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Monomer reactivity ratios of itaconic acid and acrylamide copolymers determined by using potentiometric titration method

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Abstract

Itaconic acid (methylene succinic acid)–acrylamide (IA–AAm) copolymers were synthesised with solution polymerisation by using potassium persulphate. The potentiometric titration method was used to determine the copolymer compositions. The results were evaluated by various methods. The monomer reactivity ratios were found to be $r_{\mathrm{IA}} = 0.99 \pm 0.04$, $r_{\mathrm{AAm}} = 0.58 \pm 0.02$ with the Fineman–Ross, $r_{\mathrm{IA}} = 1.05 \pm 0.10$, $r_{\mathrm{AAm}} = 0.62 \pm 0.06$ with the Kelen–Tüdös, and $r_{\mathrm{IA}} = 1.36 \pm 0.11$, $r_{\mathrm{AAm}} = 0.77 \pm 0.06$ with the Tidwell–Mortimer methods. As expected, IA is found to be the more reactive monomer in IA–AAm copolymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactivity ratio; Itaconic acid; Acrylamide; Copolymers; Potentiometric titration

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1. Introduction

The understanding of copolymerisation kinetics has gained great importance over the last two decades. Because of this fact, the prediction of monomer reactivity ratios becomes a valuable quantitative aspect. In general, the method employs low conversions in copolymerisation reactions, and then, the instantaneous copolymer composition for a pair of monomers is found.

Acrylamide (AAm) can easily polymerise by the free-radical polymerisation technique in aqueous solution media. There are several published works on the monomer reactivity ratios of AAm with a number of vinyl monomers [1–3]. On the other hand, it is known that itaconic acid (methylene succinic acid) (IA) homopolymers with high conversions and molecular weights are difficult to obtain; however, IA is more reactive in its copolymers [4–7].

The pH of the system during copolymerisation, the polymerisation method employed, and homogeneity of the system have been shown to effect the values of reactivity ratios of IA–AAm copolymerisation reactions [7–9]. It is known that the reactivity of acrylamide monomers as well as acidic monomers reacting with acrylamide increase with increasing pH [10–12].

PIA is a polyelectrolyte formed from weakly acidic repeating units, IA ($\mathrm{p}K_1 = 3.85$, $\mathrm{p}K_2 = 5.45$) [13]. The quantitative determinations of this type of polyacids have been studied experimentally by the use of potentiometric and conductometric titration methods. Reactivity ratios of itaconic acid with most of the monomers have been measured systematically in nonaqueous, unbuffered solutions [14–20].

In this work, the reactivity ratios of IA–AAm copolymers are determined by using the potentiometric titration method to obtain copolymer compositions. The copolymer samples are synthesised by free-radical polymerisation in aqueous solutions with a wide range of initial monomer compositions. All copolymerisation reactions are allowed to proceed to low conversion (<15%) only.

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Table 1
The polymerisation conditions and copolymer compositions obtained from potentiometric measurements data for the IA–AAm copolymers

Copolymer no.	Initial monomer composition of itaconic acid (f_{IA})	Conversion (%)	Copolymer composition of itaconic acid (F_{IA})
1	9.84	13.80	0.16
2	21.40	5.45	0.23
3	35.31	8.89	0.40
4	52.21	4.52	0.65
5	73.20	2.42	0.75

2. Experimental

2.1. Synthesis

Copolymers with five different initial compositions are synthesised by a procedure described earlier [20]. The characteristics of the samples are given in Table 1.

2.2. Potentiometric titration method

The monomer reactivity ratios of purified polymers are determined by the potentiometric titration method. The WTW 523 model pH meter is used for the potentiometric measurements.

Potentiometric titrations are carried out in a glass cell kept at a constant temperature of 25°C. For each titration experiment, the cell is filled with 30 ml 0.1 N NaCl solution in which 0.1 g of the solid polymer was dispersed by magnetic stirring. After the polymer is completely dissolved, the solution is titrated with 0.1 N NaOH, which is added from a microburette. The pH values observed are plotted versus the millilitres of titrant. Compositions of copolymers and monomer reactivity ratios were determined from the inflection points in the titration curves.

