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EXPERIMENTAL INVESTIGATION OF TERNARY AZEOTROPY IN THE COPOLYMERIZATION OF ACRYLONITRILE, STYRENE, AND MALEIC ANHYDRIDE

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ABSTRACT

The nonexistence of various points of ternary azeotropy calculated for the donor-acceptor terpolymer system acrylonitrile, styrene, and maleic anhydride, published in the literature, is demonstrated by gas chromatographic residual monomer analysis.

INTRODUCTION

The problem of ternary azeotropes has been extensively considered in the literature [1-8] without, however, sufficient experimental investigation.

Contradictory results concerning the existence and position of the point of ternary azeotropy have been published for the donor-acceptor copolymer system acrylonitrile (AN)/styrene (St)/maleic anhydride (MA). For the system investigated, Wittmer et al. [1] calculated an azeotrope at (0.92/49.79/49.28) mol%, and Jenner and Kellou [7] computed values at (18/50/32) and (22/40/38) mol%. Calculations by Ham [2] and by us [9] have shown that the only possible way to obtain points of ternary azeotropy is to use the

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Alfrey-Goldfinger equation [10], but that is not valid for the present system [2, 11]. The results in Ref. 7 are not reproducible. In order to prove our conclusions in Ref. 9, this paper deals with an experimental check of the points calculated for ternary azeotropy by using gas chromatographic determination of the residual monomer concentrations.

EXPERIMENTAL

Polymerization

The polymerization of the system AN/St/MA was carried out at a total monomer concentration of 8 mol/L in butanone-2 at 60°C under N_2. The initiator was 0.02 mol/L AIBN. The initiator and the monomers were purified by the usual methods. The conversion was less than 7%, and the terpolymer composition was determined by elemental analysis.

Gas Chromatography

The polymerization conditions were the same, except that 1,4-dioxane was the solvent (the peak of this solvent does not interfere with the peaks of the monomers), and the monomer concentration was 2 mol/L.

At a certain conversion, a sample was taken and injected into a gas chromatograph (Chromatron). The polymer was separated in a high-temperature cell inserted ahead of the column. The column was packed by Sterchamol 93 coated with poly(ethylene glycol) and KOH in 5:2 wt% ratio. H_2 was used as carrier gas, and a thermal conductivity detector was used. The peak areas were integrated by a data station AG 4000.

RESULTS AND DISCUSSION

Figure 1 shows terpolymer compositions of the system AN/St/MA obtained by systematic variations of the monomer feed composition. These experimental results indicate that the azeotrope, if such a point really exists for the present system, should be found at low AN contents and at a St/MA ratio of approximately 1:1. Therefore, the ternary azeotropes AN/St/MA reported by Jenner and Kellou [7] do not seem to reflect reality. The value calculated by Wittmer et al. [1] using the Alfrey-Goldfinger equation cannot be excluded by the experimental results represented in Fig. 1. However, a comparison of

