Azeotropy in Terpolymerization

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ABSTRACT

This work deals with the determination of the various azeotropies in radical terpolymerization: unitary azeotropy ($m_i = M_i$); binary azeotropy ($m_i/m_j = M_i/M_j$), and ternary or true azeotropy ($M_j = m_j$ for j = 1, 2, 3). General analytical solutions are given which are easily handled by a computer. In addition, these calculations show the existence of pseudo-azeotropy where the deviation between polymer and monomer feed compositions is very small, not only at the beginning of the reaction, but also with increasing conversion.

INTRODUCTION

In relation to the practical interest of synthesizing copolymers of homogeneous composition. a number of studies have been devoted to the problem of azeotropy, i. e., the possibility of preparing a copolymer whose composition is exactly the same as that of the initial monomer feed. In such a case there would be no compositional drift as the reaction proceeds. This problem can be solved very

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simply in binary copolymerization; however, it is much more complex when the number of monomers is larger than two.

In spite of several attempts, no general solution to the problem of azeotropy in terpolymerization has been given so far. The first answer was proposed by Slocombe [1], who developed a graphical method in which initial monomer composition and terpolymer composition are the two extremities of an arrow on the triangular diagram. One gets closer the azeotrope when the length of the arrow converges finally towards a single point in the case of a true ternary azeotrope. Tarasov et al. [2, 3] first tried to obtain a mathematical solution for ternary azeotropy. They started from the Alfrey-Goldfinger [4] equations, using some simplifications in their calculations to determine the ternary azeotropic point and give criteria for existence of that point which is unique. Wittmer et al. [5], using reactivity ratios given in the literature, found 37 ternary azeotropic compositions for over more than 700 terpolymerization systems studied through a computerized iterative method; they finally concluded that the ternary azeotrope does exist only for systems having, at least, a copolymerization binary azeotrope.

On the contrary, Ring [6, 7], from more rigorous calculations, gave criteria allowing one to assume the existence of ternary azeotropy, whether a copolymerization binary azeotrope is observed or not. Chan et al. [8] used a three-dimensional iterative process to compute the ternary azeotropic composition. Their results are in agreement with those of Tarasov. They also verified on a theoretical basis that the compositions of monomer feed and terpolymer at that composition remain the same up to complete conversion. Ham [9] proposed simplified equations for the determination of the various azeotropies and did conclude that if ternary (true) azeotropy is very unusual, the occurrence of binary (partial in Ham's work) azeotropy is quite frequent. Ham introduced the concept of such an azeotropy where the ratio M_i/M_j in the monomer feed is equal to the ratio m_i/m_j in the copolymer. However, Ham assumed the validity of the following relationship between reactivity ratios:

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21} \tag{1}$$

However, Eq. (1) is a consequence of the Q-e scheme of Alfrey and Price, which is not always valid.

O'Driscoll [10, 11] introduced the concept of limited azeotropy, where the azeotropy is valid for only one of the monomers ($M_i = m_i$). For its determination, it screened all the possible compositions and graphically plotted azeotropic curves for each monomer, using Ham's simplified equations. Wittmer [5] for the same type of

calculation used the equations of Alfrey-Goldfinger. In the following, we call this kind of azeotropy "unitary azeotropy."

Recently, Braun [12] proposed a computer program for the determination of ternary azeotropy from reactivity ratios of the literature. From the equations of Alfrey-Goldfinger, he derived a fourth-degree equation for M_i, resolved by an iterative process that determines the "zeros" of a polynomial.

Dealing with azeotropy in multicomponent copolymerization ($n \geq 3$) Valvassori et al. [13] proposed solutions for true azeotropy ($M_i = m_i$, $i = 1, 2, 3, \ldots, n$) but considering copolymerization equations which are very difficult to use successfully. It seems thus from the literature that no general solution for azeotropy in terpolymerization has been given, but only approximations by iterative processes, on simplified and often oversimplified equations, not always valid.

In this paper, we present for each kind of azeotropy (unitary, binary, or ternary) a general solution based on the terpolymerization equation of Alfrey-Goldfinger, thus consequently valid for each system, with a mathematical development corresponding to the classical solutions of fourth-degree equations (method of Ferrari, see Appendix) or cubic equations (method of Cardan [14]). Computer programs were written in Fortran IV giving the various azeotropic compositions.

In addition, this type of rigorous calculations allows the validity of the assumptions of the previous authors to be discussed. (Computer programs are available on request.)

THEORETICAL

The most general basic equations for terpolymerization, i. e., the relation between terpolymer and monomer feed compositions are those derived by Alfrey and Goldfinger [4] [Eqs. (2) and (3)]:

$$\frac{m_1}{m_2} = \frac{M_1 \left[\dfrac{M_1}{r_{31}r_{21}} + \dfrac{M_2}{r_{21}r_{32}} + \dfrac{M_3}{r_{31}r_{23}} \right] \left[M_1 + \dfrac{M_2}{r_{12}} + \dfrac{M_3}{r_{13}} \right]}{M_2 \left[\dfrac{M_1}{r_{12}r_{31}} + \dfrac{M_2}{r_{12}r_{32}} + \dfrac{M_3}{r_{32}r_{13}} \right] \left[M_2 + \dfrac{M_1}{r_{21}} + \dfrac{M_3}{r_{23}} \right]} \qquad (2)$$

$$\frac{m_1}{m_3} = \frac{M_1 \left[\dfrac{M_1}{r_{31}r_{21}} + \dfrac{M_2}{r_{21}r_{32}} + \dfrac{M_3}{r_{31}r_{23}} \right] \left[M_1 + \dfrac{M_2}{r_{12}} + \dfrac{M_3}{r_{13}} \right]}{M_3 \left[\dfrac{M_1}{r_{13}r_{21}} + \dfrac{M_2}{r_{23}r_{12}} + \dfrac{M_3}{r_{13}r_{23}} \right] \left[M_3 + \dfrac{M_1}{r_{31}} + \dfrac{M_2}{r_{32}} \right]} \qquad (3)$$

where

$$M_i = (M_i) / \sum_1^3 (M_i)$$

is the molar fraction of monomer M_i in monomer feed, and

$$m_i = (m_i) / \sum_1^3 (m_i)$$

is the molar fraction of monomer M_i in the copolymer. The $r_{ij} \neq 0$ are the reactivity ratios, parameters characterizing the reactivity of a given macroradical ($\sim M_i \cdot$) towards monomers, defined as the ratio of rate constants of homo- and copolymerization ($r_{ij} = k_{ii}/k_{ij}$).

