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Heavy metals complexes of poly(sodium 4-styrenesulfonate) — thermogravimetric studies

Summary — The paper analyzes thermal properties of poly(sodium 4-styrenesulfonate) bound with different metal ions [Cu(II), Ni(II), Zn(II), Pb(II), Cr(III)] and in the acidic form. Solid samples of polyelectrolyte bound with different counter-ions were prepared and their mass losses in the temperature range of 25—1000 °C were recorded. TG and DTG curves were used to estimate the activation energy of thermal degradation of sulfonic groups bound with different counter-ions. For studied polyelectrolyte counter-ions, the sulfonic group thermal stability increases in the following sequence: H < Ni < Cu < Na < Zn < Pb < Cr(III).

Keywords: polyelectrolyte, heavy metal complexes, thermogravimetry.

KOMPLEKSY METALI CIĘŻKICH Z POLI(4-STYRENOSULFONIANEM SODU) — BADANIA TERMOGRAWIMETRYCZNE

Streszczenie — Oddziaływania polimer-metal stanowią podstawę ultrafiltracji wspomaganej polimerami (ang. *polymer enhanced ultrafiltration*, PEUF) — techniki separacji umożliwiającej zatrzymywanie jonów metali na membranie ultrafiltracyjnej po uprzednim związaniu ich z makrocząsteczką polimeru. Jednym z polimerów o doświadczalnie potwierdzonej skuteczności takiego działania jest poli(4-styrenosulfonian sodu) (PSSS). Przedstawiono wyniki badań termograwimetrycznych próbek poli(4-styrenosulfonianu sodu) związanego z jonami metali [Cu(II), Ni(II), Zn(II), Pb(II), Cr(III)] oraz PSSS w postaci wodorowej i sodowej. Zarejestrowano krzywe TG i DTG suszonych na powietrzu próbek PSSS w różnej postaci jonowej (rys. 1). Rozkład termiczny badanych próbek (prowadzony w atmosferze powietrza) przebiegał trójstopniowo, z wyjątkiem postaci sodowej, w przypadku której zarejestrowano 4 etapy rozkładu (tabela 1). Pierwszy etap rozkładu próbek, odnotowany do temperatury 200—300 °C, był związany z utratą wody hydratacyjnej. Kolejny etap ubytku masy wynikał z rozkładu grupy sulfonowej i występował w różnych zakresach temperatury, w zależności od postaci jonowej polimeru. Stosując 3 metody, opierając się na równaniach (1)—(5), oszacowano energię aktywacji E_a rozkładu grupy sulfonowej polielektrolitu połączonej z badanymi jonami (rys. 2—4, tabela 2). Stwierdzono wzrost stabilności termicznej grupy sulfonowej, zależny od rodzaju przeciwjonu, w kolejności: H < Ni < Cu < Na < Zn < Pb < Cr(III). Ostatni etap dekompozycji przebiegał w temp. >500 °C i był efektem rozkładu matrycy polimerowej. Masy próbek po zakończonym procesie rozkładu wskazywały na obecność w mineralnej pozostałości siarczanów (Na, Pb) lub tlenków (Cu, Zn, Ni, Cr) metali.

Słowa kluczowe: polielektrolit, kompleksy metali ciężkich, termograwimetria.

INTRODUCTION

The thermogravimetric (TG) and derivative thermogravimetric (DTG) studies are widely used to characterize the thermal stability of polymers and to estimate the kinetic parameters of their thermal decomposition. They are also employed to investigate polymer-metal complexes, such as cellulose acetate complexes with transition metals [1], metal complexes of poly(acrylic acid) [2] or crosslinked chitosan [3].

The polymer-metal interactions provide a basis for the polymer enhanced ultrafiltration (PEUF), a membrane technique enabling metal ions separation from aqueous solutions and industrial effluents. It combines two processes *i.e.* binding of metal ions by water soluble macromolecules and their separation using an ultrafiltration membrane. The PEUF is typically performed applying two types of polymers: chelating polymers which form coordinate covalent bonds with metal ions and polyelectrolytes of ion-exchange properties. Polymers such as poly(acrylic acid) [4—7], polyethylenimine [6—8], and chitozan [8, 9] are most often used for enhanced ultrafiltration separation of heavy or toxic metals [4, 5, 7—9] as well as radionucleides [6] from aqueous streams (effluents).