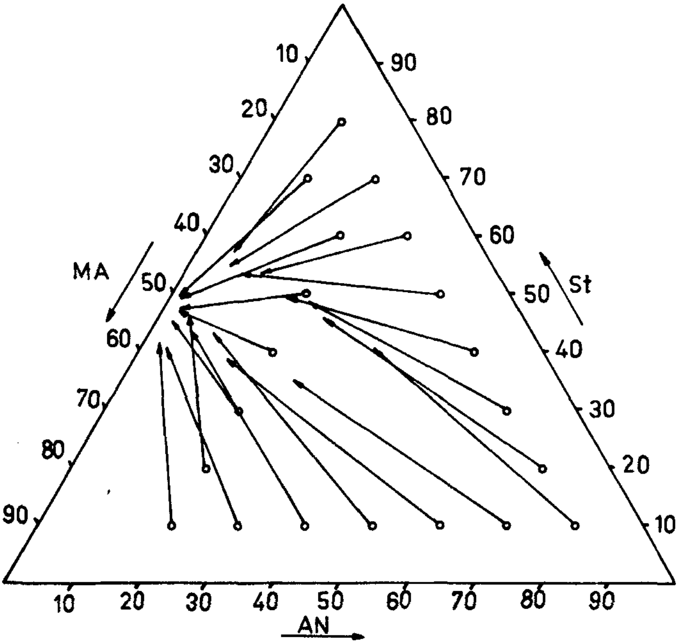

FIG. 1. Plot of experimentally determined terpolymer compositions as functions of the monomer feed compositions. The open circles represent the monomer feed compositions and the ends of the arrows are the polymer compositions.

copolymer compositions calculated by the Alfrey-Goldfinger equation for the same feed compositions (Fig. 2) shows clearly that this equation does not describe the polymerization behavior of this system. This is discussed in detail by Sandner, Klug, and Groebe [11].

In order to support or to reject the calculated ternary azeotropes by experimental investigation, we observed the dependence of the residual monomer composition on the conversion for several monomer mixtures, particularly for the calculated azeotropes published in the literature. Such azeotropes are characterized by constant residual monomer composition over the whole range of conversion.

In order to get statistically reliable results, the residual monomer composition for every monomer feed composition and every conversion was deter-

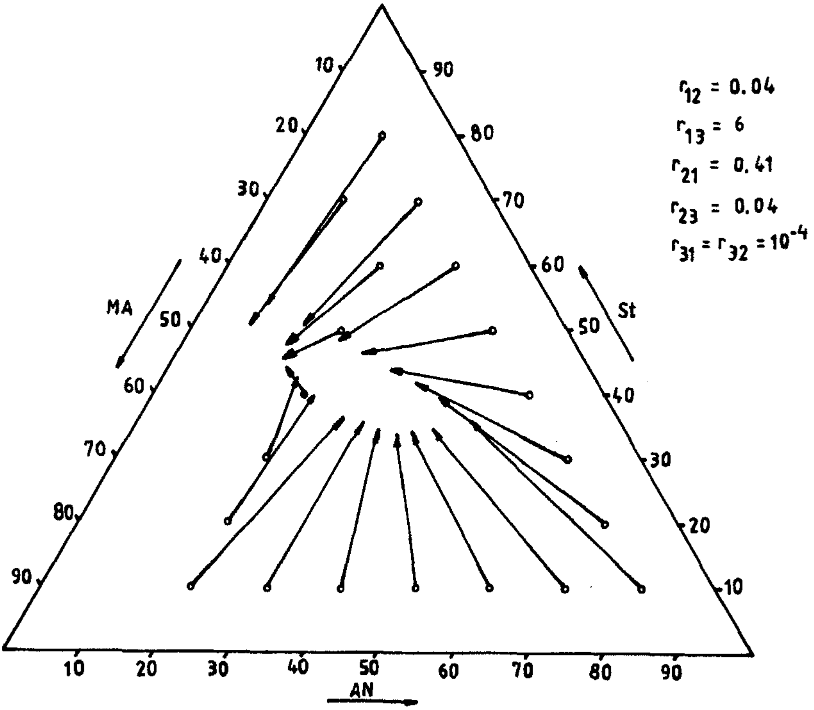

FIG. 2. Plot of terpolymer compositions calculated by the Alfrey-Goldfinger equation [10] as functions of the monomer feed compositions. The open circles represent the monomer feed compositions and the ends of the arrows are the polymer compositions.

mined at least three times by gas chromatography. To obtain a quantitative expression, we plotted the logarithm of the ratio of peak areas, St/AN, versus the corresponding conversion (Fig. 3). Such plots result in approximately straight lines (correlation coefficients greater than 0.965). The MA contents in the monomer mixture are not investigated in this paper. The slopes of the lines in Fig. 3 were submitted to a 95% significance test (error probability 5%). The monomer compositions studied, the straight lines slopes observed, and the confidence limits of these slopes are summarized in Table 1.

