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Computer Program for the Calculation of Ternary Azeotropes

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ABSTRACT

A computer program is described which enables the azeotropic composition of ternary systems to be calculated from known reactivity ratios. Supplementary to this, triangular diagrams showing the dependence of polymer composition on monomer composition may be drawn by a plotter program and give a rapid synopsis of the polymerizing system.

Since the beginning of ternary copolymerization, the possible existence of azeotropes has been a question of great interest. The so-called terpolymerization equation was published by Alfrey and Goldfinger in 1944 [1], and since then many publications have been concerned with the problem of ternary azeotropy [2-10].

For binary copolymerization, there is a simple relationship between the composition of the monomer and the polymer at the azeotropic point. Such is not the case for ternary copolymerizations. For this latter case the mathematical relationships are so complex that no direct solution is possible without the aid of a computer. We here describe a computer program which calculates the azeotropic composition by direct solution of the equations for a ternary azeotrope.*

*The program is available on request.

An early worker in this field was Slocombe [2]. He developed a graphical method in which the composition of the monomer and polymer were shown on the same triangular diagram. The polymer composition is indicated as the point of an arrow which begins at the monomer composition. In the case of an azeotrope, the arrow reduces to a point.

Tarasov et al. [3, 4] first approached the problem mathematically by placing Eq. (2) into Eq. (1) (see below). The three equations so obtained, which contained three unknowns, were modified by several mathematical simplifications to enable the calculation of the azeotropic points for three terpolymerization systems.

Ham [7] obtained a simplified terpolymerization equation from which he concluded that the existence of ternary azeotropes was doubtful [5, 6]. Such a generalization is not of great significance, however, since the conditions he assumed to simplify the terpolymerization equation are only infrequently met [11].

Wittmer et al. [8] investigated over 700 terpolymerization systems for which literature data were available. By an iterative method they found that 37 of the systems contained azeotropic points. It was also noted that ternary azeotropes only exist for systems which contained at least one binary azeotrope.

In contrast to this, Ring [9, 10] concluded that the presence of a binary azeotrope was not a necessary precondition for ternary azeotrope formation.

On the assumption that ternary azeotropes do exist, we have developed a FORTRAN IV computer program which calculates the ternary azeotrope composition from the known reactivity ratios.

The basic equation for all calculations is the aforementioned terpolymerization equation [1]:

$$\frac{m_1}{m_2} = \frac{M_1\left[\frac{M_1}{r_{31}r_{21}} + \frac{M_2}{r_{21}r_{32}} + \frac{M_3}{r_{31}r_{23}}\right]\left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}}\right]}{M_2\left[\frac{M_1}{r_{12}r_{31}} + \frac{M_2}{r_{12}r_{32}} + \frac{M_3}{r_{32}r_{13}}\right]\left[M_2 + \frac{M_1}{r_{21}} + \frac{M_3}{r_{23}}\right]}$$

$$\frac{m_1}{m_3} = \frac{M_1\left[\frac{M_1}{r_{31}r_{21}} + \frac{M_2}{r_{21}r_{32}} + \frac{M_3}{r_{31}r_{23}}\right]\left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}}\right]}{M_3\left[\frac{M_1}{r_{13}r_{21}} + \frac{M_2}{r_{23}r_{12}} + \frac{M_3}{r_{13}r_{23}}\right]\left[M_3 + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}}\right]} \qquad (1)$$

In Eq. (1), r_{ij} ($i \neq j$; $i, j = 1, 2, 3$) are the reactivity ratios for the three binary copolymerizations, while M_i and m_i are, respectively,

the mole fractions of the particular monomer in the monomer mixture and the resultant polymer. The basic condition to be met in an azeotrope is that the monomer and polymer composition are identical, i.e.,

$$m_i = M_i \tag{2}$$

Furthermore, we know that

$$\sum_{i=1}^{3} m_i = 1 \qquad \sum_{i=1}^{3} M_i = 1 \tag{3}$$

Substituting in Eq. (1) from Eqs. (2) and (3) yields two equations of the type

$$a_{11}M_2^2 + a_{12}M_3^2 + a_{13}M_2M_3 + a_{14}M_2 + a_{15}M_3 + a_{16} = 0 \tag{4}$$

$$a_{21}M_2^2 + a_{22}M_3^2 + a_{23}M_2M_3 + a_{24}M_2 + a_{25}M_3 + a_{26} = 0 \tag{5}$$

