

Copolymerization of Systems Containing Three Components

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change in the quality of transmitted light. These phenomena are the more pronounced, the greater the concentration of the solution. The color change is rapid and completely reversible with respect to temperature change.

Quantitative spectrophotometric measurements confirm the qualitative visual observations as to change in color distribution of transmitted light. The absorption coefficient of a given solution for blue light is but slightly increased by the above temperature change, while that for red light is increased considerably—by a factor of two or more for sufficiently concentrated solutions. The change for light of intermediate wave-lengths falls smoothly between these extremes.

Previous studies^{1, 2} have shown the absorption spectrum of very dilute metal-ammonia solutions to be continuous, with a pronounced maximum in the infra-red. Were this absorption band to undergo the normal broadening with temperature increase, the visible absorption spectrum would be affected in a fashion the reverse of that described above. The most probable interpretation of the present studies postulates the presence in the solutions of two different colored components, the equilibrium between these being dependent upon concentration and temperature. The component favored by high concentrations and low temperatures (which will be termed *B*) would appear to display also a continuous absorption spectrum, but with a band maximum lying nearer the visible region than that of the other component (which will be termed *A*). This would account for the observed differential increase of total absorption toward longer wave-lengths on cooling a relatively concentrated solution. The experimental results would indicate that the conversion of *B* into *A* is an endothermic process and must involve an increase in the number of particles.

Comparison with solid solutions of alkali metals in alkali halide crystals³ affords a clue as to the difference between the *A* and *B* components. In these systems the *F* centers and *F'* centers (consisting, respectively, of single electrons and electron pairs trapped at vacant negative ion lattice sites) show different continuous absorption bands, the maximum of the *F* band lying at shorter wave-length. Absorption in both bands results in ejection of a conduction electron, the corresponding work function being greater for the *F* centers. Correspondingly, the *F'* centers are thermally unstable with respect to dissociation into *F* centers. In the present studies, it is suggested that the *A* component consists of single electrons trapped in cavities in the liquid dielectric medium⁴ while the *B* component consists of electron pairs similarly trapped. However, the order of thermal stability of *A* and *B* components would appear to be reversed as compared with that of *F* and *F'* centers. Correspondingly, the positions on the wave-length scale of the corresponding band maxima are in all probability also reversed.

Theoretical treatment⁴ of the electron pair trapped in a liquid medium of high dielectric constant predicts it to be stable with respect to dissociation into single electrons trapped in separate cavities, and that its ground state should be diamagnetic. The trapped single electron should have a paramagnetic susceptibility corresponding to elec-

tron spin. Experimental studies^{5, 6} of the concentration and temperature dependence of the magnetic susceptibility of dilute metal-ammonia solutions are at least qualitatively explained by the above proposed equilibrium between trapped pairs and trapped single electrons. However, in attempting to calculate equilibrium constants from the magnetic data, it should be noted that the cavities occupied by both are very large⁴ (of the order of 7×10^{-8} cm in radius) and that consequently the diamagnetic susceptibilities are far from negligible. The absorption spectrum studies offer hope of greater accuracy.

¹ G. E. Gibson and W. L. Argo, *J. Am. Chem. Soc.* **40**, 1327 (1918).

² E. Vogt, *Zeits. f. Electrochemie* **45**, 597 (1939).

³ For literature references, see N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford Press, 1940).

⁴ Richard A. Ogg, Jr., *J. Am. Chem. Soc.* (January, 1946), in press.

⁵ E. Huster, *Ann. d. Physik* **33**, 477 (1938).

⁶ S. Freed and N. Sugarman, *J. Chem. Phys.* **11**, 354 (1943).

Copolymerization of Systems Containing Three Components

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IN a previous letter¹ on this subject, we presented equations for the composition of the initial copolymer formed from a given mixture of 3 monomers, (*A*, *B*, and *C*).²

$$\frac{a}{b} = \frac{[\beta^a \gamma^b AB + \gamma^a \beta^a A^2 + \gamma^a \beta^c AC]}{[\alpha^b \gamma^a AB + \gamma^b \alpha^b B^2 + \gamma^b \alpha^c BC]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[B + \beta^a A + \beta^c C]} \quad (1)$$

$$\frac{a}{c} = \frac{[\beta^a \gamma^b AB + \gamma^a \beta^a A^2 + \gamma^a \beta^c AC]}{[\alpha^c \beta^a AC + \beta^c \alpha^b BC + \beta^c \alpha^c C^2]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[C + \gamma^a A + \gamma^b B]} \quad (2)$$

