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Terpolymer Azeotropy

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ABSTRACT

Data supporting the theory and conjectured existence of terpolymer azeotropes are examined. It is shown that the theory is based on questionable assumptions. It is also shown that the use of $r_{32} = r_{31} = 0$, for example, leads to fatal flaws in the prediction of terpolymer azeotropes. Furthermore, specific reactivity ratios used in predicting terpolymer azeotropes are questioned.

In 1960 Tarasov et al. [1] derived equations for the calculation of terpolymer azeotropes, given the binary reactivity ratios for each of the individual comonomer pairs.

In 1964 Ham [2] derived simplified equations for the description of terpolymerization which led in 1966 to the thesis that terpolymer azeotropes may not exist since they would require violation of the Q-e scheme. The equation

$$P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba} = p \qquad (1)$$

where P_{ij} is the probability of monomer j adding to radical i in the presence of i, j, and k monomers, for example, is based on the assumption that terpolymer sequences such as

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$M_1M_3M_2 \ldots M_1$ and $M_1M_2M_3 \ldots M_1$

occur with equal probability. From Eq. (1):

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21} \tag{2}$$

can be derived. This same equation follows from the Alfrey-Price Q-e scheme [3].

It was further pointed out by O'Driscoll and Ham [4] that the Tarasov equations [1] depended upon the implicit assumption that

$$r_{12}r_{23}r_{31} \neq r_{13}r_{32}r_{21} \tag{3}$$

In 1967 an encyclopedic study was summarized by Wittmer et al. [5]. The title of the paper was "Concerning the Existence of Azeotropes in Copolymerizations of More than two Monomers." Employing 653 binary reactivity ratios, all possible combinations of three monomers were examined (for 119 monomers, only a single combination was available) using an IBM 7090 computer and numerical integration. Based on these studies, 37 ternary azeotropes were "found" and their compositions reported. However, no actual confirming experiments were reported.

These reported ternary azeotropes were in addition to those earlier ones calculated and reported by Tarasov [1]: acrylonitrile-2,5-dichlorostyrene-methyl methacrylate, acrylonitrile-2,5-dichlorostyrene-styrene, and diethyl fumarate-styrene-vinylidene chloride.

In the intervening years other ternary azeotropes have been reported. These include MMA-glycidyl methacrylate-styrene by Ring [6] and N,N-dimethylaminoethyl methacrylate-styrene-AN by Probst and Kolb [7]. In connection with the former, which was reported to have been experimentally confirmed, it should be pointed out $r_{12} \approx r_{21} \approx 1$.

In spite of the above studies, controversy continues concerning ternary azeotropes and whether they exist. Of course, it is a well-nigh impossible task to prove the nonexistence of terpolymer azeotropes. Most of the studies share one important characteristic: the lack or paucity of experimental confirmation. Only in the cases of Ring and Probst-Kolb were actual attempts made to reproduce the azeotrope reported. Although Probst-Kolb obtained uniform terpolymers at advanced conversions, they do not seem to be certain of the existence of an azeotrope.

Since experimental terpolymer results are generally not available, criticism may only be directed at the remaining evidence. It seems probable that the area where the most valid questions may be raised is that of the binary reactivity ratios employed in the calculations. It seems significant, for example, that many of the reactivity ratios used by Wittmer had a value of 0. An ongoing difficulty in the kinetic analysis of copolymerization has been the necessity of using null values in attempting to elucidate certain copolymerizations.

Wittmer, for example, attempts to deal with the problem by using values of 1×10^{-5} instead of the reported 0 values. This allows calculation where results could not otherwise be obtained. However, such a choice of value can lead to serious problems in the following situation: If monomer M_3 cannot add to M_3 radical, then $r_{31} = 0$ and $r_{32} = 0$. However, it does not follow that if $k^{33}/k^{31} = 0$ and $k^{33}/k^{32} = 0$ that k^{31}/k^{32} is fixed. Yet it is implicit in assuming $k^{33}/k^{31} = 1 \times 10^{-5}$ and $k^{33}/k^{32} = 1 \times 10^{-5}$ that $k^{31}/k^{32} = 1$. There exists today considerable evidence that k^{31} is often very different from k^{32}. For example, Sandner et al. [8] report that k^{31}/k^{32} for acrylonitrile-styrene-maleic anhydride is ~0.08, depending to some degree on monomer composition. Tomescu et al. [9] studied acrylonitrile-α-methylstyrene-maleic anhydride and found $R = k^{31}/k^{32} = 0.0032$.