Unitary Azeotropy

In this case, the molar amount of one of the three monomers is the same in the copolymer and in the monomer feed:

$$M_i = m_i \tag{4}$$

Let

$$F_1 = M_1 \left[\frac{M_1}{r_{31}r_{21}} + \frac{M_2}{r_{21}r_{32}} + \frac{M_3}{r_{31}r_{23}} \right] \left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right] \tag{5}$$

$$F_2 = M_2 \left[\frac{M_1}{r_{12}r_{31}} + \frac{M_2}{r_{12}r_{32}} + \frac{M_3}{r_{32}r_{13}} \right] \left[M_2 + \frac{M_1}{r_{21}} + \frac{M_3}{r_{23}} \right] \tag{6}$$

$$F_3 = M_3 \left[\frac{M_1}{r_{13}r_{21}} + \frac{M_2}{r_{23}r_{12}} + \frac{M_3}{r_{13}r_{23}} \right] \left[M_3 + \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}} \right] \tag{7}$$

The composition of the terpolymer is now

$$m_i = F_i / \sum_1^3 F_i \tag{8}$$

From Eqs. (4) and (8), one gets for unitary azeotropy

$$\sum_i F_i = F_i/M_i \tag{9}$$

Substituting Eqs. (5)-(7) in Eq. (9) gives:

$$\sum_i F_i = a_{11}M_1{}^3 + a_{12}M_2{}^3 + a_{13}M_3{}^2 + a_{14}M_1{}^2M_2 + a_{15}M_1{}^2M_3$$

$$+ a_{16}M_1M_2{}^2 + a_{17}M_1M_3{}^2 + a_{18}M_2{}^2M_3 + a_{19}M_3{}^2M_2$$

$$+ a_{10}M_1M_2M_3 \tag{10}$$

Thence:

$$F_1/M_1 = a_{21}M_1{}^2 + a_{22}M_2{}^2 + a_{23}M_3{}^2 + a_{24}M_1M_2 + a_{25}M_1M_3$$

$$+ a_{26}M_2M_3 \tag{11}$$

where $a_{1k} = f(r_{ij})$ are functions of the reactivity ratios only. But obviously

$$M_3 = 1 - M_1 - M_2 \tag{12}$$

and finally one gets for monomer M_1:

$$b_{11}M_1{}^3 + b_{12}M_1{}^2 + b_{13}M_1 + b_{14} = 0 \tag{13a}$$

where now b_{1k} are functions of the reactivity ratios (r_{ij}) and of the proportion of monomer M_2. These values are given by Eqs. (14). For $A_{ij} = 1/r_{ij}$:

$$b_{11} = (1 - 2A_{31})(A_{13}A_{21} - A_{13}A_{23}) + A_{31}(A_{21} - A_{23}) \tag{14a}$$

$$b_{12} = A_{13}A_{23}(3 - 4A_{31}) + A_{31}(A_{23} + 2A_{21}A_{13}) + M_2[A_{31}A_{21}(2A_{12} - 3A_{13})$$

$$+ A_{32}A_{13}(2A_{32} - 3A_{21}) + A_{23}A_{12}(1 - 3A_{31}) + A_{21}A_{32} - A_{31}A_{23}] \tag{14b}$$

$$b_{13} = A_{13}A_{23}(4A_{31} - 3) - A_{13}A_{31}A_{21}(1 + 1/A_{21} - 1/A_{31})$$

$$+ M_2\big[A_{31}A_{21}(A_{13} - A_{12}) + A_{21}A_{32}(4A_{13} - 1)$$

$$+ A_{31}A_{23}(1 + 4A_{12} - 6A_{13}) + A_{13}A_{23}(6 - 4A_{32})$$

$$- 2(A_{13}A_{21} + A_{23}A_{12})\big] + M_2^{2}\big[A_{13}A_{23}(4A_{32} + 2A_{31} - 3)$$

$$+ A_{12}A_{31}(1 - 3A_{23}) + A_{13}A_{21}(1 - 3A_{32})$$

$$+ 2A_{12}A_{32}(A_{21} - A_{23}) - A_{32}A_{13} + 2A_{23}A_{12}\big] \tag{14c}$$

$$b_{14} = A_{13}A_{23}(1 - A_{31}) + M_2\big[A_{13}A_{23}(2A_{32} - 3) + A_{23}A_{12}(1 - A_{31})$$

$$+ A_{13}(2A_{31}A_{23} - A_{21}A_{32})\big] + M_2^{2}\big[A_{13}A_{23}(3 - 4A_{13})$$

$$+ (A_{12} - A_{13})(A_{31}A_{23} - A_{21}A_{32}) + 2A_{23}A_{12}(A_{32} - 1) + A_{32}A_{13}\big]$$

$$+ M_2^{3}\big[(A_{12}A_{32} - A_{32}A_{13})(1 - 2A_{23}) + A_{23}(A_{12} - A_{13})\big] \tag{14d}$$

Similarly, c_{1k} (k = 1, 2, 3, 4) are obtained from b_{1k}, permuting in reactivity ratios r_{ij}: i = 1 $\longrightarrow$ i = 2, j = 2 $\longrightarrow$ j = 1; and d_{1k} permuting i = 1 $\longrightarrow$ i = 3, j = 3 $\longrightarrow$ j = 1.

Similarly, one gets for monomer M_2:

$$c_{11}M_2^{3} + c_{12}M_2^{2} + c_{13}M_2 + c_{14} = 0 \tag{13b}$$

and for monomer M_3:

$$d_{11}M_3^{3} + d_{12}M_3^{2} + d_{13}M_3 + d_{14} = 0 \tag{13c}$$

Thus unitary azeotropic compositions for monomer M_1 are the solutions of the cubic equations (13) when M_2 varies from 0 to 1.0 (for physical considerations). The well known method of Cardan has been used to solve this equation analytically, and only positive and real roots are to be considered. Same calculations, of course, are performed for the other monomers M_2 and M_3.

So, if a solution does exist, it is not a point or several points but segments of curves limited in the inner area of the triangular diagram.

Binary Azeotropy

The ratio between amounts of two monomers is the same in the copolymer and in the monomer feed

$$M_i/M_j = m_i/m_j \qquad\qquad i, j = 1, 2, 3 \qquad (15)$$

From Eqs. (5)-(8), and taking into account Eq. (15), one gets for this type of azeotropy

$$F_i/M_i = F_j/M_j \qquad\qquad\qquad (16)$$

Thence, if $i = 1$ and $j = 3$, for instance

$$a_{31}M_1{}^2 + a_{32}M_1M_2 + a_{33}M_1M_3 + a_{34}M_2{}^2 + a_{35}M_2M_3 + a_{36}M_3{}^2 = 0 \qquad (17)$$

or, on dividing by $M_3{}^2$:

$$b_{21}(M_1/M_3)^2 + b_{22}(M_1/M_3) + b_{23} = 0 \qquad\qquad (18a)$$

where b_{2k} are functions of the reactivity ratios (r_{ij}) and of the ratio M_2/M_3. Solutions for binary azeotropy are computed from Eq. (18) as a function of M_2/M_3 ($M_2/M_3 \geq 0$, $M_3 \neq 0$). For physical considerations, only positive real square roots must be considered, and in that case too, the binary azeotropy corresponds to segments of curves in the inner part of the triangular diagram.

The other binary azeotropic compositions are derived from the same type of calculations. For $i = 1$ and $j = 2$:

$$c_{21}(M_1/M_2)^2 + c_{22}(M_1/M_2) + c_{23} = 0 \qquad\qquad (18b)$$

which gives solutions as a function of the ratio M_2/M_3.
For $i = 2$ and $j = 0$:

$$d_{21}(M_2/M_3)^2 + d_{22}(M_2/M_3) + d_{23} = 0 \qquad\qquad (18c)$$

The solution now being a function of the ratio M_1/M_3.
The values of b_{ik} are reported in Eqs. (19) ($i = 3, 4, 5$).

Let $A_{ij} = 1/r_{ij}$

$$b_{21} = A_{31}A_{21} (1 - A_{13}) \tag{19a}$$

$$b_{22} = [A_{21}A_{32} (1 - A_{32}) + A_{31}A_{12} (A_{21} - A_{23})] M_2/M_3$$

$$+ A_{31}A_{23} (1 - A_{31}) + A_{13}A_{21}(A_{31} - 1) \tag{19b}$$

$$b_{23} = A_{32}A_{12} (A_{21} - A_{23})(M_2/M_3)^2$$

$$+ [A_{23}A_{12}(A_{31} - 1) + A_{13}A_{32} (A_{21} - A_{23}] M_2/M_3$$

$$+ A_{13}A_{23}(A_{31} - 1) \tag{19c}$$

Similarly, c_{2k} (k = 1, 2, 3) are obtained from b_{2k} permuting in reactivity ratios: r_{ij} : i = 2 $\longrightarrow$ i = 3; j = 3 $\longrightarrow$ j = 2; and d_{2k} permuting i = 1 $\longrightarrow$ i = 2; j = 2 $\longrightarrow$ j = 1.

