Improves Process Performance," *Instrum. Technol.*, **20**, 71 (1973).

———, *Multivariable Computer Control, A Case Study*, North Holland (1976).

Hamilton, J. C., D. E. Seborg and D. G. Fisher, "An Experimental Evaluation of Kalman Filtering," *AIChE J.*, **19**, 901 (1973).

Jutan, A., "State Space Modelling and Multivariable Stochastic Control of a Pilot Plant Packed Bed Reactor," Ph.D. thesis, McMaster University (1976).

———, J. P. Tremblay, J. F. MacGregor and J. D. Wright, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part I—State Space Reactor Modelling, *AIChE J.*, **23**, 732 (1977).

Jutan, A., J. F. MacGregor, and J. D. Wright, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part II—Data Collection, Parameter Estimation and Stochastic Disturbance Identification," *AIChE J.*, **23**, 742 (1977).

Jazwinski, A. H., *Stochastic Processes and Filtering Theory*, Academic Press, New York, (1970).

Michelsen, M. L., H. B. Vakil, and A. S. Foss, "State Space Formulation of Fixed Bed Reactor Dynamics," *Ind. Eng. Chem. Fund.*, **12**, *3*, 323 (1973).

MacGregor, J. F., "Optimal Discrete Stochastic Control Theory for Process Application," *Can. J. Chem. Eng.*, **51**, 468 (1973).

Noton, A. R. M., *Introduction to Variational Methods in Control Engineering*, Pergamon Press, New York (1965).

Orlikas, A., *Kinetic Study of the Hydrogenolysis of n-Butane on Nickel Catalyst*, M.Eng. thesis, McMaster University, Hamilton, Canada (1970).

Shinsky, F. G., "Stable Distillation Control Through Proper Pairing of Variables," *ISA Trans.*, **10**, No. 4, 403 (1971).

Sage, A. P. and Melsa, J. L., *Estimation Theory with Applications to Communications and Control*, McGraw-Hill (1971).

———., *Optimum Systems Control*, Prentice-Hall, Englewood Cliffs, N.J. (1968).

Shaw, I. D., *Modelling and Discrimination Studies in a Catalytic Fluidized Bed Reactor*, Ph.D. thesis, McMaster University, Hamilton, Canada (1974).

Tremblay, J. P., *Computer Control of a Butane Hydrogenolysis Reactor*, M.Eng. thesis, McMaster University, Hamilton, Ontario, Canada (1973).

———, and J. D. Wright, "Computer Control of a Butane Hydrogenolysis Reactor," *Can. J. Chem. Eng.*, **52**, 845 (1974).

———, *Real Time Computer Data Acquisition and Control Systems: An Application to Model Reference Adaptive Control of a Packed Bed Tubular Reactor*, Ph.D. thesis, McMaster University, Hamilton, Ontario, Canada (1977).

Vakil, H. B., M. L. Michelsen, and A. S. Foss, "Fixed Bed Reactor Control with State Estimation," *Ind. Eng. Chem. Fund.*, **12**, No. 3, 328 (1973).

Manuscript received December 14, 1976; revision received June 10, and accepted June 22, 1977.

Calculation of Phase Equilibria for Ethylene/Low-Density Polyethylene Mixtures

We have used recent ethylene/low-density polyethylene gas sorption data to calculate phase equilibria for ethylene/polyethylene mixtures from 0 to 30.3 MN/m^2 (0 to 300 atm), the pressure range normally used in the flash separation step in low-density polyethylene manufacture. The computations show significant differences from results obtained by extrapolation of the results of a previous study to the relatively low pressure range considered here.

STEPHEN C. HARMONY
DAVID C. BONNER
and
HUBERT R. HEICHELHEIM

Chemical Engineering Dept.
Texas Tech University
Lubbock, Texas 79409

SCOPE

The purpose of our study of ethylene/low-density polyethylene phase equilibrium was to calculate phase equilibrium between ethylene and polyethylene using corresponding states analysis applicable to low-density gases as well as to dense liquids and gases. Our emphasis is primarily on the pressure range in which ethylene is removed from polyethylene in industrial production after the reaction to produce polyethylene. Estimates of ethylene/low-density polyethylene phase equilibria have been published previously. However, the present analysis uses an improved statistical mechanical model of gas/polymer equilibrium. The parameters used in the model are obtained from recently published ethylene/polyethylene phase equilibrium data.

CONCLUSION AND SIGNIFICANCE

We have used an improved model for phase equilibria in gas/polymer solutions to calculate phase equilibria for ethylene/low-density polyethylene mixtures, taking into account polymer molecular weight distribution. The calculations indicated differences in phase compositions at less than 30.3 MN/m^2 (300 atm) from those of a previous study of such a magnitude that design of the flash separation and ethylene recycle steps in a low-density polyethylene process could be affected. Further, the new model predicts ethylene partial pressures in polyethylene solutions well at low pressures characteristics of devolatilization conditions in low-density polyethylene manufacture.

Correspondence concerning this paper should be addressed to David C. Bonner, Chemical Engineering Department, Texas A&M University, College Station, Texas 77843.