The applicability of this procedure is demonstrated for the well-known binary azeotrope AN/St (38.5/61.5) mol%. Line (a) in Fig. 3 illustrates the

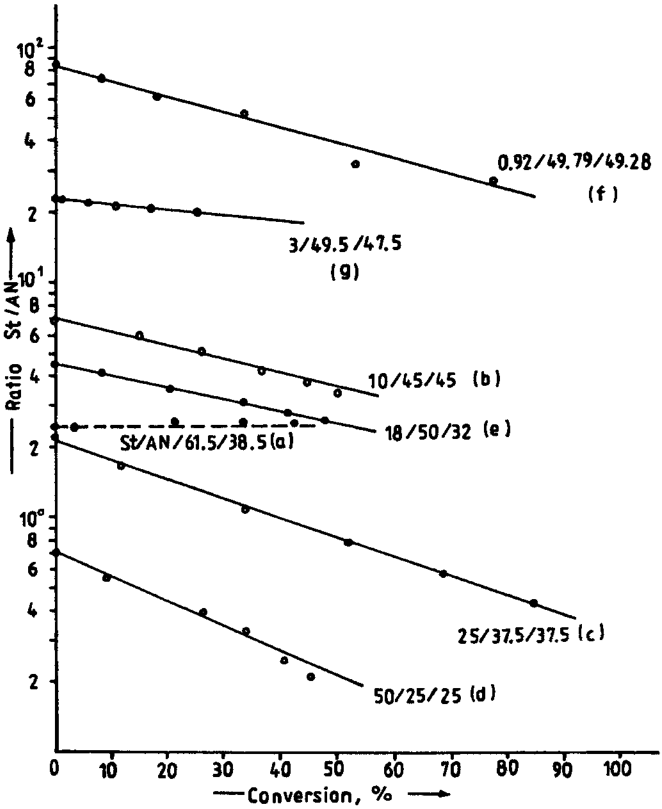

FIG. 3. Peak area ratios for residual St/AN (determined by gas chromatography) as functions of conversion for terpolymerization of AN/St/MA.

almost constant residual monomer composition up to high conversions. The confidence limits show that this slope is zero with a statistical certainty of 95%.

Curves (b), (c), and (d) were obtained by terpolymerization experiments with equimolar quantities of St and MA in the monomer feed. An increasing dependence of the residual monomer composition on the conversion can be observed with increasing AN content in the monomer mixture. Slopes significantly different from zero are also obtained in cases (e), (f), and (g), in which the azeotropes calculated by Jenner [7] and Witmer [1] and by us [9]

TABLE 1. Terpolymerization Data for the System AN/St/MA (see Fig. 3)

	Monomer feed composition AN/St/MA, mol%	Straight line slope X 10^3	Confidence limit of the slope X 10^3 (95% significance level)
a	38.5/61.5/0.0	0.474	±1.36
b	10.0/45.0/45.0	-14.3	±1.04
c	25.0/37.5/37.5	-19.5	±0.552
d	50.0/25.0/25.0	-25.9	±1.94
e	18.0/50.0/32.0	-12.4	±0.878
f	0.92/49.79/48.28	-16.0	±1.46
g	3.0/49.5/47.5	-5.67	±0.94

(using the method of O'Driscoll [3]) on the basis of the complete terpolymerization equation [10] are checked experimentally. Both Jenner's and Wittmer's mixtures show distinctly changing residual monomer compositions, even at low conversions, i.e., both mixtures are not behaving azeotropically. The last conclusion applies also for the point calculated by us [9]. Although the slope of curve (g) is much less than the others, it is also significantly different from zero with a statistical certainty of 95%.

CONCLUSIONS

It is demonstrated that application of commonly used calculations of ternary azeotropes without testing of experimental validity results in fatal errors.

Calculation of the ternary azeotrope by the valid equations derived by Ham [2] shows no point of azeotropy for the system AN/St/MA.

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