Dealing with the same kind of azeotropy, but assuming the generality of the identity (1), Ham [9] derived another set of equations which are linear relationships: :

$$M_1/M_3 = h_{13}(M_2/M_3) + h_{01} \tag{19}$$

$$M_1/M_2 = h_{12}(M_3/M_2) + h_{03} \tag{20}$$

$$M_2/M_3 = h_{23}(M_1/M_3) + h_{02} \tag{21}$$

The values of the coefficients h, which are functions of reactivity ratios only, are reported in Eqs. (22).

$$h_{13} = (A_{12}A_{31} - A_{13}A_{32})/[A_{31} (A_{13} - 1)] \tag{22a}$$

$$h_{01} = A_{13} (A_{31} - 1)/[A_{31} (A_{13} - 1)] \tag{22b}$$

$$h_{12} = (A_{21}A_{13} - A_{12} A_{23})/[A_{21} (A_{12} - 1)] \tag{22c}$$

$$h_{23} = A_{31}A_{21} (A_{13} - A_{12})/(A_{31}A_{12} - A_{32} A_{21} A_{13}) \tag{22d}$$

$$h_{02} = (A_{21}A_{13} - A_{31}A_{12}A_{23})/(A_{31}A_{12} - A_{32}A_{21}A_{13}) \qquad (22e)$$

$$h_{03} = A_{12}(A_{21} - 1)/[A_{21}(A_{12} - 1)] \qquad (22f)$$

As will be seen, these equations give deviations from ours, except for systems which obey the Q-e scheme of Alfrey and Price, which is not generally valid. Nevertheless, it is worth noting that both sets of equations give the same azeotropic composition corresponding to binary copolymerization if such a composition does exist.

Ternary Azeotropy

First, it is to be noted that intersections of unitary azeotropic curves [Eqs. (13)] or of binary azeotropic curves [Eqs. (18)] give graphical solutions for the problem of ternary azeotropy, if any $(0 < m_i < 1$ and $0 < M_i < 1)$. But mathematical calculations appear to be much more interesting, because they give an analytical—therefore general—solution, if not too much complex.

When ternary azeotropy occurs, the composition of the terpolymer is exactly the same as the composition of the monomer feed, thence no drift in the composition will be observed as the reaction proceeds.

$$m_i = M_i \qquad \qquad \text{for i = 1, 2, 3} \qquad (23)$$

Equation (23) is fulfilled when Eqs. (18) and (19) for binary azeotropy are simultaneously encountered, i. e.,

$$F_1/M_1 = F_3/M_3 \qquad (24a)$$

$$F_1/M_1 = F_2/M_2 \qquad (24b)$$

Expressing these equations, as was done for Eq. (17), one gets:

$$a_{31}M_1^2 + a_{32}M_1M_2 + a_{33}M_1M_3 + a_{34}M_2^2 + a_{35}M_2M_3 + a_{36}M_3^2 = 0 \qquad (17)$$

$$a_{61}M_1^2 + a_{62}M_1M_2 = a_{63}M_1M_3 + a_{64}M_2^2 + a_{65}M_2M_3 + a_{66}M_3^2 = 0 \qquad (25)$$

It is possible to elimininate M_3 by substituting Eq. (12) in Eqs. (17) and (25):

$$a_{81}M_1{}^2 + a_{82}M_1M_2 + a_{83}M_1 + a_{84}M_2 + a_{85}M_2{}^2 + a_{86} = 0 \qquad (26)$$

and

$$a_{81}M_1{}^2 + a_{82}M_1M_2 + a_{83}M_1 + a_{84}M_2 + a_{85}M_2{}^2 + a_{86} = 0 \qquad (27)$$

From Eqs. (26) and (27), M_1 may be expressed as a function of M_2:

$$M_1 = (a_{91}M_2 + a_{92}M_2{}^2 + a_{93})/(a_{94}M_2 + a_9 \qquad (28)$$

Finally, substitution of Eq. (28) in Eq. (26) gives an equation in M_2 only:

$$b_{31}M_2{}^4 + b_{32}M_2{}^3 + b_{33}M_2{}^2 + b_{34}M_2 + b_{35} = 0 \qquad (29)$$

The classical method by Ferrari gives analytical solutions for this fourth order equation. Theoretically, four roots might exist, but only positive roots lower than 1.0 have to be considered ($0 \leq M_i < 1$).

Ternary azeotropy coefficients are given in Eqs. (30).

$$a_{81} = (1 - A_{12})(A_{31}A_{21} - A_{31}A_{23}) + (A_{32} - A_{31})(A_{13}A_{21} - A_{13}A_{23}) \qquad (30a)$$

$$a_{82} = (1 - A_{12})(A_{21}A_{32} - A_{31}A_{23}) + (1 + A_{21})(A_{32}A_{13} - A_{12}A_{31})$$

$$+ (A_{32}A_{31})(A_{13}A_{21} - 2A_{13}A_{23} + A_{12}A_{23}) \qquad (30b)$$

$$a_{83} = (1 - A_{12})A_{23}A_{31} + (A_{32} - A_{31})(2A_{13}A_{23} - A_{13}A_{21}) \qquad (30c)$$

$$a_{84} = (1 - A_{21})(A_{32}A_{13}) + (A_{32} - A_{31})(2A_{13}A_{23} - A_{12}A_{23}) \qquad (30d)$$

$$a_{85} = (1 - A_{21})(A_{32}A_{13} - A_{12}A_{32}) + (A_{32} - A_{31})(A_{12}A_{23} - A_{13}A_{23}) \qquad (30c)$$

$$a_{86} = A_{2J}A_{1?}(A_{31} - A_{32}) \qquad (30f)$$

$$a_{91} = a_{84} - a_{81}a_{74}/a_{71} \qquad (30g)$$

$$a_{92} = a_{85} - a_{81}a_{75}/a_{71} \qquad (30h)$$

$$a_{93} = a_{86} - a_{81}a_{76}/a_{71} \tag{30i}$$

$$a_{94} = a_{81}a_{72}/a_{71} - a_{82} \tag{30j}$$

$$a_{95} \approx a_{81}a_{73}/a_{71} - a_{83} \tag{30k}$$

$$b_{31} = a_{94}(a_{82}a_{92} + a_{85}a_{94}) + a_{81}a_{94}^{2} \tag{30l}$$

$$b_{32} = a_{94}(a_{91}a_{82} + a_{92}a_{83} + a_{84}a_{94} + 2a_{85}a_{95}) + a_{92}$$

$$+ a_{92}(2a_{81}a_{91} + a_{82}a_{95}) \tag{30m}$$

$$b_{33} = a_{91}(a_{91}a_{81} + a_{82}a_{95} + a_{83}a_{94}) + a_{94}(a_{82}a_{93} + 2a_{84}a_{95} + a_{86}a_{94})$$

$$+ a_{92}(2a_{81}a_{93} + a_{95}a_{83}) + a_{85}a_{95}^{2} \tag{30n}$$

$$b_{34} = a_{93}(2a_{81}a_{91} + a_{82}a_{95} + a_{83}a_{94}) + a_{95}(a_{83}a_{91} + a_{84}a_{95} + 2a_{86}a_{94}) \tag{30p}$$