Low-density polyethylene is manufactured at temperatures as great as 533°K and pressures as great as 303 MN/m^2 (3 000 atm). The mixture leaving the reactor, which typically contains 20 wt % polyethylene, is decompressed to approximately 5.05 MN/m^2 (50 atm) to separate the unreacted ethylene from the polyethylene. At sufficiently low pressures, the mixture forms two phases, one primarily ethylene and the other primarily polyethylene. In the manufacturing process, the ethylene phase is purified to remove the low, molecular weight polyethylene waxes and oils, compressed and recycled into the reactor.

Significant energy savings could be realized if the separation step were accomplished at a higher pressure, reducing the energy needed to recompress the recycled ethylene. At the higher pressures, however, a significant amount of polyethylene will be present in the ethylene rich phase, and a significant amount of ethylene will be present in the polyethylene rich phase. For the rational design of energy saving separation processes, the design engineer must be able to predict the effects of pressure and temperature on the compositions of the two equilibrium phases.

In this work, we use a recently developed free volume theory of polymer solutions (Cheng and Bonner, 1977*b*) and the computational algorithm of Bonner et al. (1974) to calculate phase equilibrium for ethylene/low-density polyethylene mixtures at pressures to 20.2 MN/m^2. Such a computation was previously not reliably possible at pressures below approximately 30.3 MN/m^2. The polymer solution model used by Bonner et al. (1974) is applicable only to mixtures of dense fluids and should not be used for ethylene/polyethylene mixtures at pressures less than 30.3 MN/m^2.

POLYMER SOLUTION THEORY

The first qualitatively correct theory of polymer solutions was proposed independently in 1941 by Huggins (1941) and Flory (1941). The Flory-Huggins theory considers a polymer molecule as a chain of r roughly spherical segments. By considering the number of ways the polymer segments and solvent molecules can be arranged in a three-dimensional lattice, the entropy of athermal mixing, also called the combinatory entropy of mixing, is derived:

$$\Delta S_{\text{comb}} = -k(N_1 \ln \Phi_1 + N_2 \ln \Phi_2) \tag{1}$$

In this and all following expressions, the subscript 1 refers to solvent, and the subscript 2 refers to polymer.

The Flory-Huggins theory is extended to nonathermal mixtures by adding an empirical van Laar enthalpy of mixing to $-T\Delta S_{\text{comb}}$ to obtain the Gibbs energy of mixing. Subsequent differentiation of the expression for Gibbs energy of mixing gives the chemical potential of the solvent:

$$(\mu_1 - \mu_1{}^0)/RT = \ln(\Phi_1) + (1 - 1/r)\Phi_2 + \chi\Phi_2{}^2 \tag{2}$$

In the original development of the Flory-Huggins theory, χ was assumed to be independent of concentration and proportional to $1/T$.

The Flory-Huggins theory gives only a semiquantitative representation of the thermodynamic activity of polymer solutions. When χ is calculated from activity data, it is found in many cases to vary with concentration (Bonner and Prausnitz, 1973). The parameter χ often does not vary with $1/T$ as proposed by the van Laar model. Since the Flory-Huggins theory is based on the rigid lattice model, it gives no equation of state for the mixture.

A more exact representation of the properties of polymer solutions is given by the free volume or corresponding states theory of Prigogine (1957) and Flory (1965). Prigogine and co-workers viewed a polymer molecule as a chain of r segments, each having $3c$ external degrees of freedom. In the free volume approach, a suitable partition function is formulated for the mixture based on the Flory-Huggins combinatory factor and a reasonable representation for the intermolecular potential (Flory, 1965). According to statistical mechanics, the equation of state and other thermodynamic properties can be derived from a partition function. Of particular interest here are the equation of state

$$p(T, V) = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} \tag{3}$$

and the chemical potential

$$\frac{\mu_i - \mu_i{}^0}{kT} = -\left[\left(\frac{\partial \ln Z}{\partial N_i}\right)_{T,V,N_j} - \overset{j\neq i}{\underset{N_j \to 0}{\lim}}\left(\frac{\partial \ln Z}{\partial N_i}\right)_{\substack{T,V,N_j\\ j\neq i}}\right] \tag{4}$$

The partition function proposed by Flory for polymer solutions is

$$Z = Z_{\text{comb}}(\lambda\nu^*)^{Nrc}(\tilde{\nu}^{1/3} - 1)^{3Nrc}\exp(Nrc/\tilde{\nu}\tilde{T}) \tag{5}$$

Differentiation of Equation (5) yields a reduced equation of state:

$$\frac{\tilde{p}\tilde{\nu}}{\tilde{T}} = \frac{\tilde{\nu}^{1/3}}{\tilde{\nu}^{1/3} - 1} - \frac{1}{\tilde{\nu}\tilde{T}} \tag{6}$$

The characteristic parameters p^*, ν^*, and T^* are related by (Flory, 1965)

$$p^*\nu^* = ckT^* \tag{7}$$

Equations (5), (6), and (7) are formally the same for pure components and mixtures. When Equations (5), (6), and (7) are used for mixtures, p^*, ν^*, T^*, c, N, and r are mixture properties which can be calculated from the pure component properties, as will be shown below.

