Thermodynamic Properties of Liquid Polyethylene

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Synopsis

Thermodynamic properties of molten polyethylene are calculated for the temperature range 100° to 300°C and for pressures up to 3000 atmospheres. The calculations are based on limited experimental data augmented by a corresponding-states correlation and an empirical equation of state. Specific volume, internal energy, enthalpy, entropy, and solubility parameter are presented as functions of temperature and pressure. The results of this study may be useful for engineering design in the high-pressure polyethylene process.

INTRODUCTION

Low-density polyethylene is produced commercially at high pressures. For rational engineering design, it is necessary to know the thermodynamic properties of molten polyethylene as a function of temperature and pressure. Typical industrial reactors may operate at pressures up to thousands of atmospheres and at temperatures in the region of 100° to 300°C. At these conditions, experimental density data for polyethylene are scarce and heat-capacity data have been obtained only at atmospheric pressure. However, a corresponding-states correlation for liquid polymers permits reliable extrapolation of measured polyethylene volumetric data at atmospheric pressure, and use of the isothermal Tait equation allows extrapolation to higher pressures. Further, from available heat-capacity data and ideal-gas enthalpy data for n-alkanes, good estimates can be made for liquid polyethylene's enthalpy, internal energy, entropy, and solubility parameter in the pressure and temperature range of industrial interest.

CORRESPONDING-STATES THEORY

Simha and Havlik[1] have demonstrated that corresponding-states theory can be used to correlate volumetric properties of various liquid oligomers and high polymers. They showed that plots of volume–temperature data at atmospheric pressure could be superimposed by judicious selection, for each substance, of two reducing constants, V^* and T^*, which are independent of temperature and pressure. Their volume–temperature master curve has been shown to be accurately described by the empirical equation[2]

$$\ln \tilde{V}_0 = -7.28 \times 10^{-2} + 9.0752 \tilde{T}^{3/2}. \tag{1}$$
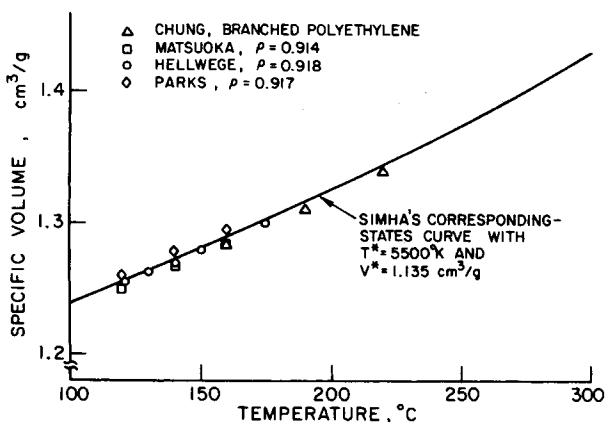
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Fig. 1. Specific volume of liquid polyethylene at atmospheric pressure (ρ = density of solid polyethylene at 25°C in g/cm³).

The reduced temperature $\tilde{T}$ and the reduced volume $\tilde{V}_0$ are defined by $\tilde{T} = T/T^*$ and $\tilde{V}_0 = V(1 \text{ atm})/V^*$. A plot of ln V_0 versus $T^{1/2}$ gives a straight line from which T^* and V^* can be obtained. Using available low-density ($\rho_{\text{solid, 25°C}} < 0.935$ g/cm³) polyethylene data,[3-6] T^* and V^* were obtained. The values $T^* = 5500°$K and $V^* = 1.135$ cm³/g were chosen as representative. Figure 1 compares experimental specific volume data with results calculated from eq. (1). The maximum deviation of experimental specific volumes from the corresponding-states curve is less than 1%.