3. Results and discussion

3.1. Copolymer composition analysis by potentiometric titration

The copolymer composition for the system involving IA, which contains two carboxylic acid groups, is ascertained by potentiometric titration of the acidic comonomer. For this purpose, mixtures of homopolymers of PAAm and PIA are prepared with different compositions. The titration volumes corresponding to the last inflections of the potentiometric titration curves of these mixtures in aqueous solution are plotted against the contents of PIA to make a calibration curve (Fig. 1). Then the inflection points of the potentiometric titration curves of the copolymers (Fig. 2) are put on the reference curve (Fig. 1) to estimate the acidic comonomer content in the copolymers and the copolymer composition is found directly from this curve. The results are given in Table 1.

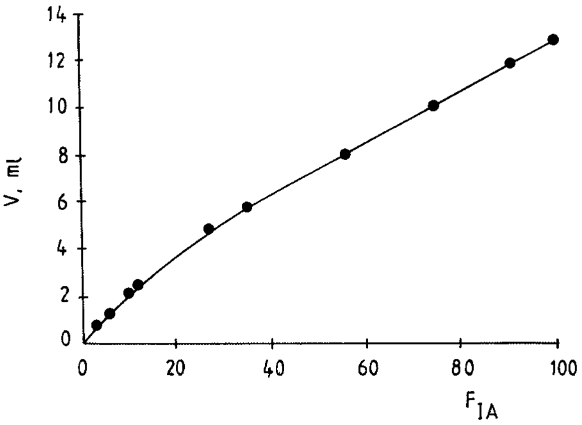

Fig. 1. Calibration curve used to obtain copolymer compositions, where *V* corresponds to the last inflection point of the potentiometric titration curve.

3.2. Monomer reactivity ratios

Several different methods are applied to the experimental results to calculate the monomer reactivity ratios. The linear analysis of the data used included the Finemann–Ross [21], Mayo–Lewis [22,23], Kelen–Tüdös [24], and to consider the effect of conversion, extended Kelen–Tüdös [23,25] methods. The results obtained from each of these methods are tabulated in Table 2. Improved non-linear least squares method for calculating the reactivity ratios of copolymers (as outlined by Tidwell–Mortimer [23,26,27]) is also applied to these data (Table 2).

Table 2 shows the variations between the values obtained by using different methods in determining monomer reactivity ratios. The precision of the experimentally determined monomer reactivity ratios depends on the experimental design and technique used to analyse the data. The non-linear least square analysis is a more precise method than other commonly used ones from a statistical point of view.

4. Conclusions

The samples used to calculate the reactivity ratios of IA and AAm are synthesised in aqueous solutions. Initial pH values of polymerisation solutions are in the acidic range (pH ≅ 3–5). It is known that the amount of itaconic acid entering the polymer depends strongly on