In the derivation of the corresponding states theory of Prigogine and Flory, consideration was limited to dense, liquid phases. Cheng (1977*b*) has formulated a new partition function for pure components and mixtures which overcomes this limitation. The distinguishing feature of the new partition function is based on a concept introduced by Beret and Prausnitz (1976). The contributions of the rotational, vibrational, and electronic modes of motion to the partition function vanish at the low-density limit. The partition function proposed by Cheng (1977*b*) is

$$Z = Z_{\text{comb}}(\lambda\nu^*)^{Nrc}(\tilde{\nu}^{1/3} - 1)^{3Ncr}\left(\frac{1}{\tilde{\nu}}\right)^{N(rc-1)}\exp(Nrc/\tilde{\nu}\tilde{T}) \tag{8}$$

From Equation (8) one obtains a reduced equation of state

TABLE 1. PURE COMPONENT CHARACTERISTIC PARAMETERS

Species	Specific hard core volume, v^*_{sp}/ kg/m^3 × 10^{-3}	Characteristic temperature, T*/°K	Characteristic pressure, p^*/MNm^{-2}	Temperature and pressure range used
Low-density polyethylene*	1.02	6 730	414.0	393°-573°K 1.01-14.1 MN/m^2
Ethylene†	1.30	1 708	391.5	366°-533°K 0.101-14.1 MN/m^2

* Data source: Beret and Prausnitz (1975*a*).

† Determined by Cheng from data of Benzler and Koch (1955).

$$\frac{\tilde{p}\tilde{\nu}}{\tilde{T}} = \frac{1}{rc} + \frac{1}{(\nu^{1/3} - 1)} - \frac{1}{\tilde{\nu}\tilde{T}} \tag{9}$$

where $\tilde{p}$, $\tilde{\nu}$, and $\tilde{T}$ are defined as in Equation (6). The relationship between the characteristic parameters p^*, ν^*, and T^* is given by Equation (7). For a pure component, Equation (9) can be rewritten using Equation (7) and the definition of v_{sp}^*:

$$\frac{\tilde{p}\tilde{\nu}}{\tilde{T}} = \frac{RT^*}{p^* M v_{sp}^*} + \frac{1}{(\tilde{\nu}^{1/3} - 1)} - \frac{1}{\tilde{\nu}\tilde{T}} \tag{10}$$

Equation (10) reduces to the ideal gas equation of state $pMv_{sp}/RT = 1$ at the low-density limit, making it equally applicable for dense and dilute phases.

Binary Mixtures

Following the development of Flory (1965), Cheng (1977*b*) formulated a one-fluid, corresponding states theory for binary mixtures of gas and liquid polymers. The partition function remains the same as Equation (8), with N, r, and c defined as follows:

$$N = N_1 + N_2$$

$$\frac{1}{r} = \frac{\Psi_1}{r_1} + \frac{\Psi_2}{r_2} \tag{11}$$

$$c = \Psi_1 c_1 + \Psi_2 c_2$$

The equation of state remains formally the same as Equation (9). Following Flory (1965), the characteristic parameters for the mixture are

$$p^* = \Psi_1\theta_1 p_1^* + \Psi_2\theta_2 p_2^* + 2(\Psi_1\Psi_2\theta_1\theta_2)^{1/2} p_{12}^*$$

$$T^* = \frac{p^*}{\Psi_1 p_1^*/T_1^* + \Psi_2 p_2^*/T_2^*} \tag{12}$$

$$\nu^* = \nu_1^* = \nu_2^*$$

The parameter p_{12}^* accounts for the intermolecular potential of binary interactions. Not that the assumption $\nu_1^* = \nu_2^*$ is nonrestrictive, since the size of each segment may be arbitrarily chosen. Owing to this assumption, the segment ratio r_1/r_2 is given by

$$\frac{r_1}{r_2} = \frac{M_1 v_{1sp}^*}{M_2 v_{2sp}^*} \tag{13}$$

One must arbitrarily fix either r_1 or r_2 to determine the other. We have set r_1 equal to unity.

If we use Equations (7) and (13), Equation (9) for the mixture becomes

$$\frac{\tilde{p}\tilde{\nu}}{\tilde{T}} = \frac{RT^*}{p^*}\left(\frac{\Psi_1}{M_1 v_{1sp}^*} + \frac{\Psi_2}{M_2 v_{2sp}^*}\right) + \frac{1}{(\tilde{\nu}^{1/3} - 1)} - \frac{1}{\tilde{\nu}\tilde{T}} \tag{14}$$

The reduced volume of the mixture can be obtained from the equation of state. A good first approximation is

$$\tilde{\nu} = \Psi_1\tilde{\nu}_1 + \Psi_2\tilde{\nu}_2 \tag{15}$$

Chemical Potential

From Equations (4) and (8), the chemical potential of the solvent is given by

$$\frac{\mu_1 - \mu_1^0}{kT} = \ln \Psi_1 + (1 - r_1/r_2)\Psi_2$$

$$+ \frac{\nu_1^* r_1}{k}\left[3\frac{p^*_1}{T^*_1}\ln\left(\frac{\tilde{\nu}_1^{1/3} - 1}{\tilde{\nu}^{1/3} - 1}\right) + \frac{p}{T}(\tilde{\nu}^{4/3} - \tilde{\nu}_1^{4/3})\right.$$

$$\left. + \frac{1}{T}\left(\frac{p^*}{\tilde{\nu}^{2/3}} - \frac{p_1^*}{\tilde{\nu}_1^{2/3}}\right) + \frac{p_1^*}{T_1^*} - \frac{p^*}{T^*}\right] + \left(\frac{p_1^*\nu_1^* r_1}{kT_1^*} - 1\right)$$

