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Partial Molar Volume Anomaly in Supercritical Mixtures and the Free Radical Polymerization of Ethylene

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SUMMARY

The anomalous properties of the supercritical region require that, when the pressure-coefficient of the rate constant is expressed according to transition-state theory, the meaning of the term "volume of activation" be analyzed with care. Applications to the polymerization of ethylene are shown.

A kinetic interpretation of the free radical polymerization of ethylene is easiest where all components exist in a single supercritical fluid phase. It has been shown that under such conditions one can sometimes account, at least qualitatively, for the effect of pressure on polymerization rate, molecular weight, and short-chain branching through transition-state theory [1]. In an incompressible mixture the pressure-coefficient of the rate constant, k_r , is then given by

$$\frac{\partial \ln k_r}{\partial P} = - \frac{\Delta V^\ddagger}{RT} \quad (1)$$

where ΔV^\ddagger is the "volume of activation." By making reasonable inferences about the pressure dependence of the rate constants for initiation and

termination, and by assuming solution ideality, one arrives at the approximate relation

$$\frac{\partial \ln k_{\text{pol}}}{\partial P} \sim - \frac{\Delta V_{\text{pol}}}{RT} \quad (2)$$

where k_{pol} is the over-all rate constant for polymerization and ΔV_{pol} the volume change of polymerization per monomer unit. Equation (2) represents quite adequately many rate data for liquid-phase polymerizations [2], and is qualitatively consistent with data obtained in several kinetic studies of ethylene polymerizing in the homogeneous supercritical phase [1].

It is becoming increasingly clear, however, that a relation such as Eq. (2), which implicitly links ΔV^\ddagger with the properties of the pure components, must fail badly in many supercritical systems because of their abnormal volumetric properties. For example, the partial molar volume of vinyl chloride in mixtures with ethylene is strongly negative in the supercritical phase over a rather broad range in pressure and composition [3], and the same has been found true for n-heptane in mixtures with ethane [4]. This partial molar volume anomaly is therefore not confined to supercritical mixtures of components with differing polarity, but also appears to be a characteristic of the less volatile component in supercritical mixtures of molecules with substantial size difference. As a result, Eq. (2) is likely to be even qualitatively incorrect through part of the supercritical region. A derivation of the more general, and correct, relation is in order, and the result will be seen to be capable of accounting for some kinetic phenomena in ethylene polymerization which had been difficult to rationalize.

For the general case of a nonideal, compressible, multicomponent solution, whether liquid, gaseous, or supercritical, we can write according to transition-state theory

$$k_T = \frac{\kappa T}{h} K_c^\ddagger \quad (3)$$

where K_c^\ddagger is defined by the product $\prod c_i^{\nu_i}$, and where c_i and ν_i stand for molar concentrations and stoichiometric coefficients, respectively, and κ for the Boltzmann constant. K_c^\ddagger is therefore equivalent to the K_c used in equilibrium thermodynamics, with the sole exception that the activated complex takes the place of the product. The definitions of K^\ddagger , K_γ^\ddagger , K_f^\ddagger , and K_ϕ^\ddagger , the equilibrium constants for the activated complex

in terms of activities, activity coefficients, fugacities, and fugacity coefficients, respectively, are similar to those of K_c^\ddagger . γ'_i represents the activity coefficient based on the molarities, c_i , γ_i that based on the mole fractions, y_i . We obtain

$$k_r = \frac{\kappa T}{h} K_c^\ddagger = \frac{\kappa T}{h} K^\ddagger (K_\gamma^\ddagger)^{-1} = \frac{\kappa T}{h} K^\ddagger (K_\gamma)^{-1} (K_y^\ddagger)^{-1} K_c^\ddagger \quad (4)$$

K_c^\ddagger can be eliminated by writing the molarities of the active species, c_i , in terms of the mole fractions, y_i . One then has

$$k_r = \frac{\kappa T}{h} K^\ddagger (K_\gamma^\ddagger)^{-1} \left(\frac{n}{V}\right)^{\sum \nu_i} \quad (5)$$

where n is the total number of moles of all species present and V is the volume. Equation (5) is suitable for differentiation with respect to pressure. Performing such a differentiation at constant temperature one obtains

$$\frac{\partial \ln k_r}{\partial P} = \frac{\partial \ln K^\ddagger}{\partial P} + \frac{\partial \ln K_\gamma^\ddagger}{\partial P} + \sum \nu_i \left(\frac{\partial \ln n}{\partial P} + \beta \right) \quad (6)$$

where β is the isothermal compressibility, equal to $-(1/V) (\partial V / \partial P)_{T,y}$.

