

Nonaqueous Potentiometric Titration of Copolymers Containing Itaconic Acid or its Monoesters

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The method of nonaqueous potentiometric titration enables to determine the content of itaconic acid or its monoesters in copolymers which are insoluble in water. This simple and suitable method requires a small amount of the sample. The determination of inflection point on the titration curve is performed numerically. The method was used for the composition determination of the following copolymers: styrene with itaconic acid, methyl methacrylate with itaconic acid, and methyl methacrylate with 4-methyl itaconate.

The content of itaconic acid (1-propene-2,3-dicarboxylic acid, IA) and its monoesters in the copolymers is widely changed upon conditions used for their preparation.

There are several methods in the literature which were used for the determination of itaconic acid content in the copolymers. Both elemental analysis of C and H [1] and acid-base titration of the copolymer sodium salt [2] in the presence of indicator seem to be not very precise. More precise results were obtained by the potentiometric titration of the copolymer potassium salt. However, this method is not suitable for the copolymers with higher content of carboxylic component. Some disadvantages of this method (slow equilibrium achievement, complicated inflection point determination) were removed by the conductometric titration [2–4]. The high-frequency titration [5] seems to be very precise, but this method requires sophisticated equipment.

The above-mentioned methods were carried out in an aqueous medium. It means that they can be used only for polymers partly or fully water-soluble. The copolymers containing low amount of itaconic acid are not water-soluble yet interesting possibilities of the applications need to find suitable conditions for their composition determination.

prepared by esterification of itaconic acid [6]. Styrene (S) and methyl methacrylate (MMA) were washed with aqueous sodium hydroxide solution to remove the inhibitor. After drying over anhydrous calcium chloride, monomers were twice distilled under reduced pressure in an argon atmosphere. 1,4-Dioxane was distilled at 101 °C. Methanol, potassium hydroxide, and oxalic acid were of anal. grade.

The copolymers of styrene with itaconic acid P(S-co-IA) were prepared by the emulsion polymerization initiated by a redox system (potassium persulfate and sodium dithionite) at 40 °C. The copolymers of MMA with IA P(MMA-co-IA) and of MMA with MI P(MMA-co-MI) were prepared through the solution polymerization in 1,4-dioxane initiated with AIBN at 40 °C.

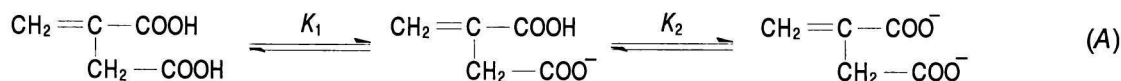
Potentiometric titrations of the copolymers were carried out in nitrogen atmosphere using a pH-meter OP-208/1 (Radelkis) with a combined glass electrode OP-080801 (Radelkis). The mass concentration of the copolymers in the dioxane–methanol mixture (volume ratio = 5 : 1) was 2 mg cm⁻³. The methanolic solution of potassium hydroxide with the amount of substance concentration 0.01 mol dm⁻³ was used as a titrant.

EXPERIMENTAL

Itaconic acid (Pfizer) was recrystallized from the acetone–water mixture. 4-Methyl itaconate (MI) was

RESULTS AND DISCUSSION

Itaconic acid is a dicarboxylic acid with the following values of equilibrium constants: $K_1 = 1.40 \times 10^{-4}$ and $K_2 = 3.56 \times 10^{-6}$ [7].



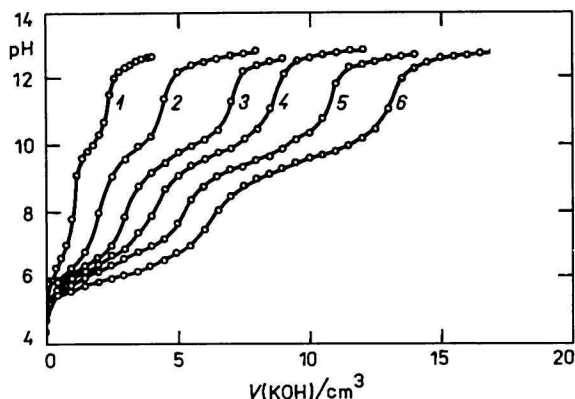


Fig. 1. Potentiometric titration of IA in methanol with 0.0105 M-KOH. Mass concentration of IA ρ (mg cm⁻³): 1. 4.3×10^{-2} , 2. 8.7×10^{-2} , 3. 13.0×10^{-2} , 4. 17.3×10^{-2} , 5. 21.6×10^{-2} , 6. 26.0×10^{-2} .

