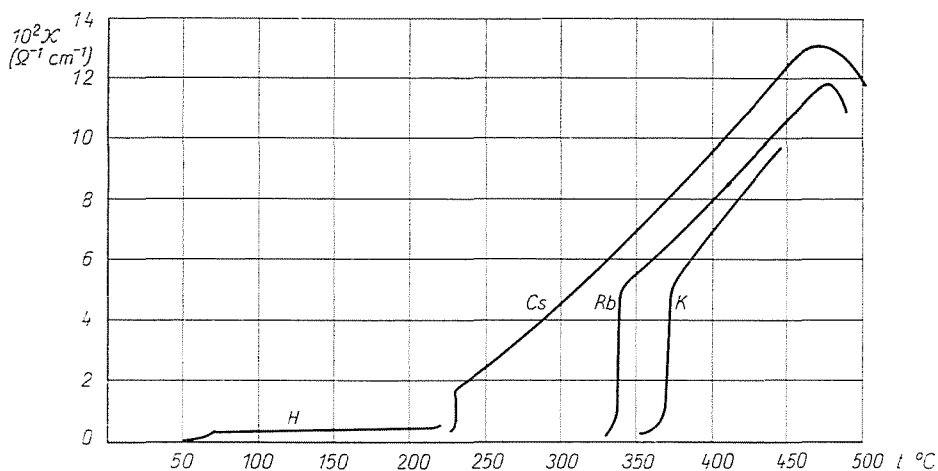


Fig. 2. Specific electric conductivity of benzene sulfonic acid and its alkaline salts vs. temperature

The benzene sulfonic acid has however different properties from other points of view, too. Namely, the sample preparation method brought about significant deviations in the results (Fig. 3). An appropriate amount of the

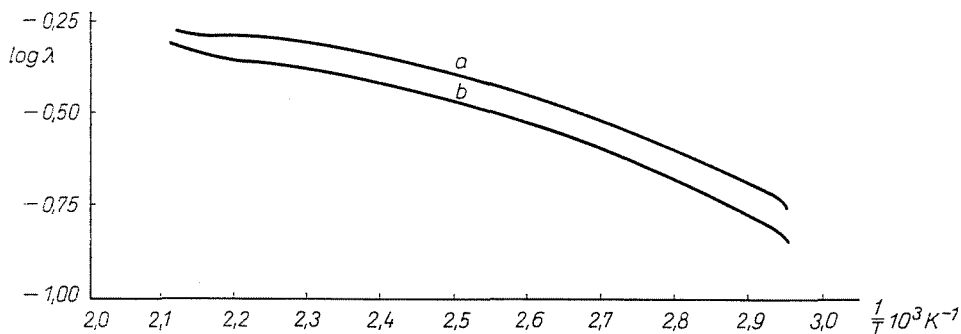


Fig. 3. Specific electric conductivity of benzene sulfonic acid vs. temperature, for various pretreatments

solid sample was placed first into the measuring cell and heated above its melting point. Thereupon the air was expelled from the melt that was cooled down again. The α values were found to differ from each other according to the rate of the cooling. Curves *a* and *b* in Fig. 3 were recorded in experiments when the sample was cooled down at a rate of 40 $^\circ\text{C}$ and 70 $^\circ\text{C}$ per hour respectively. For cooling rates between the two limits mentioned, the shifts in the

α values were reproducible and proportional to the rate. This "memory effect" like character in the behaviour of the compound hints at a correlation between the structure of the solid sample and its melt exerting an influence upon the α values.

Table 2
 λ values of alkaline acetates at melting
and decomposition temperatures

Acetates	λ melting point	λ begin of decomp.
$\Omega^{-1} \text{ cm}^2 \text{ g equivalent}^{-1}$		
Li	1,4	3,2
Na	12,0	16,5
K	13,4	24,6
Rb	6,6	23
Cs	4,9	24,6

In Table 2 the equivalent conductivity (λ) values of the molten salts at the melting points and before the decomposition point, resp., are compiled.

For alkaline salts of simple anions the equivalent conductivity decreases monotonously with the increase in the atomic number, according to the ion mobility. The λ values of benzene sulfonates recorded at the melting point increase up to the rubidium salt and of acetates up to the potassium salt and they begin to decrease only thereafter. The values measured before the decomposition point show a more striking difference in this respect against alkaline halides. The interpretation of the changes in the λ values can be approached from two sides. Either, salts formed with cations of small atomic number undergo incomplete dissociation and with the increase of the atomic number the covalent bond between the cation and anion is weakened promoting the dissociation, or, a full dissociation of the anion must be supposed, frequent phenomenon for inorganic salts containing polyatomic anions. The empiric UBBELOHDE [2] rule concerning the entropy value of the melting of completely dissociated salts makes the first supposition more plausible. According to the rule, this entropy value is constant and represents 3 E.U/g ion.