$$\ln\frac{\tilde{\nu}}{\tilde{\nu}_1} - 1 - \frac{r_1}{r}(\tilde{\nu}^{1/3} - 1) + \tilde{\nu}_1^{1/3} + \frac{r_1\nu_1^*}{kT}\left[\frac{X_{12}\theta_2^2}{\tilde{\nu}}\right.$$

$$\left. - p_1^*\left(\frac{1}{\tilde{\nu}} - \frac{1}{\tilde{\nu}_1}\right) + \frac{p_1^*}{\tilde{\nu}_1} - \frac{p^*}{\tilde{\nu}}\right] \tag{16}$$

where $X_{12} = p_1^* + (s_1/s_2)p_2^* - 2(s_1/s_2)^{1/2}p_{12}^*$. A similar expression, given below, can be derived for the polymer chemical potential. Note that the term $\nu_1^* r_1/k$ can be replaced by $v_{1sp}^* M_1/R$ in Equation (16).

Determination of Characteristic Parameters

The pure component characteristic parameters can be determined from experimental pressure-volume-temperature (PVT) properties by determining the best fit for the coefficient of thermal expansion α, $(1/V)$ $(\partial V/\partial T)_p$, the thermal pressure coefficient γ, $(\partial P/\partial T)_V$, and the temperature T. The characteristic parameters are assumed to be constant over the range of pressures and temperatures used in their determination. The details of the procedure for determining pure component characteristics parameters are given in the Appendix. Low-density polyethylene parameters p^*, v_{sp}^*, and T^* were determined using the data of Beret and Prausnitz (1975). The derived characteristic parameters are shown in Table 1. Cheng (1977*b*) determined the characteristic parameters for ethylene based on the data of Benzler and von Koch (1955).

The fit of experimental PVT data for low-density polyethylene is extremely good and is certainly within the precision of the data. Typical comparisons of theory with

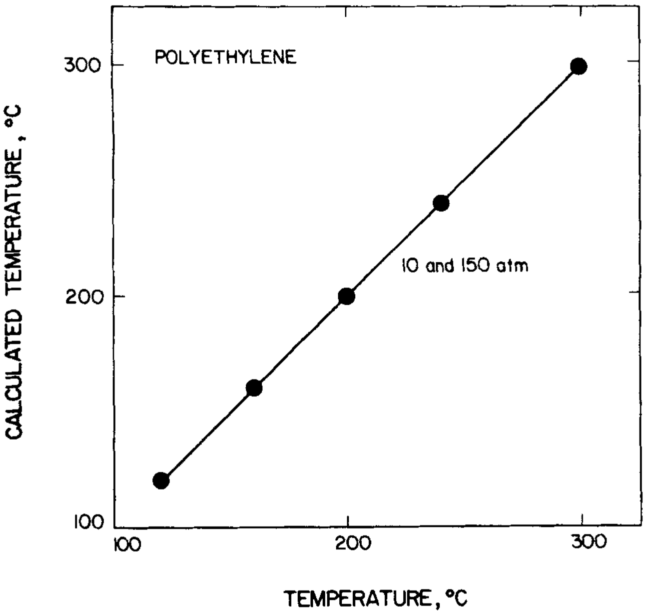

Fig. 1. Calculated temperature vs. temperature for low-density polyethylene.

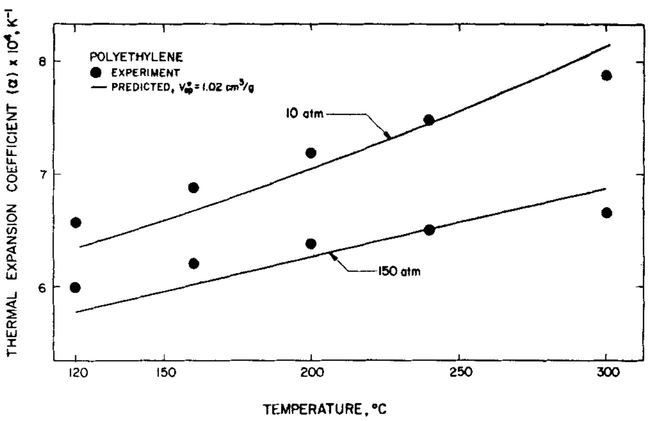

Fig. 2. Thermal expansion coefficient vs. temperature for low-density polyethylene.

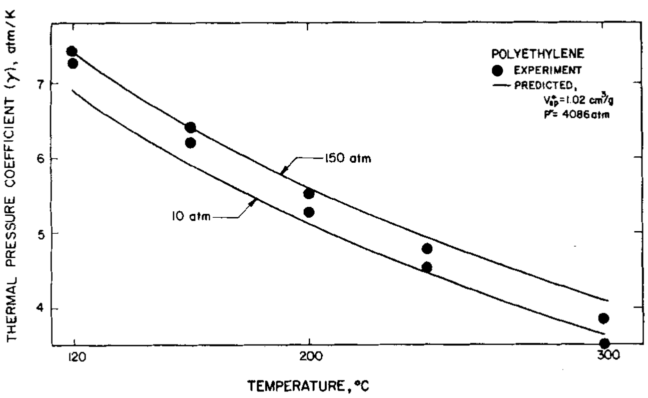

Fig. 3. Thermal pressure coefficient vs. temperature for low-density polyethylene.