$$b_{35} = a_{81}a_{93}^{2} + a_{95}a_{83}a_{93} + a_{86}a_{95}^{2} \tag{30q}$$

As mentioned above, several authors have proposed simplified solutions to the problem. O'Driscoll [11], assuming that the equations of Ham are valid, derived:

$$M_{1} = -(bA - B)/(1 - ab + A - aB + B - bA)$$

$$M_{2} = -(aB - A)/(1 - ab + A - aB + B - bA)$$

$$M_{3} = (1 - ab)/(1 - ab + A - aB + B - bA) \tag{31}$$

(correction of these equations in [11] are to be made) where:

$$a = (r_{13}/r_{12} - r_{31}/r_{32})(r_{13} - 1)$$

$$b = (r_{23}/r_{21} - r_{32}/r_{31})/(r_{23} - 1)$$

$$A = (r_{31} - 1)/(r_{13} - 1)$$

$$B = (r_{32} - 1)/(r_{23} - 1)$$

Tarasov et al. [2, 3] showed that the conditions for the ternary azeotropy to exist is that P, Q, and R given by:

$$P = (1 - \frac{1}{r_{13}})(\frac{1}{r_{32}} - 1) - (\frac{1}{r_{12}} - \frac{1}{r_{13}})(\frac{1}{r_{13}} - 1)$$

$$Q = (\frac{1}{r_{21}} - \frac{1}{r_{23}})(\frac{1}{r_{12}} - \frac{1}{r_{13}}) - (1 - \frac{1}{r_{23}})(1 - \frac{1}{r_{13}})$$

$$R = (\frac{1}{r_{31}} - 1)(1 - \frac{1}{r_{23}}) - (\frac{1}{r_{32}} - 1)(\frac{1}{r_{21}} - \frac{1}{r_{23}}) \tag{32}$$

are of the same sign and differ from zero. The composition of the azeotrope is then given by the relationship:

$$M_1 : M_2 : M_3 = R(\frac{Q}{r_{13}r_{32}} + \frac{P}{r_{12}r_{23}} + \frac{R}{r_{12}r_{13}})$$

$$: P(\frac{P}{r_{21}r_{23}} + \frac{Q}{r_{23}r_{31}} + \frac{R}{r_{21}r_{13}})$$

$$: Q(\frac{Q}{r_{31}r_{32}} + \frac{P}{r_{21}r_{32}} + \frac{R}{r_{12}r_{31}}) \tag{33}$$

O'Driscoll [11] stated that Eq. (33) is valid only for systems which do not obey the Q-e scheme, and, on the contrary, that Eq. (31) is only valid for systems which do obey this Q-e scheme.

This work confirms the validity of the equations of Tarasov and al. but not of those derived by O'Driscoll except, indeed when assumption (1) of Ham is fullfilled, that is when the Q-e scheme is verified for the reactivity ratios.

The equations proposed by Valvassori [14] for multicomponent systems (n > 3) will not be dealt with, due to their complexity, and, above all, to the fact that they are based on the simplifying assumptions of Ham, which obviously suffer of too large a lack of generality.

APPLICTAION TO EXPERIMENTAL RESULTS

In order to examplify the interest of equations and programs that we have developed in this work, several terpolymerization systems
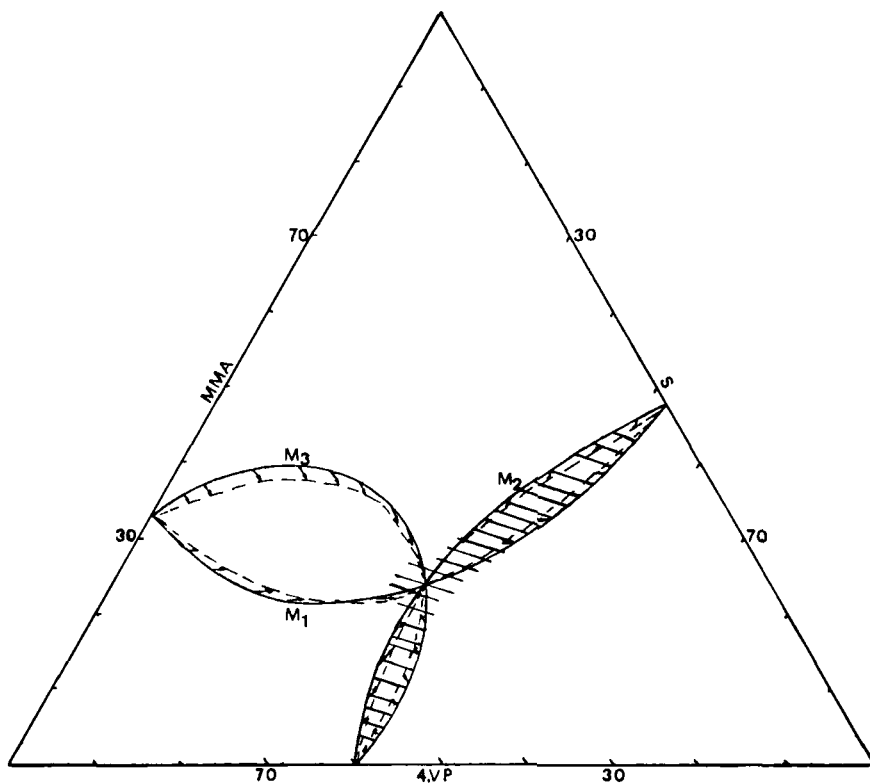
FIG. 1. Instantaneous terpolymer composition as a function of
monomer composition for the system methyl methacrylate (MMA)-
styrene (S)-4-vinylpyridine (4VP): (——) monomer composition;
(– –) terpolymer composition. The reactivity ratios used are [3]
r_{12} = 0.46; r_{21} = 0.52; r_{13} = 0.574; r_{31} = 0.79; r_{23} = 0.54; r_{32} = 0.70.
Unitary azeotropic lines; hatched ares = "pseudo-azeotropic" domains.

have been analyzed, the majority of which are related with acrylo-
nitrile (A), styrene (S), or methyl acrylate (MA) monomers that are
under study as copolymerization systems in this laboratory. Fur-
thermore, and due to the fact that one of our objectives is the
synthesis of copolymers with a good compositional homogeneity,
we have focused our attention on the compositional drift when the
reaction proceeds to higher and higher conversion. In relation with
this point, the representation of experimental points by means of
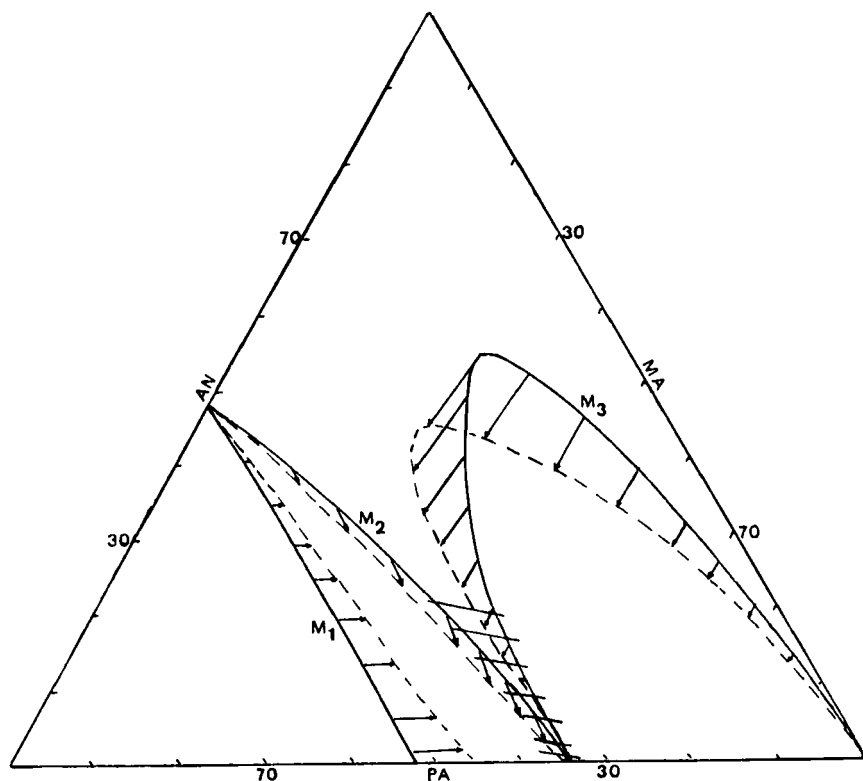arrows, as proposed by Slocombe [1] was chosen as the most
expressive.