One may allow the pure components (including the pure activated complex) at the pressure of the mixture to be the reference states, characterized by the molar volumes V_i^0 . In a closed system, one then obtains

$$\left(\frac{\partial \ln k_r}{\partial P} \right)_{T,y} = -(1/RT) \sum \nu_i V_i^0 - (1/RT) \sum \nu_i (\bar{v}_i - V_i^0) + \sum \nu_i \beta \quad (7)$$

where \bar{v}_i is the partial molar volume of component i , and where the first and second terms on the right-hand side correspond to the first and second terms on the right-hand side of Eq. (6). The second term therefore represents the contribution of solution nonideality. Equation (7) always reduces to

$$\left(\frac{\partial \ln k_r}{\partial P} \right)_{T,y} = -\sum \nu_i (\bar{v}_i / RT - \beta) \quad (8)$$

which is perfectly general for a closed system.

It is clear that the use of Eq. (2), which requires that ΔV^\ddagger be expressed in terms of the properties of the pure components, implies solution ideality, and therefore the substitution of the first term in the right-hand side of Eq. (7) for the first term in the right-hand side of Eq. (8). It is the latter, however, which must be made to represent the "volume of activation" in a nonideal system.

Alternatively, the correct general equation (8) may be obtained, even more directly, from Eq. (6) by allowing the reference states to be the ideal gases at 1 atm, in which case the first term on the right-hand side makes no contribution. Using the latter reference states, the rate constant may also be formulated in terms of fugacities and fugacity coefficients. Equation (5) becomes

$$k_r = \frac{\kappa T}{h} K_f^\ddagger (K_\gamma) \left(\frac{n}{V}\right)^{\sum \nu_i} = \frac{\kappa T}{h} K_f^\ddagger (K_\phi^\ddagger)^{-1} \left(\frac{n}{PV}\right)^{\sum \nu_i} \quad (9)$$

Since K_f^\ddagger is pressure independent, differentiation with respect to pressure and substitution in the result of the exact thermodynamic relation $RT d(\ln \phi_i) = (\bar{v}_i - RT/P) dP$ again leads to Eq. (8).

It seems likely that Eq. (8) in distinction to Eq. (2) provides the explanation for some important apparent anomalies in the kinetics of the high pressure polymerization of ethylene and in the structure of low and intermediate density polyethylene. Except in the immediate vicinity of the critical point, the contribution of the isothermal compressibility, β , to the pressure coefficient of the rate constant for propagation is unimportant, but the term $-\sum \nu_i \bar{v}_i / RT$ represents, to a first approximation, the difference in partial molar volume per monomer unit of polyethylene and of ethylene, both in supercritical solution. It is concluded that the former can be highly negative (up to several times the molar volume in absolute value), and the latter similar in magnitude to the corresponding molar volume under some conditions typical for the laboratory and commercial high pressure polymerization. This results in an abnormally high pressure-coefficient of the rate constant for propagation through the part of the supercritical region located not too far from the critical point. In particular, it is suggested that the partial molar volume anomaly (which does not, of course, occur where polymer forms as a separate crystalline phase) is likely to account largely for the fact that, even in supercritical mixtures, somewhat removed from the critical point, ΔV^\ddagger is comparable to ΔV_{po} , and not to 1/2 to 2/3 of that value, as in liquids [2]; the excessive effect of pressure on polymerization rate [5] and on short-chain branching [6] as the

pressure is dropped toward the critical value; the relatively low pressure-coefficient of the polymerization rate at temperatures where crystalline polymer precipitates [7]; and for the consequent high anomalous activation energy for polymerization at about 100 to 130°C.

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