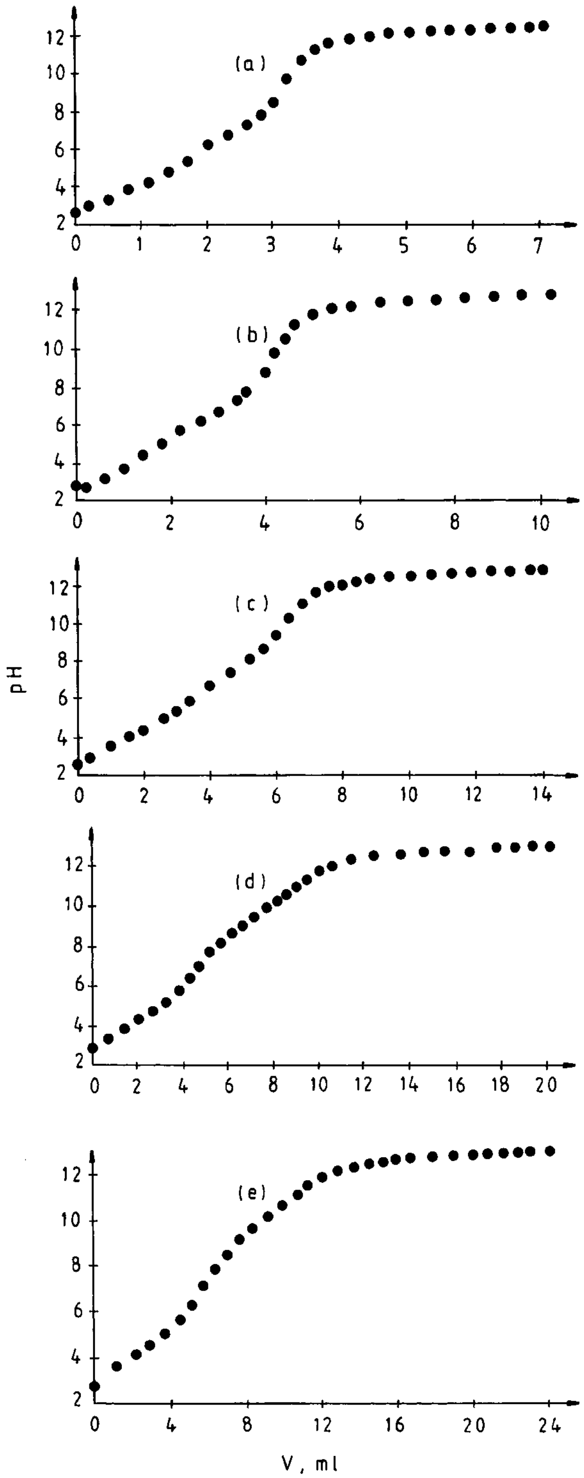

Fig. 2. Potentiometric titration curves of copolymers containing IA: (a) 9.84, (b) 21.40, (c) 35.31, (d) 52.21, and (e) 73.20 mol% in the feed (f_{IA}).

Table 2
Results of the monomer reactivity ratios calculated by using various methods

Method	r_{IA}	r_{AAm}
Finemann–Ross [21]	0.99 ± 0.04	0.58 ± 0.02
Mayo–Lewis [22,23]	1.38 ± 0.22	0.81 ± 0.10
Kelen–Tüdös [24]	1.05 ± 0.10	0.62 ± 0.06
Extended Kelen–Tüdös [23,25]	1.02 ± 0.11	0.59 ± 0.06
Tidwell–Mortimer [23,26,27]	1.36 ± 0.11	0.77 ± 0.06

the pH. The extent of ionisation of the acidic comonomer increase, and the content of the ionisable component in the copolymer decrease with an increase in the pH of the reaction mixture [7,10–12].

According to these experimental and literature results, the growing radical of the IA is found to have a greater affinity towards its own monomer unity, and the growing comonomer radical AAm also seems to prefer to combine with the IA, as is shown in all the methods used either linear or non-linear. This is the same result as the one previously reported, where copolymer compositions were calculated by the conductometric titration method [20]. In this case, the monomer reactivity ratios were found to be $r_{IA} = 1.25 \pm 0.10$, $r_{AAm} = 0.67 \pm 0.05$ with the Kelen–Tüdös, and $r_{IA} = 1.65 \pm 0.21$, $r_{AAm} = 0.88 \pm 0.08$ with the Tidwell–Mortimer methods. If the results obtained from the linear or non-linear methods are compared, it is observed that the type of experimental technique affects the calculated reactivity ratio values. The results obtained from potentiometric and conductometric techniques differ by about 20% in r_{IA} and 10% in r_{AAm}.

Fundamentally, it is known that in the case of the conductometric method, conductivity values in the vicinity of the equivalence point had no important effect on the construction of the graph, which consists of two straight lines intersecting at the inflection point. In other words, equivalence points on the conductivity curves are expected to be determined more accurately than the potentiometric counterparts.

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