FIG. 2. Instantaneous terpolymer composition as a function of
monomer composition for the system acrylonitrile (AN)-methyl
acrylate (MA)-phenyl acetylene (PA): (——) monomer composition;
(– –) terpolymer composition. The reactivity ratios used are [3]:
r_{12} = 0.84; r_{21} = 1.5; r_{13} = 0.26; r_{31} = 0.33; r_{23} = 0.62; r_{32} =
0.27. Unitary azeotropic lines; hatched area = "pseudo-azeotropic"
domains.

In order to determine the variation of polymer composition when
the conversion is increasing, a program has been written in Fortran
IV, giving the instantaneous and average compositions and also the
sequences distribution of the terpolymers. The calculations are
based on integration of the Alfrey-Goldfinger terpolymerization
equations by the Runge-Kutta-Gill method of the fourth order.
From the practical point of view it is interesting to determine
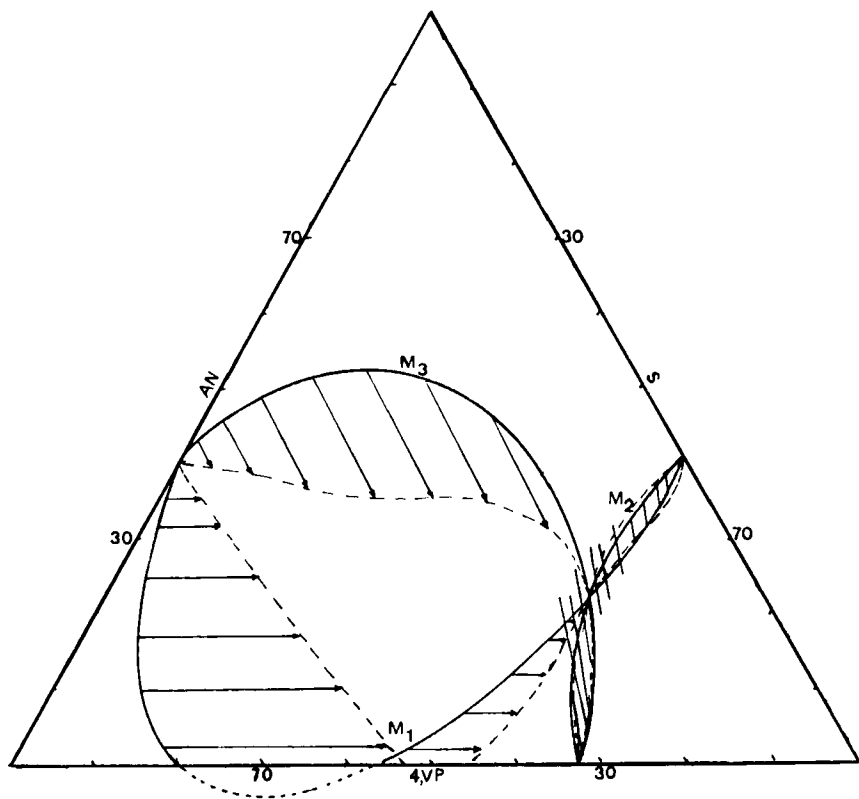not only azeotropic points or azeotropic curves, but also domains

FIG. 3. Instantaneous terpolymer composition as a function of monomer composition for the system acrylonitrile (AN)-Styrene (S)-4-vinylpyridine (4-VP): (——) monomer composition; (– –) terpolymer composition. The reactivity ratios used are [3]: r_{12} = 0.07; r_{21} = 0.37; r_{13} = 0.113; r_{31} = 0.41; r_{23} = 0.54; r_{32} = 0.07. Unitary azeotropic lines; hatched area = "pseudo-azeotropic" domains.

in which the compositional drift is very low. The arrow plot and the calculations then give the possibility to define these domains, which might be termed "pseudo-azeotropic" domains; they are hatched on our diagrams.

The lines for unitary azeotropy give the composition of a monomer mixture leading to a copolymer including for any of the monomer the same proportion as the monomer feed; they are complex curves and contain a lot of information. Particularly, their intersection, if any,
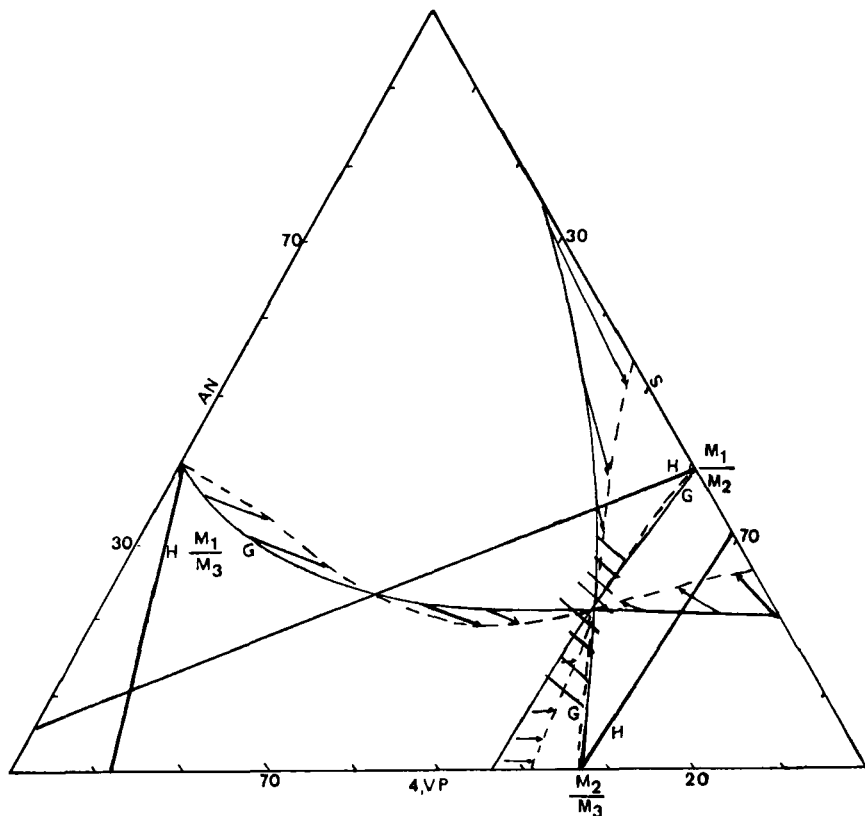
FIG. 4. Instantaneous terpolymer composition as a function of
monomer composition for the system acrylonitrile (AN)-styrene (S)-
4-vinylpyridine (4-VP) (see Fig. 3 for reactivity ratios): (——) mono-
mer composition; (– –) terpolymer composition. Binary azeotropic
lines: (G) based on Alfrey-Goldfinger equations; (H) based on Ham
equation (the ternary azeotropies according to H and G are very
different from one another); hatched area = "pseudo-azeotropic"
domains.