Here *a*, *b*, and *c* are molar concentrations of the three components in the initial polymer; *A*, *B*, and *C* are the molar concentrations in the monomer mixture; α^b , α^c , —, etc. are ratios of propagation rate constants, as follows:

$$\begin{array}{lll} \alpha^b = k_{ab}/k_{aa}, & \beta^a = k_{ba}/k_{bb}, & \gamma^a = k_{ca}/k_{cc}, \\ \alpha^c = k_{ac}/k_{aa}, & \beta^c = k_{bc}/k_{bb}, & \gamma^b = k_{cb}/k_{cc}. \end{array}$$

It was stated that "equations 1 and 2 indicate the possibility of predicting the composition of a multipolymer from information gathered from a separate study of each pair of monomers involved." This is, in general, true. Dr. G. L. Barrett³ has pointed out, however, that there is an important class of monomers for which such a calculation is impossible. Members of this class (e.g., maleic anhydride, maleic esters) possess vanishingly small rate constants for self-propagation.⁴ If monomer *C* in a 3-component polymerization is of this type, then k_{cc} is equal to zero; γ^a and γ^b are infinite. The structure of the tri-polymer depends upon all 9 of the propagation constants. In the usual case, where no constant vanishes, knowledge of the six ratios used in Eqs. (1) and (2) means implicit knowledge of all other necessary ratios. Thus (k_{ca}/k_{cb}) is fixed if the ratios (k_{ca}/k_{cc}) and (k_{cb}/k_{cc}) are known. If k_{cc} vanishes, however, experiments on the separate 2-com-

ponent systems yields only the fact that both (k_{cb}/k_{cc}) and (k_{ca}/k_{cc}) are essentially infinite. Knowledge of (k_{ca}/k_{cb}) must be obtained somehow, even though this ratio does not appear explicitly in Eqs. (1) and (2). Letting k_{cc} approach zero, Eqs. (1) and (2) take the form:

$$\frac{a}{b} = \frac{[\beta^a AB + R\beta^a A^2 + R\beta^c AC]}{[R\alpha^b AB + \alpha^b B^2 + \alpha^c BC]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[B + \beta^a A + \beta^c C]}, \quad (3)$$

$$\frac{a}{c} = \frac{[\beta^a AB + R\beta^a A^2 + R\beta^c AC]}{[\alpha^c \beta^a AC + \alpha^b \beta^c BC + \alpha^c \beta^c C^2]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[RA + B]}, \quad (4)$$

where

$$R = k_{ca}/k_{cb}.$$

If α^b , α^c , β^a , β^c , γ^a , and γ^b are known from the separate 2-component studies, a single tripolymerization experiment will yield more than enough information to determine R . (R can be determined by Eq. (3), which allows Eq. (4) to be used as a check.)

There are also cases where *two* monomers (say B and C) have vanishing rates of self-propagation. If k_{bc} and k_{cb} as well as k_{bb} and k_{cc} vanish, then all necessary ratios can be determined from separate copolymerization reactions using the monomers two at a time, and the equations relating copolymer composition to monomer composition take on the simple form:

$$\frac{a}{b} = 1 + \frac{1}{\alpha^b} \frac{A}{B} + \frac{\alpha^c}{\alpha^b} \frac{C}{B}, \quad (5)$$

$$\frac{a}{c} = 1 + \frac{1}{\alpha^c} \frac{A}{C} + \frac{\alpha^b}{\alpha^c} \frac{B}{C}, \quad (6)$$

$$\frac{b}{c} = \frac{\alpha^b B}{\alpha^c C}. \quad (7)$$

If monomers B and C can add to one another, then a tripolymerization experiment is necessary. The equations for this case also follow simply from (1) and (2):

$$\frac{a}{b} = \frac{[R_1 AB + R_1 R_2 A^2 + R_2 AC]}{[R_2 \alpha^b AB + \alpha^b B^2 + \alpha^c BC]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[R_1 A + C]}, \quad (8)$$

$$\frac{a}{c} = \frac{[R_1 AB + R_1 R_2 A^2 + R_2 AC]}{[R_1 \alpha^c AC + \alpha^b BC + \alpha^c C^2]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[R_2 A + B]}, \quad (9)$$

where

$$R_1 = k_{ba}/k_{bc}, \quad R_2 = k_{ca}/k_{cb}.$$

If separate 2-component studies have yielded the values of α^b and α^c , plus the information that B and C do not add to themselves ($k_{bb} = k_{cc} = 0$) but do add to one another (B and C form a copolymer), then a tripolymerization experiment will yield enough information to determine the unknown ratios R_1 and R_2 .

¹ T. Alfrey and G. Goldfinger, J. Chem. Phys. **12**, 322 (1944).

² These equations have been extended to the general case of n monomers by C. Walling and E. R. Briggs, J. Am. Chem. Soc. **67**, 1774 (1945).

³ Private communication.

⁴ T. Alfrey and E. Lavin, J. Am. Chem. Soc. **67**, 2044 (1945).