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Azeotropy in Terpolymerization

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LETTER TO THE EDITOR

Azeotropy in Terpolymerization

A number of papers have recently discussed the possibility of azeotropy terpolymerization of vinyl monomers (*1–4*). The analysis by Tarasov et al. (*1*) revealed the necessary and sufficient criteria for terpolymerization azeotropy with an explicit assumption that can be reduced to the statement that Eq. (1) does *not* hold:

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21} \qquad (1)$$

Equation (1) has undergone some debate in the literature (*5–8*). It is a necessary consequence of the $Q - e$ scheme and can be derived from it. Therefore, the azeotropy criteria of Tarasov et al. do not apply to monomers which obey the $Q - e$ scheme. It is the purpose of this note to explore azeotropy for ternary systems of monomers which *do* obey the $Q - e$ scheme.

Since we are dealing with monomers which obey the $Q - e$ scheme, Ham's simplified composition equation (9) is used:

$$\frac{m_1}{m_2} = \frac{M_1}{r_{21}}\left(\frac{M_2}{r_{12}} + M_1 + \frac{M_3}{r_{13}}\right) \Big/ \frac{M_2}{r_{12}}\left(\frac{M_1}{r_{21}} + M_2 + \frac{M_3}{r_{23}}\right) \qquad (2)$$

where M_i and m_i are the mole fractions of monomers i in the feed and terpolymer and r_{ij} is the binary reactivity ratio for monomers i and j adding to a chain ending in i. Similar equations can be written for M_1/M_3 and M_2/M_3.

True azeotropy is defined as that set of monomer feed fractions such that $m_i = M_i$ for $i = 1, 2, 3$. Ham (2) has previously defined "partial" azeotropy, where M_i/M_j remains constant for two of the three monomers as terpolymerization proceeds. O'Driscoll (3) has defined "limited" azeotropy, where $m_i = M_i$ for any one monomer. Since

$$M_1 + M_2 + M_3 = 1 \qquad (3)$$

it is obvious that if, at one feed composition, limited azeotropy is found for two monomers, or partial azeotropy for two pairs of monomers, then true azeotropy exists.

Utilizing the above definition of true azeotropy and the forms of Eq. (2) we can derive the equation defining azeotropic compositions as follows: Setting the left side of Eq. (2) equal to M_1/M_2 and rearranging gives

$$M_1(r_{12}-1)+M_2(1-r_{21})+M_3\left(\frac{r_{12}}{r_{13}}-\frac{r_{21}}{r_{23}}\right)=0 \tag{4a}$$

The analogous equation for M_1/M_3 gives

$$M_1(r_{13}-1)+M_2\left(\frac{r_{13}}{r_{12}}-\frac{r_{31}}{r_{32}}\right)+M_3(1-r_{31})=0 \tag{4b}$$

and for M_2/M_3,

$$M_1\left(\frac{r_{23}}{r_{21}}-\frac{r_{32}}{r_{31}}\right)+M_2(r_{23}-1)+M_3(1-r_{32})=0 \tag{4c}$$

Because of the restraint of Eq. (3), only two of equations (4) are independent. Dividing both sides of (4b) and (4c) by M_3 and rearranging gives

$$M_1/M_3+a(M_2/M_3)=A \tag{5a}$$

$$b(M_1/M_3)+M_2/M_3=B \tag{5b}$$

where the various terms are defined by the binary reactivity ratios:

$$a=\left(\frac{r_{13}}{r_{12}}-\frac{r_{31}}{r_{32}}\right)\Big/ r_{13}-1$$

$$b=\left(\frac{r_{23}}{r_{21}}-\frac{r_{32}}{r_{31}}\right)\Big/ r_{23}-1$$

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

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

[It should be noted that A and B, if positive, are the azeotropes for binary systems, $(M_1/M_3)_{\text{binary}}$ and $(M_2/M_3)_{\text{binary}}$. However, positive values of A and B are not necessary for the present argument.]

Solutions of equations (5) give

$$M_1/M_3=(1/1-ab)\ (B-bA) \tag{6}$$

$$M_2/M_3=(1/1-ab)\ (A-aB) \tag{7}$$

Combining Eqs. (6) and (7) with (3) gives the monomer feeds which would yield true azeotropy:

$$M_1 = (bA - B)/1 - ab + (A - aB) + (B - bA) \qquad (8)$$

$$M_2 = (aB - A)/1 - ab + (A - aB) + (B - bA) \qquad (9)$$

$$M_3 = (1 - ab)/1 - ab + (A - aB) + (B - bA) \qquad (10)$$

The necessary and sufficient criteria for true azeotropy is that M_1, M_2, and M_3 all be positive as described by Eqs. (8), (9), and (10). Whether the constraint inherent in the $Q - e$ scheme rules out ternary azeotropy in obeying systems remains to be determined.

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