In the previous works [10—12], poly(sodium 4-styrenesulfonate), a water-soluble polyelectrolyte containing sulfonic groups, was applied to enhance the ultrafiltration removal of Cu(II), Ni(II), Zn(II), Pb(II), Cr(III) from model solutions and real wastewater. This work demonstrates a thermogravimetric analysis of solid samples of poly(sodium 4-styrenesulfonate) bound to the same metal ions as well as in the hydrogen and sodium form.

The influence of counter-ion type on the sulfonic groups stability was evaluated on the basis of the recorded TG and DTG curves and the activation energy of polyelectrolyte sulfonic groups thermal decomposition was calculated. The thermogravimetric analysis enabled the polyelectrolyte — metal ion impact evaluation, which is the crucial aspect of polymer selection in PEUF.

EXPERIMENTAL

Materials

Poly(sodium 4-styrenesulfonate) — further abbreviated as PSSS, a water soluble anionic polyelectrolyte with M_w = 70 000, was purchased as a 30 % solution from Sigma-Aldrich. Model solutions of Cu(II), Zn(II), Ni(II), Pb(II) and Cr(III) were prepared using appropriate metal nitrates. The metal salts and other chemicals (sodium chlorate, hydrochloric acid) supplied by POCh S.A. were of analytical grade.

Preparation of polymer samples

The ultrafiltration process was employed to prepare solid samples of PSSS in different ionic forms. An AMICON 8400 stirred membrane cell (Millipore), with the capacity of 400 cm^3, equipped with an additional tank (800 cm^3) and a selector valve changing the ultrafiltration mode (concentration/diafiltration) was used in the research. A Sepa® CF EW polysulfone membrane (Osmonics) with molecular weight cut-off of 50 000, was used to separate the polyelectrolyte macromolecules. The membrane area amounted to 38.5 cm^2 and the process was conducted at the transmembrane pressure of 0.1 MPa.

The procedure of polymer samples preparation was as follow: 50 cm^3 of polymer solution (1.5 g of PSSS) was placed in the stirred ultrafiltration cell and 200 cm^3 of 5 % metal nitrate solution, hydrochloric acid or sodium chlorate was filtered through the cell. The residual unbound ions were diafiltered by 500 cm^3 of deionized water. In the next step, the polyelectrolyte solution was concentrated by ultrafiltration (the volume reduction up to 25 cm^3) and dried at 40 °C. The obtained polymeric samples were characterized by different colors, depending on their ionic forms. The samples of PSSS bound with Na and Zn ions were almost colorless, while those with H and Pb bonds were amber (orange-yellow), and Cu, Ni and Cr(III) forms of the polymer were in different shades of green.

Thermogravimetric analysis

The air dried polymer samples (approx. mass of 5 mg) were placed in a 0,7 cm^3 platinum crucible with a perforated lid and subjected to a controlled temperature increase in the dynamic air at a flow rate of 100 cm^3/min. The temperature was changed within the range of 25—1000 °C with a constant heating rate of 24 °C/min. The measurements were conducted using a Mettler Toledo TGA 851^e thermobalance and the STAR^e Thermal Analysis System.

Calculations

The recorded thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were used to evaluate the activation energy of sulfonic group decomposition in different ionic forms of PSSS. Three methods of activation energy determination were applied [13—15].

Broido method

The activation energy was determined from a TG curve according to the expression [13, 14]:

$$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right]=\frac{-E_a}{R}\frac{1}{T}+\ln\left(\frac{R}{E_a}\frac{Z}{\theta}T_{\max}^2\right) \quad (1)$$

and

$$\alpha=(m_0-m_t)(m_0-m_f) \quad (2)$$

where: E_a — *activation energy (J/mol)*, R — *gas constant (J/Kmol)*, T — *temperature (K)*, T_{max} — *temperature of the maximum reaction rate (K)*, Z — *frequency factor*, θ — *heating rate (K/min)*, α — *mass fraction which has undergone decomposition up to time t (temperature T), sample mass:* m_0, m_t, m_f *— initial, at time t, at the end of reaction, respectively.*

The activation energy can be determined from the slope of the linear dependence of $\ln\{\ln[1/(1-\alpha)]\} = f(1/T)$.