Furthermore, particularly in the absence of contributions from k^{33} to composition, k^{31}/k^{32} is very important in determining terpolymer composition. Indeed, the only way available for assessing k^{31}/k^{32} is from terpolymer composition studies. For this purpose there is available an equation from Alfrey and Goldfinger [10]:

$$d[M_1]:d[M_2]:d[M_3] = m_1:m_2:m_3$$

$$= [M_1]\left(R\frac{[M_1]}{r_{21}} + \frac{[M_2]}{r_{21}} + \frac{R[M_3]}{r_{23}}\right)\left([M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right):$$

$$[M_2]\left(R\frac{[M_1]}{r_{12}} + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right)\left(\frac{[M_1]}{r_{21}} + [M_2] + \frac{[M_3]}{r_{23}}\right):$$

$$[M_3]\left(\frac{[M_1]}{r_{13}r_{12}} + \frac{[M_2]}{r_{12}r_{23}} + \frac{[M_3]}{r_{13}r_{23}}\right)\left(R[M_1] + [M_2]\right) \tag{4}$$

as well as a simplified equation by Ham [2].

No equation is available for calculating ternary azeotropes employing R values. However, it is possible to employ R values indirectly by appropriate selection of r_{32} and r_{31} values, since their ratio equals R. Of course, r_{32} and r_{31} must be individually kept very small.

For example, for acrylonitrile-maleic anhydride-styrene employing

$r_{12} = 6$ $r_{21} = 1 \times 10^{-7}$

$r_{13} = 0.07$ $r_{31} = 0.37$

$r_{23} = 1 \times 10^{-7}$ $r_{32} = 0.01$

F1 = 9.23182E-03

F2 = 4.92822E-01

F3 = 4.97945E-01

in essential agreement with Wittmer. However, assuming R = 0.08 [8] and choosing appropriate small values of r_{23} and r_{21}:

$R_{12} = 6$ $r_{21} = 1 \times 10^{-5}$

$r_{13} = 0.07$ $r_{31} = 0.37$

$r_{23} = 8 \times 10^{-7}$ $r_{32} = 0.01$

F1 = 1.1724970

F2 = -7.78101E-02

F3 = -9.46868E-02

Hence, no azeotrope results. It is of interest to note that essentially the same results are obtained up to at least $r_{23} = 8 \times 10^{-4}$ and $r_{21} = 0.01$.

In conclusion, it may be asserted again, as in 1966, that azeotrope formation (in terpolymers) is very rare and may be nonexistent.

Another example is Wittmer's #31 "azeotrope"-maleic anhydride-methyl acrylate-styrene. Employing $r_{12} = 1 \times 10^{-5}$ and $r_{13} = 1 \times 10^{-5}$ (assumes $k^{31}/k^{32} = 1.0$), as well as

$r_{21} = 2.5$ $r_{23} = 0.18$

$r_{31} = 0.01$ $r_{32} = 0.75$

F1 = 4.96462E-01

F2 = 2.18426E-03

F3 = 0.501353355

in agreement with Wittmer. However, Bevington and Nicora [15] report $k^{12}/k^{13} = 0.116$. As above, choosing $r_{12} = 1 \times 10^{-5}$ and $r_{13} = 1.16 \times 10^{-6}$

F1 = -2.39515E-01

F2 = 1.315397

F3 = -7.58817E-02

indicating no azeotrope formation.

Holding $r_{12} = 1 \times 10^{-5}$ and reducing r_{13} from 1×10^{-5} to lower levels, it is found that $r_{13} = 9.97 \times 10^{-6}$ is the lowest value which yields an azeotrope. This says in effect that azeotrope formation in this system is only possible if the maleic anhydride radical does not differentiate between methyl acrylate and styrene monomers—a highly unlikely circumstance.