corresponds to the true or ternary azeotrope and, therefore, indicate
the region of lower compositional drift. But our calculations show that
other domains might also correspond to a low compositional change;
these domains may be situated along unitary azeotropic lines (MMA/
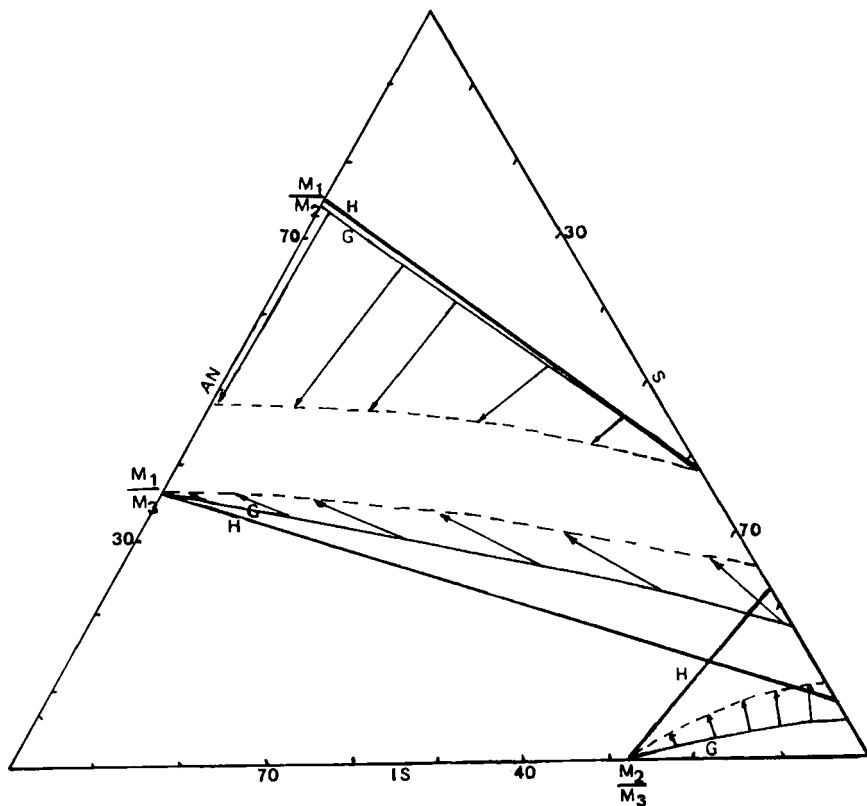S/4-VP, Fig. 1) or between arcs of these lines close enough to one

FIG. 5.   Instantaneous terpolymer composition as a function of
monomer composition for the system acrylonitrile (AN)-styrene (S)-
isoprene (IS): (——) monomer composition; (– –) terpolymer com-
position.   The reactivity ratios used are [5]: r_{12} = 0.1; r_{21} = 0.44;
r_{13} = 0.03; r_{31} = 0.45; r_{23} = 1.38; r_{32} = 2.0.   Binary azeotropic lines:
(G) based on Alfrey-Goldfinger equations (no ternary azeotrope);
(H) based on Ham equations (ternary azeotrope).

another.   However, it is not at all always valid, that the compositional
drift remains small along the azeotropic lines (AN/S/4-VP, Fig. 3)
which can present very different shapes.   Thus, in the case of the
MMA/S/4-VP system (Fig. 1) three curves intersect at one point,
and in the case of AN/MA/PA system (Fig. 2), the three curves do
not intersect (no ternary azeotrope); the behavior of the AN/S/4-VP
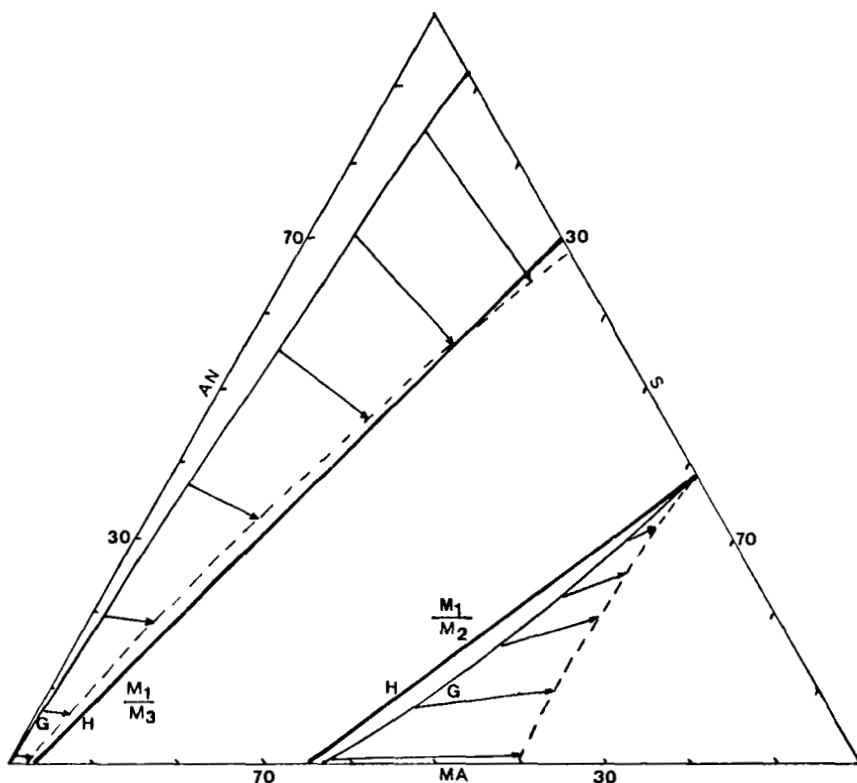
FIG. 6. Instantaneous terpolymer composition as a function of monomer composition for the system acrylonitrile (AN)-Styrene (S)-methyl acrylate (MA): (——) monomer composition; (– –) terpolymer composition. The reactivity ratios used are [16]: $r_{12} = 0.10$; $r_{21} = 0.44$; $r_{13} = 0.69$; $r_{31} = 1.02$; $r_{23} = 1.04$; $r_{32} = 0.17$. Binary azeotropic lines: (G) based on Alfrey-Goldfinger equations (no azeotropic line for M_2/M_3); (H) based on Ham equations (no azeotropic line for M_2/M_3).

system (Fig. 3) is even more complex, since the curve corresponding to the unitary azeotrope for acrylonitrile is actually constituted of two arcs.