For high pressures, we use the Tait equation:

$$1 - V/V_0 = C \ln (1 + P/B) \qquad (2)$$

where V_0 is the specific volume at atmospheric pressure and V is the specific volume at pressure P. (The argument of the logarithm in eq. (2) should correctly be written $(B + P)/(B + P_0)$, where $P_0 = 1$ atm. However, negligible errors are introduced by neglecting P_0 compared to B.) The parameter B is only a function of temperature, and the dimensionless constant C is a universal constant for all hydrocarbons equal to 0.0894, as shown by Cutler et al.[7] Simha and his co-workers[8,9] have found for various liquid polymers that the function

$$\ln B = a_1 + a_2 T \qquad (3)$$

adequately represents the temperature dependence of B when constants a_1 and a_2 are fixed by experimental data. Rearranging eq. (2) enables calculation of B from high-pressure volumetric data:

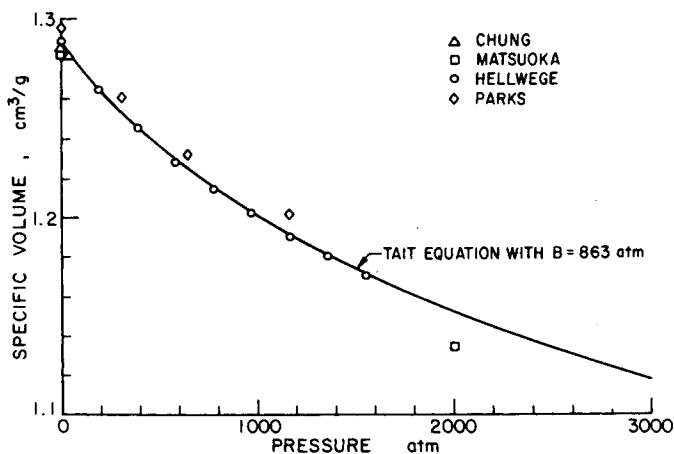$$B = P \left[e^{\frac{V_0 - V}{C V_0}} - 1 \right]^{-1}. \qquad (4)$$

Fig. 2. Effect of pressure on specific volume of liquid polyethylene at 160°C.

The low-density polyethylene data of Hellwege et al.[5] were reduced with eq. (4) and plotted in the form ln B versus T as suggested by eq. (3). The resulting straight line has the equation

$$\ln B = 7.541 - 0.00488t \tag{5}$$

where t is in degrees centigrade. B values calculated from other sources of experimental high-pressure data[4,6] were scattered about the values predicted by eq. (5).

Figure 2 compares experimental specific volumes with those obtained from the Tait equation at 160°C. Equations (1), (2), and (5) were used to calculate specific volumes for liquid polyethylene from 100° to 300°C and for pressures up to 3000 atm, shown in Figure 3. Also shown in Figure 3 are Matsuoka's[4] experimental melting points for linear and highly branched polyethylene. These can be used to estimate the conditions where molten polymer begins to solidify.

DERIVED THERMODYNAMIC PROPERTIES

To calculate other thermodynamic properties, we require heat capacity data. Wunderlich and Baur[10] report that between 37° and 177°C amorphous polyethylene's heat capacity at atmospheric pressure is well described by

$$C_P = 0.3743 + 5.58 \times 10^{-4}T \tag{6}$$

where C_P is in cal $g^{-1}°K^{-1}$ and T is in °K. We assume that this equation holds from 25° to 300°C.
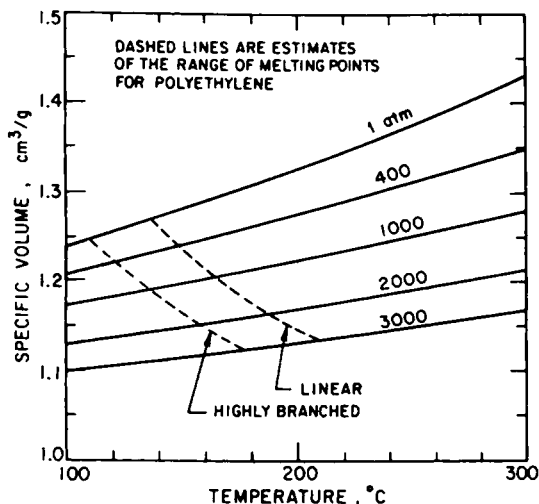
Fig. 3. Calculated specific volume of liquid polyethylene.