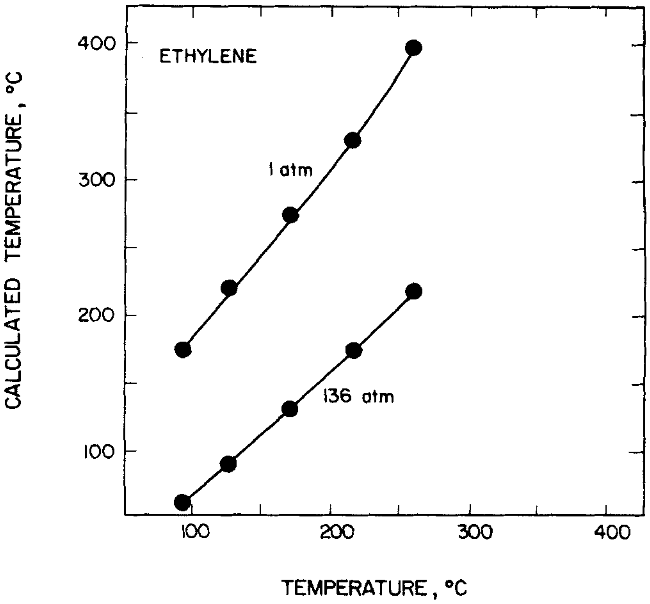

Fig. 4. Calculated temperature vs. temperature for ethylene.

polyethylene data are shown in Figures 1 to 3. The experimental fit of ethylene volume as a function of pressure and temperature (portrayed in Figure 4 as a plot calculated temperature vs. actual temperature at two pressures) is not extremely good, as is typical of an equation of state with a van der Waals potential. The fit of thermal expansion coefficient (Figure 5) and thermal pressure coefficient (Figure 6) for ethylene is quite good.

The correlation in Figure 4 could be improved by utilizing a different form for the intermolecular potential at the expense of greatly increased complexity and, as will be seen later, with little increase in the accuracy of the phase equilibrium predictions. The phase equilibrium predictions with our model are already quite good.

The reason that the model works well for gas/polymer solutions using a simple van der Waals potential is probably that ethylene partial molar volumes in molten polyethylene are of the same order of magnitude as those of liquids (Maloney and Prausnitz, 1976). Van der Waals potentials work well in density ranges typical of liquids (Flory, 1965).

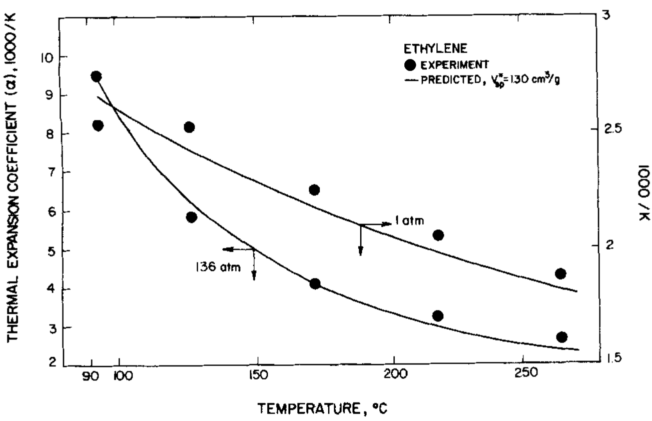

Fig. 5. Thermal expansion coefficient vs. temperature for ethylene.

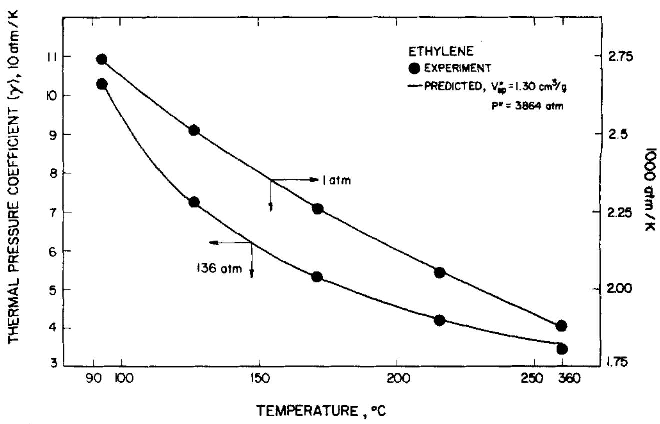

Fig. 6. Thermal pressure coefficient vs. temperature for ethylene.

The binary interaction parameter p_{12}^* can be determined from polymer solvent, phase equilibrium data using Equation (16) for the ethylene chemical potential. The procedure is presented in the Appendix. The parameter p_{12}^* was determined for the ethylene/low-density polyethylene system over the range 399° to 428°K and 0.402 to 7.07 MN/m^2 (4 to 70 atm) using the ethylene sorption data of Cheng and Bonner (1977*a*). The best fit of the data was obtained using a value for p_{12}^* of 5 784 MN/m^2 (5 727 atm).