Dave and Chopra method

The Dave and Chopra method makes use of DTG curve and the following dependence of the rate constant k for first-order reaction [13]:

$$k=\frac{-\mathrm{d}W/\mathrm{d}t}{(A-a)} \quad (3)$$

where: A — *DTG peak area expressing the mass loss (mg) in the whole decomposition stage*, a — *DTG peak area up to time t expressing the mass loss (mg) up to time t (temperature T)*, dW/dt — *DTG peak height at time t.*

According to Arrhenius equation the reaction rate constant is given as:

$$k = Ze^{-\frac{E_a}{RT}} \tag{4}$$

Combining equations (3) and (4) and converting them into logarithmic form, a linear dependence of log*k* as a function of 1/*T* can be achieved. The activation energy E_a can be determined from the slope of the line.

Coats and Redfern method

The method allows to determine the activation energy for first-order reaction on the basis of TG curves, according to equations [15]:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{ZR}{\theta E_a}\left(1-\frac{2RT}{E_a}\right) - \frac{E_a}{RT} \tag{5}$$

Drawing the left side of the equation (5) as a function of 1/*T*, a good correlation with the linear dependence was achieved and activation energy can be calculated.

RESULTS AND DISCUSSION

Figure 1 depicts TG/DTG curves of PSSS in different ionic forms. Table 1 summarized the results of the thermal decomposition of polymer samples.

In all the recorded curves, three stages of thermal degradation can be distinguished, except PSSS_Na, where four decomposition stages occur. The first stage of decomposition corresponds to the loss of volatile compounds (hydration water) and appeared up to 200—300 °C. The mass loss observed in the stage varies between 9.25 % (PSSS_Pb) and 21.56 % (PSSS_Ni). The values of mass loss enable the evaluation of hydrate stoichiometry of polyelectrolyte in different ionic forms (Table 1).

The second degradation stage, referring to thermal desulfonation, occurred in different temperature ranges, depending on the counter-ions bound to polyelectrolyte functional groups. The lowest desulfonation temperature (beginning at 275.5 °C) was recorded for the acidic form of polyelectrolyte, while the highest thermal stability was found for the sulfonic group bound with Zn ions (beginning of the decomposition at 466.3 °C). All ionic forms of PSSS, except PSSS_H and PSSS_Ni, demonstrated the one-step decomposition of sulfonic groups. Analyzing the thermal degradation of sodium salts of some polymeric sulfonic acids, Jiang and co-authors suggested the radical cleavage of the C-S bond and two possible pathways of further desulfonation step, leading to sulfur dioxide and sodium sulfate or sulfur dioxide, water and sodium sulfite as the main products of sulfonic group decomposition [16]. The sample masses recorded after the desulfonation of PSSS_Na, PSSS_Pb and PSSS_Cr indicate the similar fragmentation as in the first proposed pathway, leading to SO_2 and appropriate metal sulfate formation. A good correspondence between the theoretical, calculated mass (3.7202 mg; 4.4131 mg; 3.6229 mg, respectively for Na, Pb and Cr) and the final sample mass of this decomposition stage (m_{If}) can be observed. In the case of PSSS_Cu, PSSS_Zn and PSSS_Ni, the agreement between the recorded and calculated values of the sample masses of this degradation stage is not so good, which may be due to partial decomposition of metal sulfates to oxides. The sample mass observed in the two-step desulfonation of PSSS_H corresponds to the calculated values, assuming SO_2 evolution (the 1st step, the calculated value 2.9514 mg) and SO_2 and 0.5 H_2O evolution per monomer unit (the 2nd step, the calculated value 2.7301 mg). Both SO_2 and H_2O were confirmed by Jiang and co-workers in volatile products during thermal degradation of poly(4-styrenesulfonic acid), within the temperature range 200—400 °C [16].

The third stage of mass loss observed in the thermogravimetric curves above 500 °C, can be attributed to the decomposition of polymer matrix. The final sample masses (above 900 °C) indicate that the solid residues remained as metal sulfates (Na, Pb) or oxides (Cu, Zn, Ni,

T a b l e 1. Summary of thermogravimetric analysis of PSSS in different ionic forms[*)]