First, we calculate changes in entropy and enthalpy with temperature. At 1 atmosphere,

$$S(T_2, 1 \text{ atm}) - S(T_1, 1 \text{ atm}) = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT \qquad (7)$$

$$H(T_2, 1 \text{ atm}) - H(T_1, 1 \text{ atm}) = \int_{T_1}^{T_2} C_P \, dT. \qquad (8)$$

To find the effect of volume on entropy, we use the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \qquad (9)$$

Rewriting the Tait equation

$$P = B\left[e^{\frac{V_0 - V}{CV_0}} - 1 \right] \qquad (10)$$

yields

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{B}\left(\frac{dB}{dT}\right) + \frac{V}{C}\frac{(B+P)}{V_0^2}\left(\frac{dV_0}{dT}\right). \qquad (11)$$

Integration of eq. (11) between V_0 and V at constant temperatures gives

$$S(V,T) - S(V_0,T) = \left[\frac{d \ln B}{dT}\right][B(V_0 - V) - CV_0 P]$$

$$+ \left[\frac{d \ln V_0}{dT}\right][B(V_0 - V) - P(V + CV_0)]. \qquad (12)$$

We arbitrarily chose a base entropy $S(100°C, 1 \text{ atm}) = 1.0$ cal g^{-1} °C^{-1} to obtain positive entropies at the pressures of interest. Equations (7) and (12) yield $S(T,P)$ as shown in Figure 4.
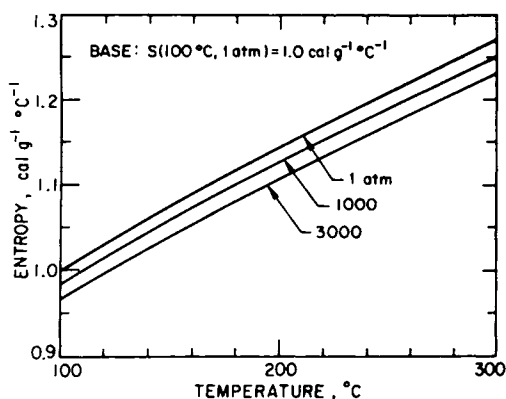
Fig. 4. Calculated entropy of liquid polyethylene.

Internal energy U is given by

$$dU = TdS - PdV. \tag{13}$$

Substituting eq. (10) into eq. (13) and integrating between V_0 and V at constant temperature gives

$$U(V,T) - U(V_0,T) = T[S(V,T) - S(V_0,T)]$$
$$+ V_0CP - B(V_0 - V). \tag{14}$$

Enthalpy H is found from the definition

$$H = U + PV. \tag{15}$$

Using a base enthalpy $H(100°C, 1 \text{ atm}) = 100$ cal/g, eqs. (8), (14), and (15) were used to give $H(T,P)$ as shown in Figure 5. Figure 6, based on eqs. (8), (14), and (15), shows the internal energy of liquid polyethylene.

POLYETHYLENE IN THE IDEAL-GAS STATE

Figure 6 also shows an estimate of the internal energy of polyethylene in the ideal-gas state (denoted by superscript 0). This estimate was calculated by least-squares fitting of ideal-gas enthalpy data for n-alkanes,[11] with $15 \leq N \leq 20$, where N is the carbon number. This calculation assumes that the specific enthalpy is given by

$$H^0(N) = H_\infty^0 + H_e^0/N \tag{16}$$

where H_∞^0 is the enthalpy of 1 g of infinitely long polyethylene molecules, $(CH_2)_{N \to \infty}$, in the ideal-gas state, and H_e^0 is the specific enthalpy associated with CH_3 endgroups. Since $PV = RT/M$ for an ideal gas, were M is molecular weight, eq. (15) gives
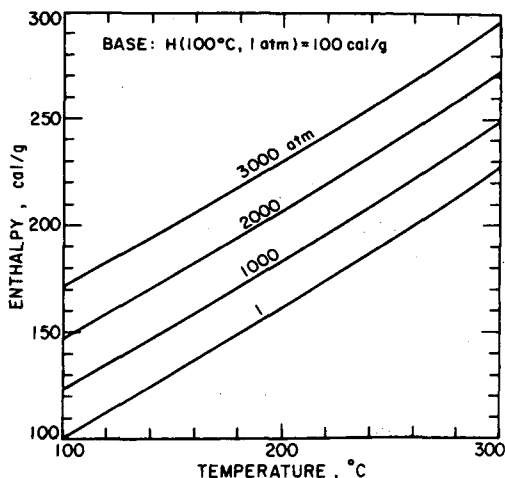
$$H^0 = U^0 + RT/M. \tag{17}$$