Equilibrium Equations

When phases α and β, containing ethylene and n species of low-density polyethylene, are at the same temperature and pressure, phase equilibrium can be determined by solving the $n + 1$ equations

$$\begin{gathered} \mu_1{}^\alpha = \mu_1{}^\beta \\ \mu_{21}{}^\alpha = \mu_{21}{}^\beta \\ \vdots \\ \mu_{2i}{}^\alpha = \mu_{2i}{}^\beta \\ \vdots \\ \mu_{2n}{}^\alpha = \mu_{2n}{}^\beta \end{gathered} \tag{17}$$

where the superscripts refer to the α and β phases, and the second subscript refers to a polymer with a particular molecular weight. Equations (17) can be rewritten by subtracting the pure component chemical potential ($\mu_i{}^0$) from each side, resulting in

$$(\mu_1 - \mu_1{}^0)^\alpha = (\mu_1 - \mu_1{}^0)^\beta \tag{18a}$$

$$(\mu_{21} - \mu_{21}{}^0)^\alpha = (\mu_{21} - \mu_{21}{}^0)^\beta \tag{18b}$$

$$(\mu_{2i} - \mu_{2i}{}^0)^\alpha = (\mu_{2i} - \mu_{2i}{}^0)^\beta \tag{18c}$$

$$(\mu_{2n} - \mu_{2n}{}^0)^\alpha = (\mu_{2n} - \mu_{2n}{}^0)^\beta \tag{18d}$$

Equation (16) can be used for the ethylene chemical potential if the second term is modified to read $[1 - (r_1/(r_2)_n)]\Psi_2$, where $(r_2)_n$ is the number-average polymer chain length in the phase being considered. The equation for the chemical potential of polymer species i of molecular weight M_i is

$$\begin{aligned} \frac{\mu_{2i} - \mu_{2i}{}^0}{kT} = {} & \ln \Psi_{2i} - \left(\frac{r_{2i}}{r_1} - 1 \right) + \Psi_2 \frac{r_{2i}}{r_1} \left[1 - \frac{r_1}{(r_2)_n} \right] \\ & + \frac{\nu_1{}^* r_{2i}}{k} \left[3 \frac{p_2{}^*}{T_2{}^*} \ln \left(\frac{\tilde{\nu}_2{}^{1/3} - 1}{\tilde{\nu}^{1/3} - 1} \right) + \frac{p}{T} (\tilde{\nu}^{4/3} - \tilde{\nu}^{4/3}) \right. \\ & \left. + \frac{1}{T} \left(\frac{p^*}{\tilde{\nu}^{2/3}} - \frac{p_2{}^*}{\tilde{\nu}_2{}^{2/3}} \right) + \frac{p_2{}^*}{T_2{}^*} - \frac{p^*}{T^*} \right] + \left(\frac{p_2{}^* \nu_1{}^* r_{2i}}{kT_2{}^*} - 1 \right) \\ & \ln \frac{\tilde{\nu}}{\nu_2} - 1 - \frac{r_{2i}}{r} (\tilde{\nu}^{1/3} - 1) + \tilde{\nu}_2{}^{1/3} + \frac{r_{2i} \nu_1{}^*}{kT} \left[\frac{X_{21} \theta_1{}^2}{\tilde{\nu}} \right. \\ & \left. - p_2{}^* \left(\frac{1}{\tilde{\nu}} - \frac{1}{\tilde{\nu}_2} \right) + \frac{p_2{}^*}{\tilde{\nu}_2} - \frac{p^*}{\tilde{\nu}} \right] \end{aligned} \tag{19}$$

where $X_{21} = p_2{}^* + (s_2/s_1) p_1{}^* - 2(s_2/s_1)^{1/2} p_{12}{}^*$, Ψ_{2i} is the segment fraction of polymer species i, r_{2i} is the chain length of polymer species i, and $\Psi_2 = \sum_{i=1}^{n} \Psi_{2i}$ is the total polymer segment fraction.

We have assumed that $p_2{}^*$, $v_{2sp}{}^*$, and $T_2{}^*$ are independent of polymer chain length. Orwoll and Flory (1067) show that this is a good assumption, provided that the polymer chain length is large. We also assume that $s_1/s_2 = 1$. Estimates of s_1/s_2 based on lattice models and van der Waals radii vary from 0.7 to 1.4; therefore, the value $s_1/s_2 = 1$ provides a reasonable estimate (Bonner et al., 1974).

RESULTS

The computational algorithm of Bonner et al. (1974) was used with the Cheng free volume theory to predict phase equilibria for the ethylene/low-density polyethylene

TABLE 2. PHASE EQUILIBRIUM AT DESIGN CONDITIONS

Temperature, °K	Pressure, MNm^{-2} (atm)	A	B	$\overline{M}_n$, light phase	$\overline{M}_n$, heavy phase
413	7.07 (70)	0.00412	1.16	50	13 259
413	15.2 (150)	0.00403	3.04	51	13 254
413	20.2 (200)	0.00448	4.35	55	13 258
473	7.07 (70)	0.00834	0.618	72	13 319
473	15.2 (150)	0.00752	1.71	70	13 304
473	20.2 (200)	0.0104	2.37	83	13 334

(20 wt % overall polymer concentration)
A—Weight percent of total polyethylene retained in light phase.
B—Weight percent of total ethylene retained in heavy phase.