The potentiometric acid-base titration of IA in the methanolic medium gives titration curves with two inflection points. They correspond to the gradual neutralization of both carboxylic groups (Fig. 1). The titration makes possible to determine the IA content using both inflection points to an accuracy of ± 0.05 mg (Table 1). The calibration of this determination can be expressed by the following equation

$$m'(IA) = a + bm(IA) \quad (1)$$

$$a = (0.0 \pm 0.1) \text{ mg} \quad (2)$$

$$b = 1.00 \pm 0.02 \quad (3)$$

$(r = 0.9991)$

where $m'(IA)$ is the mass of IA in mg determined by the titration and $m(IA)$ is the mass of IA in mg weighted for the titration.

Table 1. Potentiometric Titration of IA in Methanol with 0.0105 M-KOH

$m(IA)$ mg	$V_1(KOH)$ cm ³	$V_2(KOH)$ cm ³	$m'_1(IA)$ mg	$m'_2(IA)$ mg
7.8	5.74	11.58	7.84	7.91
6.5	4.77	9.58	6.52	6.54
5.2	3.83	7.65	5.23	5.22
3.9	2.98	5.85	4.07	3.99
2.6	2.00	3.93	2.73	2.68
1.3	0.94	2.00	1.28	1.36

1 — calculated from the first inflection point; 2 — calculated from the second inflection point.

The presence of carboxylic groups in the IA containing copolymers enables to determine their composition on the basis of the direct acid-base potentiometric titration. The method requires to prepare the copolymer solution in an appropriate solvent in which the pH change is measurable. The mixture of 1,4-dioxane and methanol in the volume ratio 5 : 1 has been found the most suitable medium

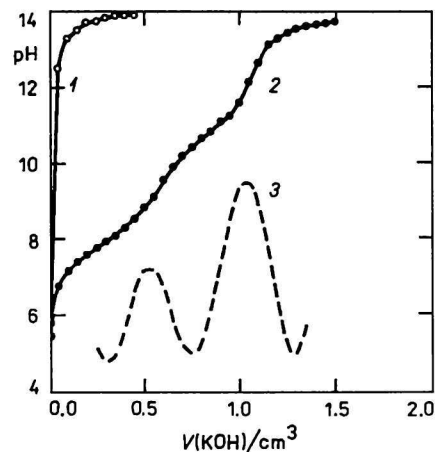


Fig. 2. Potentiometric titration of P(S-co-IA) (0.0490 g) in nonaqueous solution with 0.0109 M-KOH. 1. Blank, 2. polynomial, 3. the first derivation.

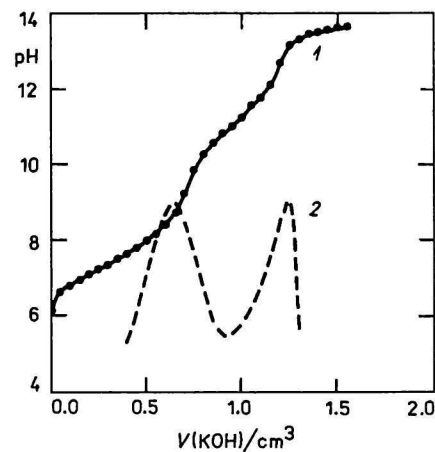


Fig. 3. Potentiometric titration of P(MMA-co-IA) (0.0424 g) in nonaqueous solution with 0.0109 M-KOH. 1. Polynomial, 2. the first derivation.

for the titration. The addition of methanol at the beginning of titration was essential to increase the medium polarity. At these conditions the titration curves with clear inflections were obtained despite of a low concentration of the copolymer samples and titrant. The inflection point position was numerically estimated from the titration curves using the polynomial. Consumption of the titrant in an equivalent point was evaluated from the first derivation maximum.