The lines of binary azeotropy, which then correspond to copolymers for which the ratio of two given monomers is the same in the polymer and in the monomer mixture, also are complex with different shapes (Figs. 4 and 5) and carry the same information relative to true azeotrope and "pseudo-azeotropic" domains. So, when a ternary azeotrope
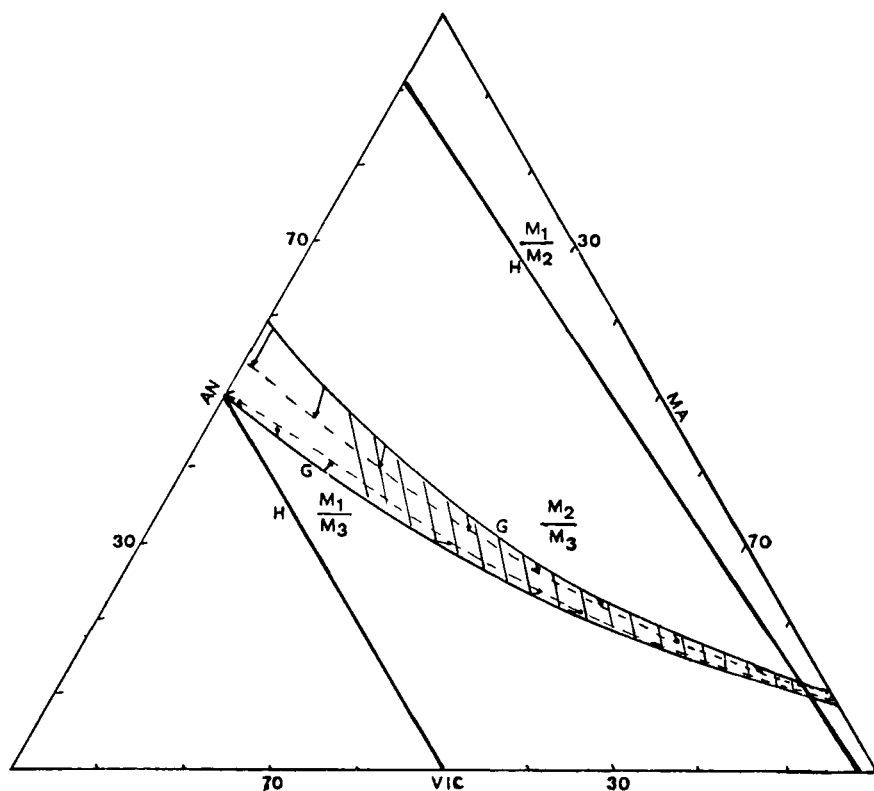
FIG. 7. Instantaneous terpolymer composition as a function of monomer composition for the system acrylonitrile (AN)-me*hvl acrylate (MA)-vinyl isocyanate (VIC): (——) monomer composition; (– –) terpolymer composition. The reactivity ratios used are [3]: $r_{12} = 0.69$; $r_{21} = 1.04$; $r_{13} = 0.19$; $r_{31} = 0.16$; $r_{23} = 1.38$; $r_{32} = 0.14$. Binary azeotropic lines: (G) based on Alfrey-Goldfinger equations (no azeotropic line for M_1/M_2); (H) based on Ham equations (no azeotropic line for M_2/M_3); hatched area = "pseudo-azeotropic" domain.

does exist, the curves intersect at the same point (Figs. 3 and 4) as expected.

But, whereas in the case of unitary azeotropy, three curves, one for each monomer always appear, for binary azeotropy, it is possible not to observe the azeotropic line for some monomer pairs (A-S-AM, Fig. 6). For the determination of these binary azeotropic lines— termed partial azeotropic by Ham [9]—this author used a set of
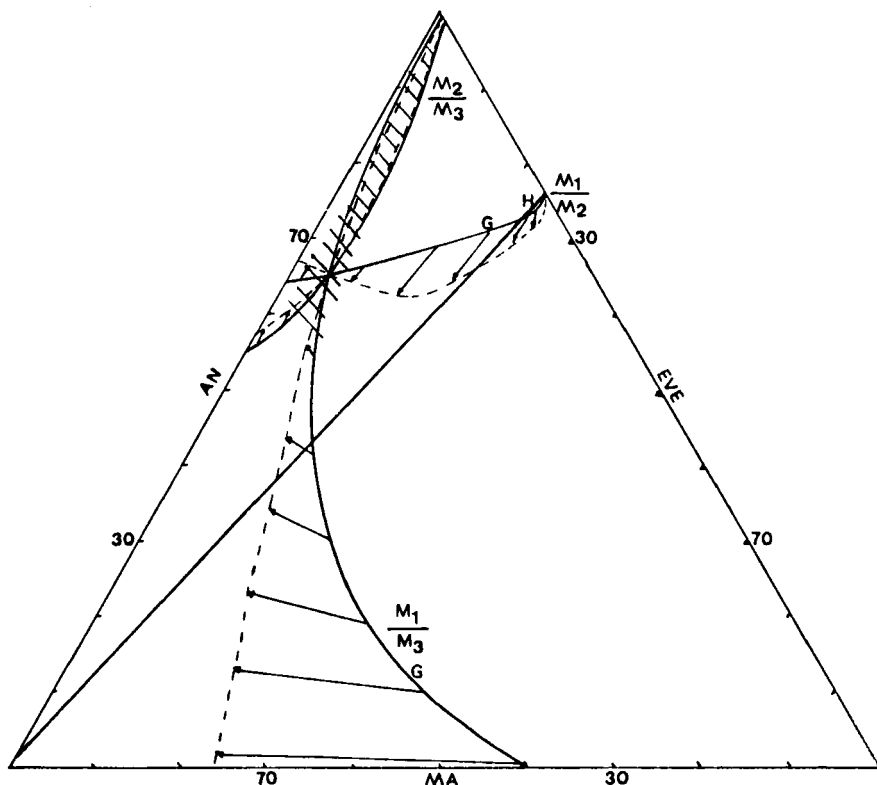
FIG. 8. Instantaneous terpolymer composition as a function of monomer composition for the system acrylonitrile (AN)-ethyl vinyl ether (EVE)-methyl acrylate (MA): (——) monomer composition; (– –) terpolymer composition. The reactivity ratios used are [7]: $r_{12} = 0.7$; $r_{21} = 0.03$; $r_{13} = 1.04$; $r_{31} = 0.69$; $r_{23} = 0.001$; $r_{32} = 3.3$. Binary azeotropic lines: (G) based on Alfrey-Goldfinger equations (ternary azeotrope); (H) based on Ham equations (no azeotropic line for M_1/M_3 and M_2/M_3); hatched area = "pseudo-azeotropic" domain.

equations [cf. Eqs. (21), (23), (24)] based on the identity $r_{12} r_{23} r_{31} = r_{13} r_{32} r_{21}$ which is a consequence of the Q-e scheme for reactivity ratios. The corresponding straight lines are reported on the diagrams. Large deviations may be observed between these lines and the curves (Fig. 4) calculated without simplifying assumption; however, sometimes the agreement is acceptable (cf. c $M_1/M_2 = m_1/m_2$, Fig. 6). Furthermore, Ham's equations may give a binary azeotropic line
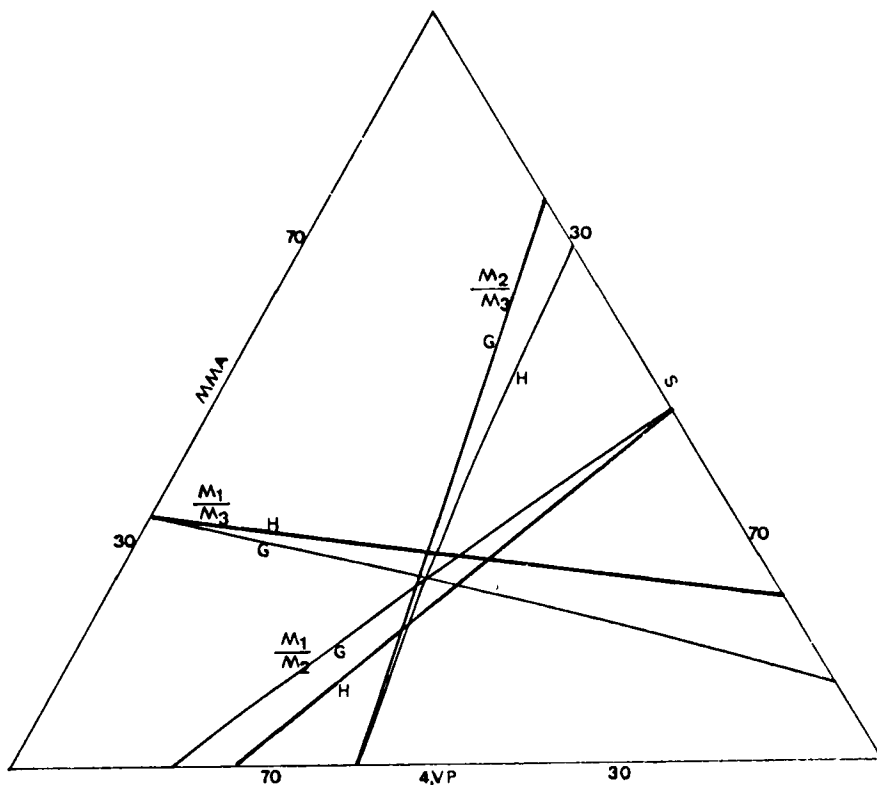
FIG. 9. Instantaneous terpolymer composition as a function of monomer composition for the system methyl methacrylate (MMA)-styrene (S)-4-vinylpyridine (4-VP): See Fig. 1 for reactivity ratios; $r_{13}r_{32}r_{21} = 0.2089$; $r_{12}r_{23}r_{31} = 0.1962$. Binary azeotropic lines: (G) based on Alfrey-Goldfinger equations (ternary azeotrope); (H) based on Ham equations (three ternary azeotropes).