Polymer-ion	m_0, mg	Δm_I, %	nH$_2$O ($\Delta m_{I\ theor.}$), %	$m_{I\ f}$, mg	$T_{II\ i}$—$T_{II\ f}$, °C	$T_{II\ max.}$ °C	$m_{II\ f}$, mg	Δm_{II+III} %	m_f, mg	$m_{f\ theor.}$, mg
PSSS_H	5.6520	-17.81	2 H_2O (-16.36)	4.6455	275.6—386.4 (457.2)	318.6	3.1196 (2.6831)	-81.55	0.0362	
PSSS_Na	5.1056	-13.74	2 H_2O (-14.88)	4.4043	415.5—468.0	449.0	3.8206	-56.97	1.4955	1.5169 (Na_2SO_4)
PSSS_Cu(II)	5.5878	-16.18	5 H_2O (-17.32)	4.6835	315.1—354.2	332.8	3.6759	-68.79	0.8400	0.8665 (CuO)
PSSS_Zn(II)	5.6312	-19.13	6 H_2O (-20.02)	4.5538	466.3—510.2	483.0	3.3903	-65.58	0.8608	0.8583 (ZnO)
PSSS_Ni(II)	5.9148	-21.56	6 H_2O (-20.28)	4.6393	429.5—511.7	486.7	3.1295	-64.68	0.8136	0.8151 (NiO)
PSSS_Pb(II)	5.4741	-9.25	3 H_2O (-8.61)	4.9679	396.6—438.8	414.9	4.4499	-48.36	2.3205	2.6264 ($PbSO_4$)[**)]
PSSS_Cr(III)	5.1540	-16.35	7 H_2O (-17.33)	4.3115	412.4—500.6	427.0	3.6635	-50.77	1.6944	1.0892 (Cr_2O_3)[***)]

[*)] m_0 — initial mass; Δm_I — mass loss in stage I; nH$_2$O ($\Delta m_{I\ theor.}$) — degree of hydration and, in parenthesis, theoretical mass loss in stage I; $m_{I\ f}$ — final mass of stage I; $T_{II\ i}$—$T_{II\ f}$ — initial and final temperature of stage II; $T_{II\ max.}$ — temp. of DTG peak in stage II; $m_{II\ f}$ — final mass of stage II; Δm_{II+III} — mass loss in stages II and III; m_f — final mass; $m_{f\ theor.}$ — theoretical final mass assuming given in parenthesis form of residue.

[**)] Temperature of $PbSO_4$ decomposition *ca*. 1000 °C.

[***)] 1.5662 mg — assuming 1 Cr(III) at 2 mer unit.

