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FURTHER IMPROVEMENT TO THE ANALYTICAL SOLUTION OF BINARY COPOLYMER COMPOSITION EQUATION AND SUGGESTED PROCEDURE FOR DERIVING MONOMER REACTIVITY RATIOS

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ABSTRACT

The previously published analytical method of Joshi and Joshi [1] has been improved by incorporating the principle of self-regression. The applicability of this procedure in estimating reactivity ratios from copolymerization experimental data has been demonstrated for two representative cases.

INTRODUCTION

In the previously published analytical procedure [1] for obtaining parameters r_1 and r_2 of the differential binary copolymer composition equation, a least square procedure was adopted, giving equal weight to all the experimental lines of Mayo Lewis (ML) plot. In this paper we improve this procedure by using self regression analysis (SRA) which takes into account errors in the independent variable (M_2) and the dependent variable (m_2). The suggested SRA procedure also gives appropriate weight to each experimental line of the ML plot as opposed to equal weight to all lines in the previous method. This method could well be extended to other methods of estimating reactivity ratios which are based on linearization of the copolymer composition equation [2]

$$\frac{dM_1}{dM_2} = \frac{m_1}{m_2} \cdot \frac{r_1 m_1 + m_2}{r_2 m_2 + m_1} = \frac{m_1}{m_2} \tag{1}$$

or a modified form of equation (1). Here, M_2 and m_2 are the mole fractions of monomer-2 in the feed and the copolymer respectively and r_1 and r_2 are the monomer reactivity ratios (MRR).

RESULTS AND DISCUSSION

In our earlier paper, an absolute analytical procedure was suggested for obtaining reactivity ratios of the binary copolymer system using ML plot [1]. In that procedure, each experiment represents one line on the r_1 v/s r_2 Mayo-Lewis plot [2]. Ideally, all the lines corresponding to various experiments should pass through a single point, coordinates of which would represent the reactivity ratios of the concerned system. Practically, the MRR for a given comonomer pair are the coordinates of the point which gives a minimum square total of perpendicular distance from all the N experimental lines on the ML plot. The governing equation for the reactivity ratios is given by equations 2-5 of reference [1].

Suggested Self Regression Analysis

In SRA, one of the N lines (i^{th} line with slope m_i and intercept c_i say) of the ML plot is eliminated. Using the remaining N-1 lines, r_1 and r_2 values can be estimated by the earlier Joshi-Joshi method [1] by minimizing the square total of perpendicular distance. The coordinates of this point can be denoted by ($r_{1\ N\text{-}1}$, $r_{2,\ N\text{-}1}$). Next, two new lines each passing through ($r_1 N_{\text{-}1}$, $r_{2,\ N\text{-}1}$) are generated as follows. One of the new lines has slope m_i and a new intercept, while the other has intercept c_i and a new slope. Thus, two new lines are generated for each eliminated line.

This elimination procedure is repeated for all the N lines, thereby generating 2N new lines. This stage is termed as the first self-regression.

In the second self-regression, the same elimination procedure is repeated for each of the new 2N lines to generate further 4N new lines. Such a self-regression procedure is repeated till all the generated new lines pass through a single point. The coordinates of this single point would correspond to the MRR of the copolymerization system under study wherein, appropriate weight is given to each exper-

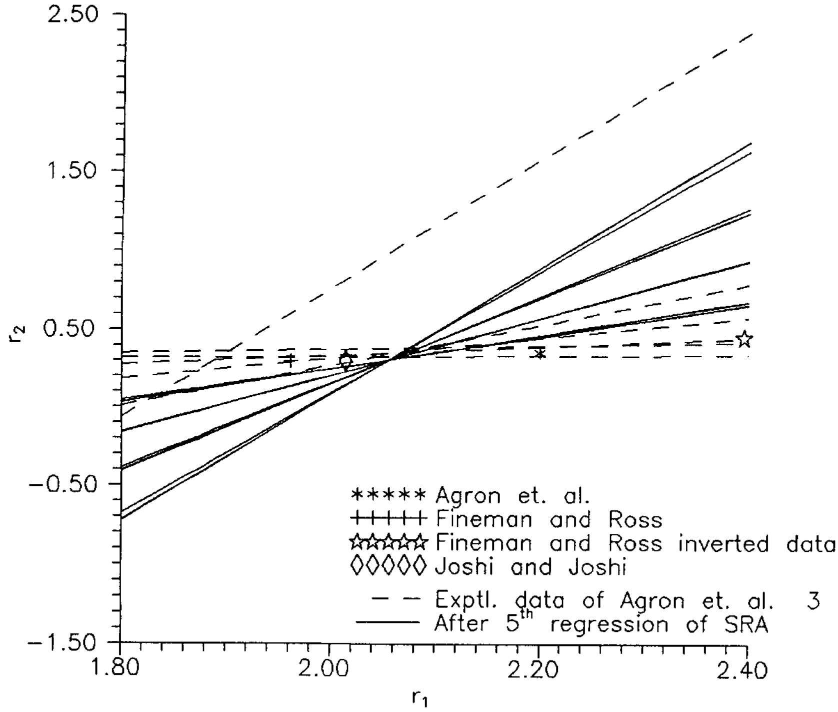

Figure 1. Mayo-Lewis plot showing copolymerization data of Agron *et al.* [3] and estimated monomer reactivity ratios by Agron et al [3], Fineman and Ross [5], Joshi and Joshi [1] and SRA method.

imental line with reference to all other experimental lines. The line with most error is automatically given least weight in the suggested SRA. Application of this procedure to experimental copolymerization data will now be presented.