when there is a ternary azeotrope, thence three binary azeotropic lines (Fig. 8).

In addition, it is quite often observed, when calculations show the existence of a true azeotrope that Ham's equations, which result in straight lines, do not intersect (Figs. 4 and 9), even when, at the best, they define a domain close to the azeotrope.

The reasons are to be sought in Ham's assumption itself. So, slightly modifying the value of a reactivity ratio (say, r_{13} in the MMA/ S/4-VP system from 0.574 to 0.539, Figs. 9 and 10) in order to equalize
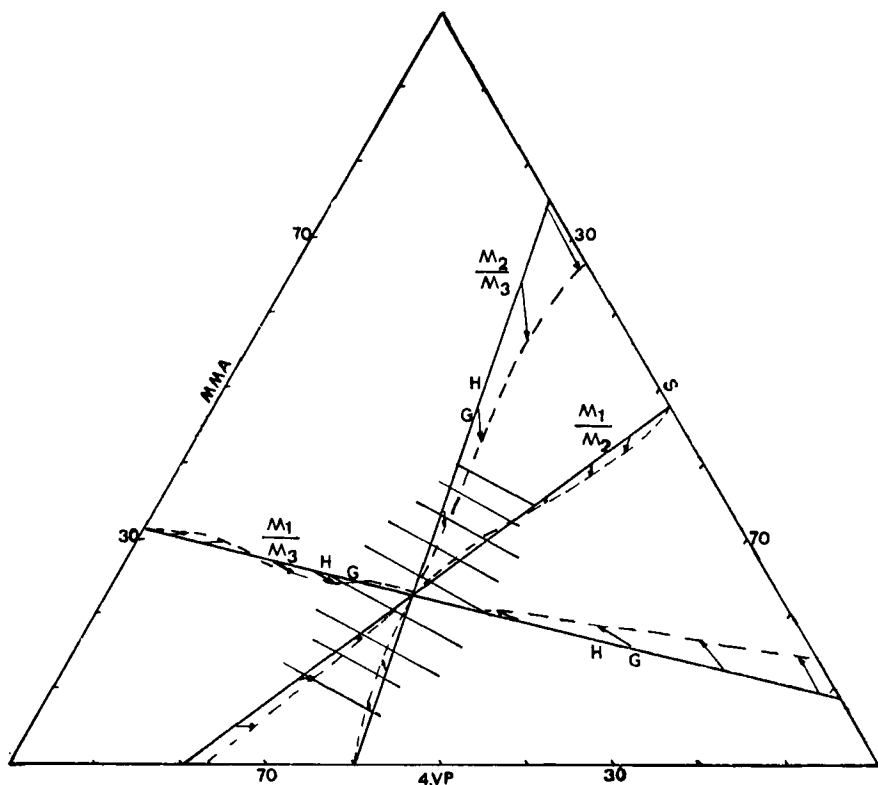
FIG. 10. Instantaneous terpolymer composition as a function of monomer composition for the system MMA/S/4-VP, but now r_{13} = 0.539 (whereas r_{13} = 0.574 in Fig. 9) $r_{13}r_{32}r_{21}$ = 0.1962 = $r_{12}r_{23}r_{31}$: (——) monomer composition; (– –) terpolymer composition. Binary azeotropic lines: G and H lines coincide; hatched area = "pseudo-azeotropic" domains.

the products of reactivity ratios, one observes that the curves are changed to Ham's straight lines, but now they intersect at the same azeotropic point (Fig. 10). No simple relationship appears between the existence of a ternary azeotrope and the existence of binary copolymerization azeotropes.

   With regard to compositional drift, it must be said that only the ternary azeotrope is actually without change as the polymerization proceeds. However, it is noteworthy that our calculations show the possibility of defining a "pseudo-azeotropic" zone in which

compositional drift will be very low (hatched area on diagrams). These calculations do not confirm another assumption by Ham [9] according to which the composition does not change along binary azeotropic lines with conversion (see for instance Figs. 5 and 8).

CONCLUSION

A general solution for the problem of the different azeotropies which may be considered in terpolymerization has been proposed, i. e., calculations which allow the determination of the monomer feed composition for a simple relationship for one or several monomers to exist between the monomer mixture and the terpolymer. These calculations do not depend on any simplifying assumptions or relationships, except that kinetics follows the classical radical copolymerization model. They show, in particular, that one must be very cautious in using the Ham's simplified equations because his basic relationship (1) may not be verified; for that reason, other methods suggested by O'Driscoll or Valvassori may lead to erroneous results, if the Alfrey-Price scheme is not obeyed by the system under consideration. On the other hand, this work has shown that, except for ternary azeotrope, a compositional drift is observed with extent of polymerization, but that it is possible to find "pseudo-azeotropic" domains along which the change in copolymer composition is very minor up to high conversion.

Outside the azeotrope and the pseudo-azeotropic domains, the compositional drift may be very important. However, in order to calculate this drift correctly, very precise values of all the six reactivity ratios are necessary, and minor changes in these values may lead to rather large errors in the predicted results. It is interesting to note, at that point, that there is no example of experimental results giving convincing evidence of an actual ternary azeotrope which coincide with calculated values.

It is however important, from the practical point of view, to have copolymers with constant composition. The apparatus we have designed in our laboratory [15, 16] allows us to prepare such copolymers, whatever the number of comonomers may be.

APPENDIX

Equations of Fourth Degree: Method of Ferrari

The equation

$$x^4 + ax^3 + bx^2 + cx + d = 0 \qquad\qquad (A-1)$$

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may be written:

$$[x^2 + (a/2)x + \lambda]^2 = [2\lambda - b + (a^2/4)]x^2 + (a\lambda - c)x + \lambda^2 - d$$

is determined so that the second member of this identity is a perfect square:

$$(a\lambda - c)^2 - 4(\lambda^2 - d)[2\lambda - b + (a^2/4)] = 0 \qquad (A-2)$$

Equation (A-2) is a cubic equation which can be theoretically solved by known methods. It is sufficient to consider for λ one of its roots and Eq. (A-1) is then decomposed in a product of quadratic factors.

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