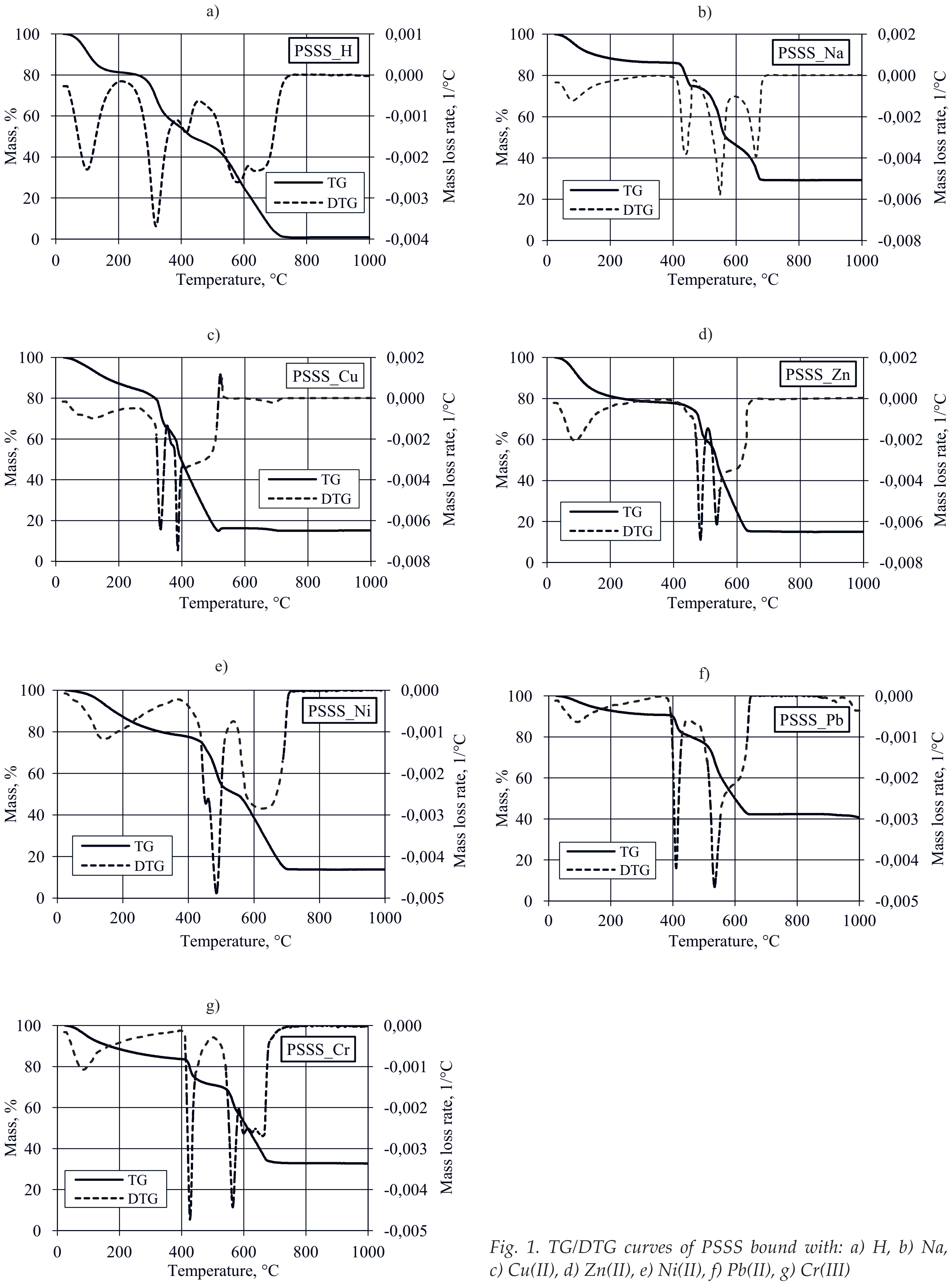

Fig. 1. TG/DTG curves of PSSS bound with: a) H, b) Na, c) Cu(II), d) Zn(II), e) Ni(II), f) Pb(II), g) Cr(III)

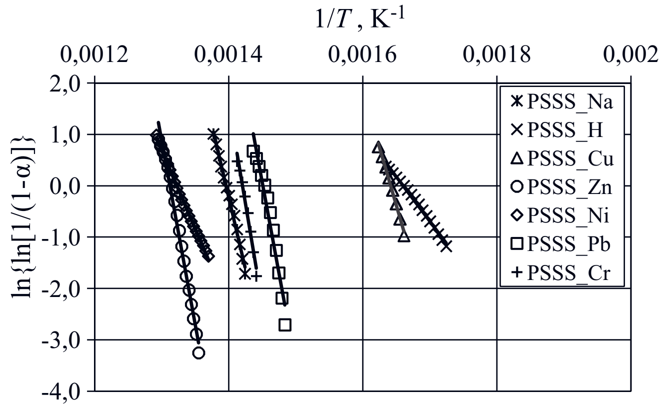

Fig. 2. The dependence of ln{ln[1/(1 – α)]} versus (1/T) — according to equation (1), Broido method

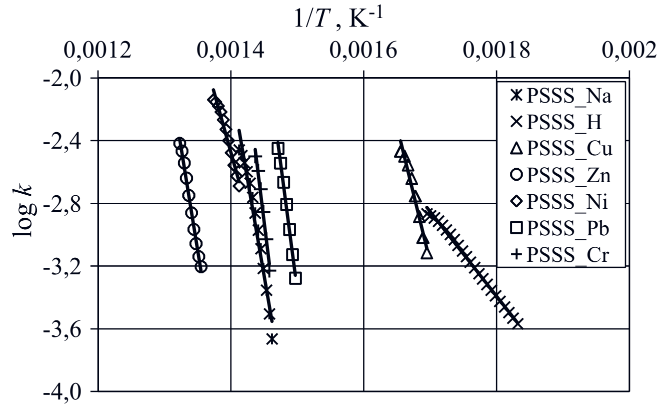

Fig. 3. The dependence of logk versus (1/T) — according to equations (3) and (4), Dave and Chopra method

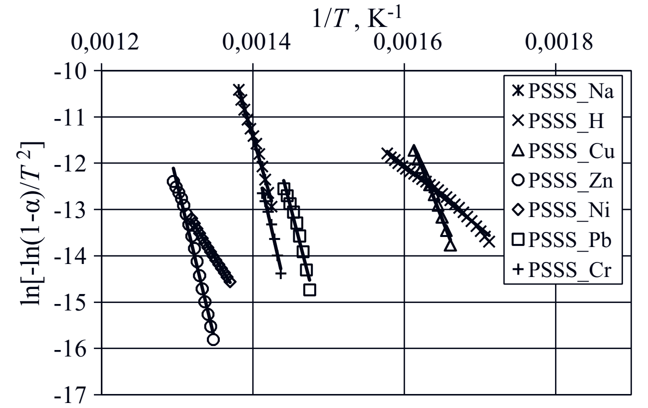

Fig. 4. The dependence of ln[-ln(1 – α)/T²] versus (1/T) — according to equation (5), Coats and Redfern method

Cr). There is a good agreement between the theoretical and experimental data, except the PSSS_Cr where probably nonstoichiometric bonds of polyelectrolyte sulfonic groups and trivalent chromium were formed.