Fig. 5. Calculated enthalpy of liquid polyethylene.

For infinitely long polyethylene, $M \to \infty$, and $H_\infty{}^0 = U_\infty{}^0$. The ideal-gas enthalpies at 100°, 200°, and 300°C are equal to the corresponding ideal-gas internal energies. These are represented by

$$U_\infty{}^0 = 59.80 + 0.3883t + 0.0004326t^2 + U_B \tag{18}$$

where $U_\infty{}^0$ and U_B are in cal/g and t is in °C. Also calculated was $U_\infty^0 (25°C) = 70.78 \text{ cal/g} + U_B$.

The constant U_B is included to scale these internal energies to the previously chosen base $H(100°C, 1 \text{ atm}) = 100 \text{ cal/g}$. To compute a numerical value for U_B, we estimated polyethylene's solubility parameter, defined by

$$\delta(T,P) = \left[\frac{U^0(T,P = 0) - U(T,P)}{V(T,P)} \right]^{1/2}. \tag{19}$$

Solubility parameters for n-alkanes[12] at 25°C, with $10 \leq N \leq 20$, were least squares fit to the equation

$$\delta(N) = \delta_\infty + \delta_e/N. \tag{20}$$

Equation (20), as well as eq. (16), is justified by an assumption suggested by Broadhurst[13]; the molar energies and volumes are linear in N, that is, each methylene repeating segment adds a constant increment to the total energy and to the total volume of a molecule. Equations (16) and (20) are appropriate for large N because they neglect terms in $1/N^2$, $1/N^3$, etc. Equation (20) gives $\delta_\infty(25°C, 1 \text{ atm}) = 8.44 \text{ (cal/cm}^3)^{1/2}$. This value for the solubility parameter is slightly higher than those obtained from solubility data for polyethylene in hydrocarbon solvents, $\delta \approx 8.0 \text{ (cal/cm}^3)^{1/2}$. This difference is not surprising since the solubility parameter is a pure-component property rigorously calculated from eq. (19). By contrast, polymer solution theories, from which δ can be obtained using solubility data, are only approximations.
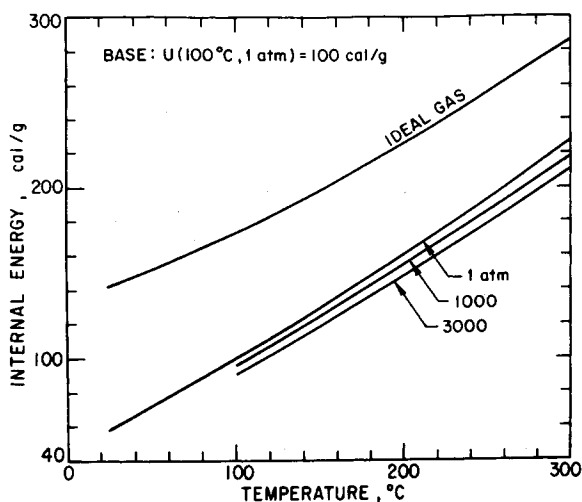
Fig. 6. Calculated internal energy of liquid polyethylene.

From the corresponding-states correlations, $V(25°C, 1$ atm$) = 1.183$ cm³/g and $U(25°C, 1$ atm$) = 57.85$ cal/g. These values combined with $U_\infty^0(25°C)$ and eq. (19) yield $U_B = 71.34$ cal/g. The ideal-gas internal energies in Figure 6 were calculated by rewriting eq. (18):

$$U_\infty^0 = 131.14 + 0.3883t + 0.0004326t^2. \tag{21}$$

Figure 7 shows solubility parameters obtained from eqs. (19) and (21) with internal energies and volumes from Figures 3 and 6.