TABLE 3. COMPARISON OF RESULTS OF THIS STUDY WITH RESULTS OF BONNER ET AL. AT 20.2 MN/m^2 (200 ATM)

	This study	Bonner et al. (1974)
Wt % of total polyethylene retained in light phase	0.0166	0.01
Wt % of total ethylene retained in heavy phase	0.936	1.10
$\overline{M}_n$, light phase	102	110
$\overline{M}_n$, heavy phase	13 400	13 350

(Temperature = 533°K; 12.5 wt % overall polymer concentration).

TABLE 4. COMPARISON OF THE CALCULATED RESULTS OF THIS STUDY WITH THE DATA OF CHENG AND BONNER (1977*a*)

Temp, °K	Pressure, MNm^{-2} (atm)	Wt % ethylene in heavy phase This study	Cheng
399	1.13 (11.2)	0.56	0.55
399	2.16 (21.4)	1.23	1.36
399	3.88 (38.4)	2.53	2.42
399	5.25 (52.0)	3.66	3.30
428	11.3 (11.2)	0.39	0.39
428	21.6 (21.4)	0.85	0.90
428	38.8 (38.4)	1.77	1.78
428	52.5 (52.0)	2.59	2.65

system. The molecular weight distribution used was the same as used by Bonner et al. (1974). To illustrate the use of the algorithm for design calculations, equilibrium phase compositions were determined for a system with an overall polymer concentration of 20 wt% at 413° and 473°K and 7.07, 15.2, and 20.2 MN/m^2. The results of these calculations appear in Table 2. Equilibrium calculations were also performed at 533°K and 20.2 MN/m^2, with 12.5% overall polymer concentration for comparison with the results of Bonner et al. (1974). These results and the results of Bonner et al. appear in Table 3. A final set of equilibrium calculations was made at 399° and 428°K; 1.13, 2.16, 3.88, and 5.25 MN/m^2; and 20% overall polymer concentration for comparison with the data of Cheng (1977*b*). These results appear in Table 4.

The results shown in Table 2 illustrate the equilibrium results which can be expected when an industrial decompression chamber is operated at various temperatures and pressures. At 7.07 MN/m^2, a pressure near that used industrially, the light phase is essentially polyethylene free, and the heavy phase contains only a small amount of the ethylene. The number average molecular weight in the heavy phase is nearly the original value. As the pressure is increased to 15.2 and 20.2 MN/m^2, the amount of polymer in the light phase remains nearly constant, while the amount of ethylene in the heavy phase increases significantly. The molecular weight distribution remains essentially unchanged in both phases.

The results listed in Table 3 show two significant differences between the 1974 results and the present results at 20.2 MN/m^2 and 533°K. First, the amount of polyethylene predicted by the 1974 study to dissolve in ethylene is underestimated by more than 60%. This has serious implications for design of the process step in which low molecular weight polyethylene must be removed from recycled ethylene.

Second, the 1974 results overestimate the amount of ethylene dissolved in polyethylene at flash separation pressure by nearly 18%. Thus, if one were to use the 1974 computations at low pressures, for which they are not intended, the amount of ethylene that the design would show must be removed from polyethylene (for reasons of air pollution) would be overestimated.

As shown in Table 4, the computations presented here also can be used to predict ethylene solubility in polyethylene with good precision.

The ethylene sorption data of Cheng (1977*a*) were used in conjunction with Equation (16) to determine the one binary interaction parameter p_{12}^*. Over the temperature range 399° to 428°K, the parameter p_{12}^* is not a function of temperature. This indicates that p_{12}^* reported here can probably be used reliably to temperatures of at least 473°K and perhaps higher.

The computations presented here are certainly more reliable for phase equilibrium computations at pressures less than 30.3 MN/m^2 than those of the model used by Bonner et al. (1974).

The data used to determine the parameters required for the computations presented here are limited to 14.1 MN/m^2. Although polyethylene PVT data used to determine characteristic parameters are relatively insensitive to pressure at less than 50.5 MN/m^2, ethylene specific volume changes behavior markedly at approximately 30.3 MN/m^2. We therefore recommend 30.3 MN/m^2 as the maximum pressure for the use of our ethylene characteristic parameters. The 1974 model is not applicable to gases at low densities, and the interaction parameter was determined from high pressure cloud point data, so that computations at 30.3 MN/m^2 or less represent an unwarranted use of the 1974 model.

CONCLUSION

A new model of polymer solutions can be used, together with a mass balance, to calculate phase equilibria for ethylene/low-density polyethylene mixtures at the pressures and temperatures used in the separation step of the high pressure manufacturing process. The calculations consider the molecular weight distribution of the polymer. With the data considered in this study, accurate results can be obtained from 399° to 473°K and 0 to 7.07 MN/m^2. Use of the parameters derived in this study is not recommended above 30.3 MN/m^2, although the parameters can probably be used reliably to 30.3 MN/m^2.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for financial support through grant ENG 74-0762. The authors also thank the Texas Tech University Computer Center for the use of their facilities.