In the case of Wittmer's #20 azeotrope, 2-chloroallyl acetate-maleic anhydride-vinyl chloride, one would expect a slightly higher reactivity for vinyl chloride than for 2-chlorallyl acetate toward maleic anhydride radical. On this basis it is most unlikely that the reported $k^{22}/k^{23} = 0.008$, relative to $k^{22}/k^{21} = 0$, is correct. However, even if one tests $k^{22}/k^{23} = 1 \times 10^{-5}$ and $k^{22}/k^{21} = 1 \times 10^{-5}$ (as well as for other values reported as 0), no azeotrope results.

Wittmer's #5 azeotrope is acrylonitrile (0.4022)-diethyl fumarate (0.058)-styrene (0.5417). The reported r_{23} (0.07 ± 0.007) and r_{21} (0) values require that acrylonitrile be infinitely more reactive than styrene toward diethyl fumarate radical—a highly unlikely possibility (k^{21}/k^{23} in acrylonitrile-maleic anhydride-styrene is 0.08). There was also no azeotrope at $r_{21} = 1 \times 10^{-5}$ and $r_{23} = 8 \times 10^{-7}$

For Wittmer's azeotrope #19 (1,3-butadiene-diethyl fumarate-styrene), values of $r_{21} = 0.25$ and $r_{23} = 0.070 \pm 0.007$ were employed. (Using the same reactivity ratios as Wittmer, his calculation of an azeotrope was confirmed.) The values require $k^{23}/k^{21} = 3.57$. Since 1,3-butadiene has an e value more negative than styrene as well as a higher Q value, it seems more probable that k^{23}/k^{21} is less than 1. However, no azeotrope resulted at r_{21}/r_{23} values less than 1.

For Wittmer's azeotrope #24 (diethyl fumarate-styrene-vinylidene chloride), values of $r_{12} = 0.07 \pm 0.007$ and $r_{13} = 0.046 \pm 0.015$ were employed, requiring $k^{13}/k^{12} = 1.52$. It seems likely that k^{13}/k^{12} would be less than 0.1, given the high Q value and negative e value of styrene and medium Q value of vinylidene chloride.

No systematic attempt has been made to review the original reactivity ratios employed by Wittmer (except those above). However, certain ones have been selected which raise the most obvious questions.

Wittmer uses for #1 azeotrope AN-ethyl acrylate-Na acrylate $r_{12} = 0.44$, $r_{21} = 0.95$. However, Brandrup [11] reports $r_{12} = 1.17 \pm 0.1$ and $r_{21} = 0.67 \pm 0.02$. An azeotrope in agreement with Wittmer results when the first pair is used, but not with the second pair.

In Wittmer azeotropes #2, 3, and 4, acrylonitrile-ethyl vinyl ether reactivity ratios of $r_{12} = 0.7 \pm 0.02$, $r_{21} = 0.03 \pm 0.02$ are employed rather than the Mayo-Walling-Lewis [12] values of $r_{12} = 5.0$, $r_{21} = 0$. Substitution leads to no azeotrope in all cases.

Four of Wittmer's azeotropes contain α-methylstyrene, a monomer widely recognized as exhibiting depropagation tendencies. Moreover, it is known that sequences of more than three α-methylstyrene units are not produced in copolymers, throwing into question the significance of α-methylstyrene r values. In the case of azeotropes #15, #29, and #32, both α-methylstyrene and methyl methacrylate are present. Curiously, Wittmer uses the 1948 values of Walling et al. [13] of $r_1 = 0.14 \pm 0.01$, $r_2 = 0.50 \pm 0.03$ rather than his own 1967 values [14] of $r_1 = 0.6$ and $r_2 = 0.55$. Testing his azeotrope #15 AN-MMA-α-methylstyrene, the same composition was obtained as reported when using the Walling values, but not when using the Wittmer values. No azeotrope was obtained in the latter case.

Testing azeotrope #29 2-fluorobutadiene-MMA-α-methylstyrene, Wittmer's calculation was confirmed with the first set of α-MeSM/MMA reactivity ratios, but not with the second (no azeotrope).

Testing azeotrope #32 MAN-MMA-α-methylstyrene, Wittmer's result was confirmed with the first set of r values, but no azeotrope was obtained with the second.

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