DISCUSSION

Figures 3–7 provide fundamental thermodynamic data which may be useful in chemical process design. Detailed numerical tables used to prepare these figures are available from the authors upon request.

Since Simha's publication of 1964, he and his co-workers have elaborated further on the theory of corresponding states and have presented several theoretical interpretations of experimental data.[9,14,15] Although not used in this paper's empirical approach, these latter publications contain valuable information for estimation of polymer thermodynamic properties. It had been reported[16] that the low-density polyethylene data of Hellwege et al.[5] could be correlated with eq. (2) only if B were pressure dependent. Later, it was discovered[9] that the definition of relative volume change used by Hellwege et al.[5] had been misinterpreted so that the conclusions of this earlier article were not valid. Our calculations show that these low-density polyethylene data are well represented by pressure-independent B values.

Analysis of volumetric data from various polyethylene samples,[3-6,17-19] including some which had high densities in the solid state, showed no systematic variation of liquid densities with chain branching, as indicated by solid density at 25°C. All the data are scattered around our calculated specific volumes shown in Figure 3. We therefore attribute the variations
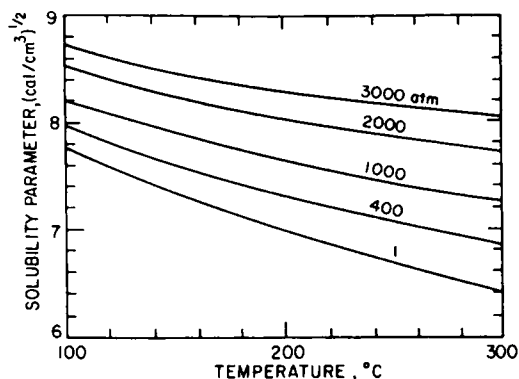
Fig. 7. Calculated solubility parameter of liquid polyethylene.

among experimental data primarily to experimental uncertainties and conclude that there is no significant difference between linear and branched polyethylene in the liquid state.   Thus, we expect that the results presented here provide a good estimate for the thermodynamic properties of liquid polyethylene, regardless of the degree of branching.

References

1. R. Simha and A. J. Havlik, *J. Amer. Chem. Soc.*, **86**, 197 (1964).
2. R. Simha and C. E. Weil, *J. Macromol. Sci.-Phys.*, **B4**, 215 (1970).
3. C. I. Chung, *J. Appl. Polym. Sci.*, **15**, 1277 (1971).
4. S. Matsuoka, *J. Polym. Sci.*, **57**, 569 (1962).
5. K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z. Z. Polym.*, **183**, 110 (1962).
6. W. Parks and R. B. Richards, *Trans. Faraday Soc.*, **45**, 203 (1949).
7. W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, *J. Chem. Phys.*, **29**, 727 (1958).
8. A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).
9. R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid-Z. Z. Polym.*, **251**, 402 (1973).
10. B. Wunderlich and H. Baur, *Advan. Polym. Sci.*, **7**, 297 (1970).
11. American Petroleum Institute, Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Pittsburgh, Pa., 1955, Table 20u-G.
12. R. F. Blanks and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **3**, 1 (1964).
13. M. G. Broadhurst, *J. Res. Nat. Bur. Stand.*, **67A**, 233 (1963).
14. R. Simha and T. Somcynsky, *Macromolecule*, **2**, 342 (1969).
15. R. Simha and P. S. Wilson, *Macromolecule*, **6**, 908 (1973).
16. V. S. Nanda and R. Simha, *J. Chem. Phys.* **41**, 3870 (1964).
17. G. N. Foster, N. Waldman, and R. G. Griskey, *J. Appl. Polym. Sci.*, **10**, 201 (1966).
18. M. G. Gubler and A. J. Kovacs, *J. Polym. Sci.*, **34**, 551 (1959).
19. R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967).