The a_{xy} terms are constants which contain the six different reactivity ratios.* These equations describe two parabolas which intersect. The intersections in the first quadrant, that is, in the region $0 \leq M_2 \leq 1$ and $0 \leq M_3 \leq 1$, give the compositions of possible azeotropes. Solution of Eqs. (4) and (5) for M_2 and equating the solutions to each other yields four possible equations for M_3. Fortunately, all are identical and may be expressed as

$$e_1M_3^4 + e_2M_3^3 + e_3M_3^2 + e_4M_3 + e_5 = 0$$

The e_i parameters are again composed of the respective reactivity ratios. Four values of M_3 are calculable from this equation and are obtained by the use of a program computing the zeros of a polynomial [12-14]. The values of M_3 obtained which lie between 0 and 1 are substituted into the equations for M_2. The values of M_2 between

*For the case in which one of the reactivity ratios r_{ij} is zero, a very small, finite value must be used, say 10^{-3}. This is apparent from inspection of Eq. (1).

0 and 1 which are obtained in conjunction with those for M_3 give the composition of the ternary azeotrope. As an addition to this program, the triangular diagram of Slocombe may be constructed with the aid of a plotter program. Such a diagram provides a rapid synopsis of the ternary system behavior, the composition of the monomer and the resulting polymer being joined by an arrow. Where the mole fractions of the monomer and polymer are identical to the second decimal place, the compositions are marked by a star which enables facile composition read-off from the diagram. Regions of interest in the diagram may be enlarged by a suitable variation of the parameters which govern the size of the diagram.

As an example of the use of this program, we have calculated the azeotropic composition for the system acrylonitrile (M_1)/ethyl

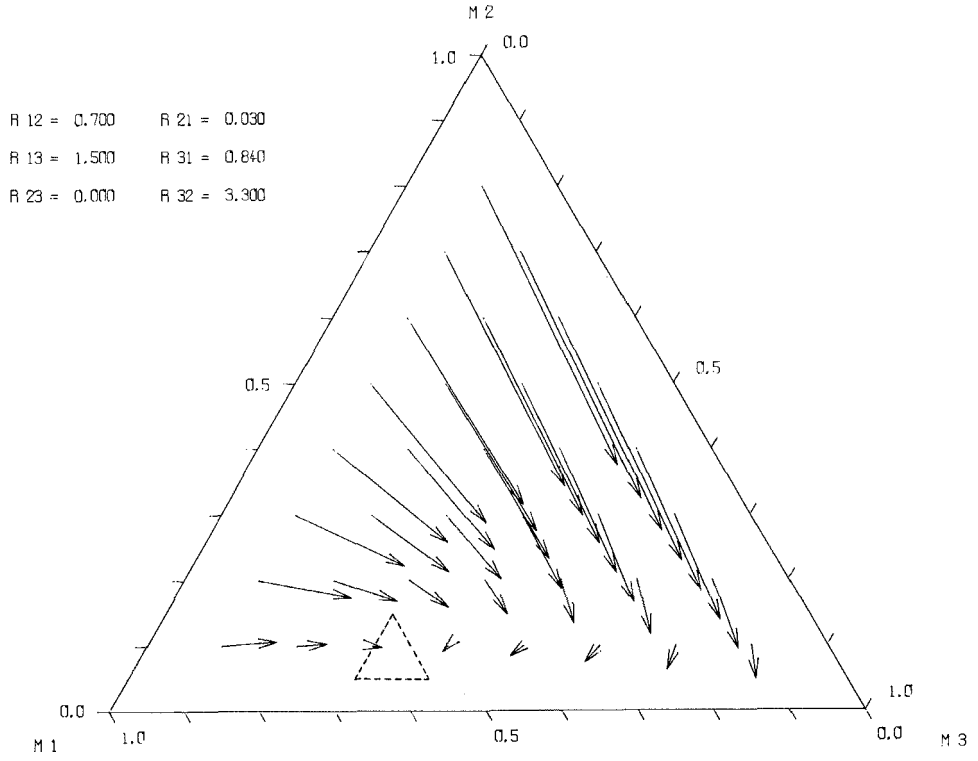

FIG. 1. Triangular diagram for the terpolymerization system acrylonitrile (M_1)/ethyl vinyl ether (M_2)/methyl acrylate (M_3). The dashed triangle is magnified in Fig. 2.