The measurements results were the following:

BzSO ₃ ⁻ Na	0,85
BzSO ₃ ⁻ K	1,3
BzSO ₃ ⁻ Rb	2,0
BzSO ₃ ⁻ Cs	3,1

Again, our viscosity results let conclude on an order of higher degree of metal ion salts of low atomic number in the molten phase and its decrease with the increase of the atomic number of the cation.

In Figs 4 and 5, the dynamic viscosity values of alkaline acetate and benzene sulfonate salts resp., are shown versus temperature increase. Our diagrams as well as the activation energy values calculated from them are all

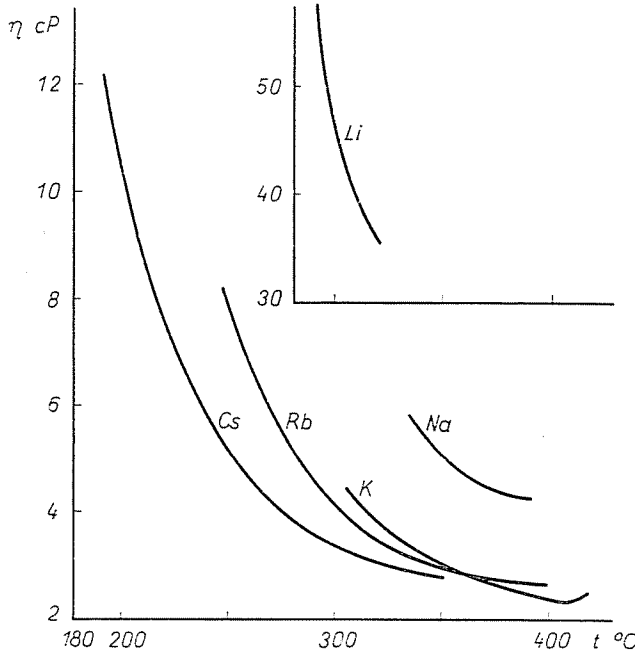


Fig. 4. Dynamic viscosity of molten alkaline acetates vs. temperature

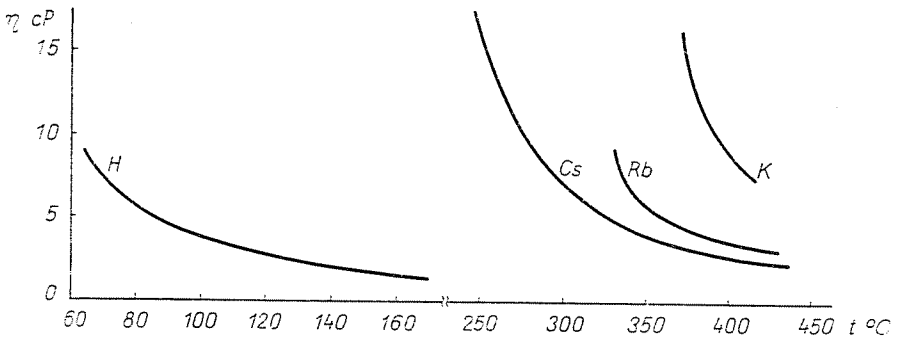


Fig. 5. Dynamic viscosity of benzene sulfonates in the melting to decomposition point range vs. temperature

demonstrating that the degree of order in the melts decreases with the increase in the cation diameter. This fact has a great significance also for the decomposition process of the melt upon further heating. KRÖNIG [3] has demonstrated lithium acetate to transform at a nearly 100 percent conversion into acetone and the resulting amount of ketone to gradually decrease to nearly zero with the increase of the atomic number of the alkaline metal. At the same time the decomposition into hydrocarbon comes into prominence. On the other hand, from the work of JAKERSON [4] and NOSZKÓ [5] it is also known that the acetolysis is a process involving the formation and decomposition of an intermediary product of dimeric structure.

Our λ and dynamic viscosity values unambiguously refer to an order of high degree for lithium acetates, to decrease along with the conversion to acetone, nearly parallel with the increase of cation diameter.

Summary

Density, electric conductivity and viscosity of alkaline acetates and benzene sulfonates have been determined as function of temperature. The degree of order in the melts was found to decrease for both series with the increase of the atomic number of the alkaline cation. The tendency in the recorded changes is analogous with the conversion of acetates into acetone, hence there is a correlation between structure of the molten salt and mechanism of its thermal decomposition.

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