It should be mentioned that the observed temperatures of sulfonic groups decomposition in poly(4-styrenesulfonate) bound with hydrogen and sodium ions are similar to that reported by Balcerowiak for the solid ion-exchanger with analogous functional groups [17, 18].

Figures 2—4 depict linear dependences which enabled the activation energy determination, according to the applied methods. Table 2 presents the values of activation energy E_a and determination coefficient R^2 calculated for different ionic forms of PSSS using TG and DTG data, according to the methods described above.

Table 2. The activation energy (E_a) of sulfonic groups thermal degradation in PSSS at different ionic forms and determination coefficient (R^2)

	Broido		Dave and Chopra		Coats and Redfern	
	E_a kJ/mol	R^2	E_a kJ/mol	R^2	E_a kJ/mol	R^2
PSSS_H	144.5	0.9937	103.3	0.9969	111.4	0.9892
PSSS_Na	464.4	0.9934	469.8	0.9705	467.2	0.9919
PSSS_Cu	377.2	0.9926	334.8	0.9722	345.8	0.9914
PSSS_Zn	597.0	0.9886	499.9	0.9947	565.2	0.9856
PSSS_Ni	253.5	0.9968	268.6	0.9724	221.1	0.9980
PSSS_Pb	558.8	0.9587	613.9	0.9939	526.3	0.9700
PSSS_Cr(III)	652.0	0.9825	667.1	0.9829	595.7	0.9846

Applying the Broido method, very high determination coefficients (at the level of 0.99) were achieved for the samples of PSSS with the majority of analyzed ions. Only for PSSS_Pb sample a slightly lower R^2 value was observed (*ca.* 0.96), which indicates a low correlation of the analytical data with the determined linear dependence estimating the activation energy. On the other hand, the Dave and Chopra method gives a very high determination coefficient for Pb as a polyelectrolyte counter-ion ($R^2 > 0.99$) and relatively high values for other PSSS ionic forms [0.97 (Ni, Cu, Na) — > 0.99 (H, Zn)]. The third method applied (Coats and Redfern) also shows a high correlation of thermogravimetric data with proposed linear functions ($R^2 = 0.97$ — > 0.99), with lower values again in the case of Pb ion.

The activation energy of polyelectrolyte sulfonic groups thermal decomposition vary considerably, depending on a counter-ion type. The lowest E_a values were found for the acidic form of polyelectrolyte. All other ionic forms of PSSS were characterized by several-fold higher activation energies. That indicates a stabilizing influence of metal ions bound to -SO_3 groups (the same effect was observed in other works concerning polymers containing sulfonic groups [16—19]). The increase in activation energy and the increase in sulfonic group thermal stability can be described by the following sequence of counter-ions bound to polyelectrolyte: H < Ni < Cu < Na < Zn < Pb < Cr(III). The three methods of activation energy determination resulted in slightly different values of E_a for the same type of counter-ion but in most cases the differences were not significant.

CONCLUSIONS

TG and DTG analysis enabled the evaluation of polymer-metal interactions which are the basis for PEUF application for heavy metal removal from aqueous solutions and industrial wastewater.

Thermal degradation of poly(4-sodium styrenesulfonate) bound with target heavy metals and in the acidic and sodium form displayed three or four (sodium form) stages of decomposition.

The first stage was related to the loss of hydration water. The second degradation stage was caused by desulfonation and occurred in the different temperature ranges, depending on the ionics form of polyelectrolyte. The polymer with metal-exchanged sulfonic group exhibited enhanced thermal stability. Depending on polyelectrolyte counter-ion, the sulfonic group thermal stability increased in the sequence: H < Ni < Cu < Na < Zn < Pb < Cr(III).

During the last stage of decomposition, the polymer matrix was degraded and inorganic residue as metal sulfates or oxides remained.

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