Application of SRA to Experimental Data

We have used copolymerization experimental data of Agron et al [3] for the system Ethyl methacrylate (M_1) and Vinylidiene chloride (M_2) which was also used for the Joshi-Joshi method [1]. Figure 1 shows the ML plot and estimated values of $r_1$and r_2 by Agron et al [3], Fineman and Ross [5], Joshi and Joshi method [1] and the lines generated by the SRA method after the 5th regression. Due to presentation constraints, only some of the linesgenerated after the 5th iteration of SRA are shown in Figure 1. However, all the lines do indeed pass through a single point. As is evident from Figure 1, the SRA method generated lines which all pass through a

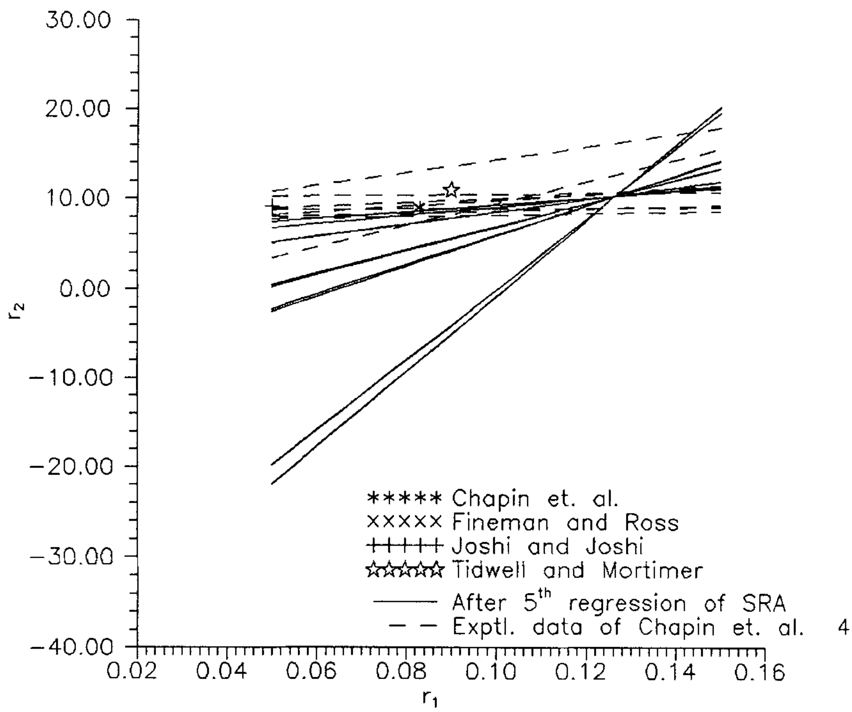

Figure 2. Mayo-Lewis plot showing copolymerization data of Chapin et al [4] and estimated monomer reactivity ratios by Chapin et al [4], Fineman and Ross [5], Joshi and Joshi [1], Tidwell and Mortimer [6] and SRA method.

single point which agrees favorably with the reactivity ratios estimated by the other methods. When the SRA method was applied to inverted data of Agron *et al.* [3], the lines generated after the 5th iteration intersected at (2.13, 0.326) while in Figure (1) the lines intersect at (2.055, 0.303). The good agreemeny in these two estimates shows the suitability of incorporating the SRA procedure in estimating monomer reactivity ratios.

As another example, we analyzed the copolymerization experimental data for the system Vinyl chloride *(M_1)* and Methyl acrylate *(M_2)* taken from the work of Chapin et al [4]. The ML plot for this system is shown in Figure 2. Here also, the agreement of the SRA method with the reactivity ratios estimates by other methods (Chapin et al [4], Fineman and Ross [5], Joshi and Joshi [1], Tidwell and Mortimer [6]) is seen to be favorable.

Recently, Rossignoli and Duever [7] have reviewed various methods of estimating reactivity ratios. Application of SRA procedure to experimental and computer simulated copolymerization data and comparison of these estimates with various methods like nonlinear least squares and error-in-variable analysis is under communication [8].

CONCLUSION

Self- regression analysis can be efficiently applied to the analytical solution of binary copolymer equation for improving the previously published procedure [1] of calculating reactivity ratios. This SRA procedure is relatively simple to incorporate in any parameter estimation procedure. The SRA method has been shown to be effective in accurate estimates of reactivity ratios from experimental copolymerization data using the ML plot.

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