vinyl ether (M_2)/methyl acrylate (M_3), for which the reactivity ratios are

$r_{12} = 0.7$ $r_{21} = 0.03$

$r_{13} = 1.5$ $r_{31} = 0.84$

$r_{23} = 0.0001$ $r_{32} = 3.3$

By the aid of an iterative method, Wittmer et al. [8] calculated the azeotropic composition to be $M_1 = 0.59$, $M_2 = 0.09$, and $M_3 = 0.32$. The same values were obtained using our program. In Fig. 1 we give the Slocombe diagram for this system as obtained using a plotter program. The region enclosed by the dashed lines was redrawn on a magnified scale (Fig. 2) by the program. One can

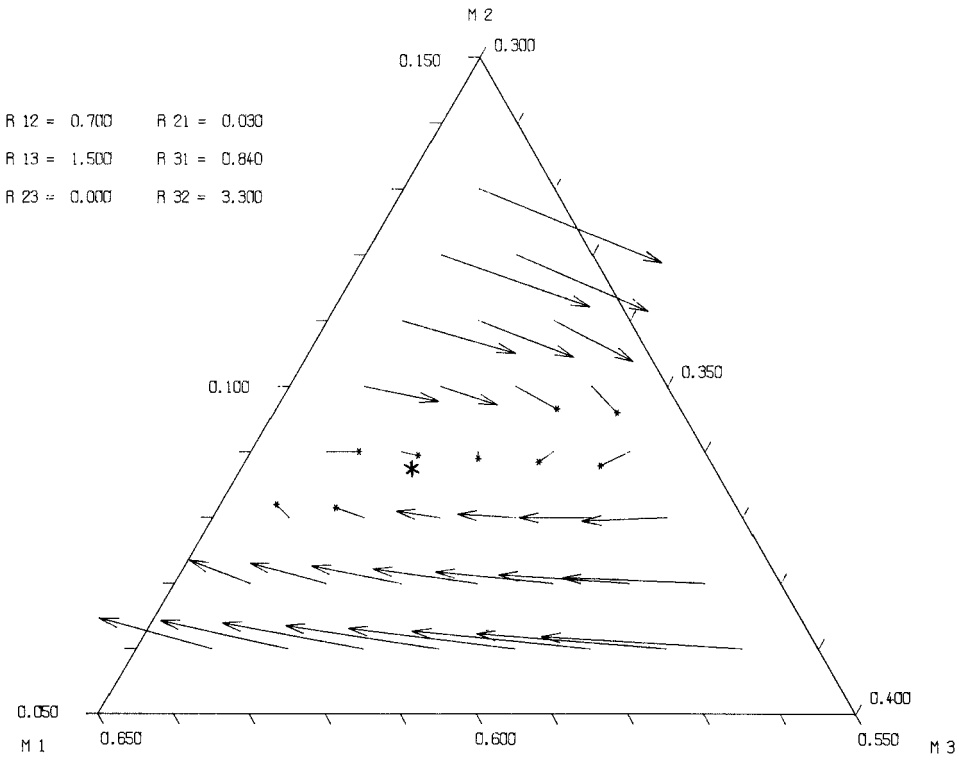

FIG. 2. Magnified triangle from Fig. 1.

clearly see from this diagram that there is a region in which the composition of both polymer and monomer are identical to the second decimal place. Since the use of infinitely variable monomer compositions would complicate the plotter program, certain standard compositions are used in all cases, and it is purely by chance that one of these corresponds to the azeotrope. The true azeotrope for the present system is marked by a cross in Fig. 2.

Azeotropic compositions calculated by our program gave excellent agreement with terpolymerization systems reported in the literature [3, 4, 8]. The advantage of our program is that it utilizes a direct solution of the terpolymerization equation, allowing the composition of the azeotrope (if one exists in the system) to be found in a very short time. Moreover, exclusion of the plotter program saves the time-consuming preparation of the Slocombe diagram.

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