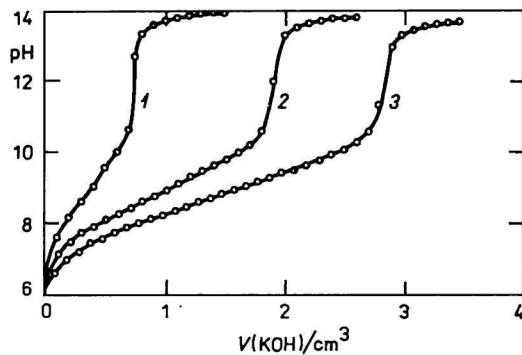
The titration curves of the P(S-co-IA) and P(MMA-co-IA) are depicted in Figs. 2 and 3. From the data in Table 2 it can be seen that this method gives sufficiently precise results with respect to the determination of relatively small amount of IA in the copolymers.

The presence of free carboxylic group was employed for the composition determination of the copolymers containing IA monoesters as well. The

Table 2. Determination of IA in P(S-co-IA) (0.0490 g) and P(MMA-co-IA) (0.0424 g) with 0.0109 M-KOH

Copolymer	$V_1(\text{KOH})$	$V_2(\text{KOH})$	$w_1(\text{IA})$	$w_2(\text{IA})$
	cm^3	cm^3		
P(S-co-IA)	0.54	1.10	0.016	0.016
P(MMA-co-IA)	0.65	1.25	0.022	0.021

1 — calculated from the first inflection point; 2 — calculated from the second inflection point; w — mass fraction of IA in copolymer.

**Fig. 4.** Potentiometric titration of P(MMA-co-MI) in nonaqueous solution with 0.0105 M-KOH. Mass concentration of P(MMA-co-MI) $\rho/(\text{mg cm}^{-3})$: 1. 13.8×10^{-2} , 2. 36.9×10^{-2} , 3. 55.4×10^{-2} .**Table 3.** Determination of MI in P(MMA-co-MI) with 0.0105 M-KOH

$m(\text{P(MMA-co-MI)})$	$V(\text{KOH})$	$m'(\text{MI})$	$w(\text{MI})$
mg	cm^3	mg	
4.15	0.69	1.05	0.254
11.07	1.88	2.86	0.258
16.61	2.80	4.26	0.257

w — mass fraction of MI in copolymer.

titration curves of P(MMA-co-MI) are in Fig. 4. As can be seen from the results in Table 3, this method is precise enough to characterize even the composition of this type of copolymers.

CONCLUSION

The method of potentiometric titration in a nonaqueous medium was purposed with the aim to determine the composition of copolymers containing itaconic acid and its monoesters, respectively. These copolymers were insoluble in water. A mixed solvent used for the titration enables both, using a low concentration of the sample and solubilization of the copolymer salt formed over titration. The titration curves showing the clear inflection were obtained. An equivalent point of the titration was numerically estimated. The proposed method is rather simple and requires only small amount of the sample. The relative error calculated from the parallel measurements was up to 5 %.

REFERENCES

1. Fordyce, R. G. and Ham, G. E., *J. Am. Chem. Soc.* 69, 695 (1947).
2. Exner, J. and Bohdanecký, M., *Chem. Listy* 48, 483 (1954).
3. Hen, J., *J. Colloid Interface Sci.* 49, 425 (1974).
4. Crisp, S., Lewis, B. G., and Wilson, A. D., *J. Dent. Res.* 54, 1238 (1975).
5. Drouglas, J., Timnick, A., and Guille, R. L., *J. Polym. Sci., A 1*, 1609 (1962).
6. Cowie, J. M. G. and Zia Haq, *Br. Polym. J.* 1977, 241.
7. Tate, B. E., in *Encyclopedia of Chemical Technology*, Vol. 13. (Kirk, R. E. and Othmer, D. F., Editors.) P. 865. Wiley, New York, 1981.

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