NOTATION

c = one third the number of external degrees of freedom per molecular segment
k = Boltzmann's constant
m = mass
M_i = molecular weight of species i
n_i = number of moles of species i
N_i = number of molecules of species i
N = ΣN_i = total number of molecules
p = pressure
p^* = characteristic pressure of mixture, defined in Equation (12)
p_i = characteristic pressure of species i
p_{12}^* = characteristic interaction pressure
p = reduced pressure = p/p^*
r = number of segments per molecule
R = gas constant
s_i = number of contact sites per segment of species i
ΔS_{comb} = entropy change on athermal mixing
T = absolute temperature
$\tilde{T}$ = reduced temperature, T/T^*
T^* = characteristic temperature of the mixture, defined in Equation (12)
T_i^* = characteristic temperature of species i
V = total volume of system
v_{isp}^* = hard core volume per gram of species i
w_i = weight fraction of i
X_{12} = Flory binary interaction parameter, defined following Equation (16)
Z = configurational, canonical partition function
Z_{comb} = configurational, canonical partition function of athermal mixing

Greek Letters

α = $1/V\ (\partial V/\partial T)_p$
γ = $(\partial P/\partial T)_v$
θ_i = site fraction of species i in solution = $s_i r_i N_i / \Sigma s_i r_i N_i$
λ = geometrical packing factor
μ_i = chemical potential of species i in solution
ν = volume per segment
ν^* = hard core volume per segment
$\tilde{\nu}$ = $\nu/\nu^* = v_{sp}/v_{sp}^*$ = reduced volume
Φ_i = volume fraction of species i

χ = Flory-Huggins interaction parameter
Ψ_i = segment fraction of species i

Subscripts

1 = low molecular weight species
2 = polymer
12 = binary interaction value

Superscripts

$\sim$ = reduced quantity
α, β = phase designations
$^\circ$ = reference value
* = characteristic value

LITERATURE CITED

Benzler, H., and A. von Koch, "Thermodynamic Properties of Ethylene from $-150°C$ to $+400°C$ and from 1 atm. to 10,000 atm.," *Chem.-Ing.-Tech.*, **27**, 71 (1955).

Beret, S., and J. M. Prausnitz, "Densities of Liquid Polymers at High Pressure. Pressure-Volume-Temperature Measurements for Polyethylene, Polyisobutylene, Poly (vinyl acetate), and Poly (dimethylsiloxane) to 1 kbar," *Macromolecules*, **8**, 536 (1975).

————, "Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules," *AIChE J.*, **21**, 1123 (1976).

Bonner, D. C., and J. M. Prausnitz, "Vapor-Liquid Equilibrium Calculations for Concentrated Polymer Solutions," *ibid.*, 943 (1973).

Bonner, D. C., D. P. Maloney, and J. M. Prausnitz, "Calculation of High-Pressure Phase Equilibria and Molecular-Weight Distribution in Partial Decompression of Polyethylene Ethylene Mixtures," *Ind. Eng. Chem., Process Design Develop.*, 13, 91 (1974).

Cheng, Y. L., and D. C. Bonner, "Solubility of Ethylene in Low-Density Polyethylene to 69 atm," *J. Polymer Sci., Phys. Ed.* (1977*a*).

————, "Solubility of Nitrogen and Ethylene in Molten, Low-Density Polyethylene at 69 atm," submitted to *J. Polymer, Sci., Phys. Ed.* (1977*b*).

Ehrlich, P., "Phase Equilibria of Polymer-Solvent Systems at High Pressures Near Their Critical Loci. II. Polyethylene-Ethylene," *J. Polym. Sci.*, **A3**, 131 (1965).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **9**, 660 (1941).

————, "Statistical Thermodynamics of Liquid Mixtures," *J. Am. Chem. Soc.*, **87**, 1833 (1965).

Huggins, M. L., "Solutions of Long-Chain Molecules," *J. Chem. Phys.*, 9, 440 (1941).

Maloney, D. P., and J. M. Prausnitz, "Solubility of Ethylene in Liquid, Low-Density Polyethylene at Industrial Separation Pressures," *Ind. Eng. Chem. Process Design Develop.*, **15**, 216 (1976).

Orwoll, R. A., and P. J. Flory, "Equation of State Parameters for Normal Alkanes. Correlation with Chain Length," *J. Am. Chem. Soc.*, 89, 6814 (1967).

Prigogine, I., *The Molecular Theory of Solutions*, pp. 323-373, North Holland Publishing Co., Amsterdam (1957).

APPENDIX: THE DETERMINATION OF CHARACTERISTIC PARAMETERS

Cheng (1977*b*) developed a method which can be used to determine the pure component characteristic parameters p^*, v_{sp}^*, and T^* from PVT data. The procedure requires the use of the thermal expansion coefficient α, $(1/V)\ (\partial V/\partial T)_p$, and the thermal pressure coefficient γ, $(\partial P/\partial T)_v$, which must be obtained from the PVT properties.

Specific Hard Core Volume, v_{sp}^*

The thermal expansion coefficient is given by

$$\alpha = \frac{1}{T} \frac{3}{3 - 6\dfrac{\gamma T - p}{\gamma T} + \dfrac{\gamma M v_{sp} - R}{\gamma M v_{sp}}\left(\dfrac{\tilde{\nu}^{1/3}}{\tilde{\nu}^{1/3} - 1}\right)} \tag{A1}$$

The only unknown quantity in Equation (A1) is the specific hard core volume v_{sp}^*, which can be determined using nonlinear least-squares regression. The procedure involves a trial-and-error search for the value of v_{sp}^* which minimizes the sum of the squares of the difference between the experimental and calculated values of α over the pressure and temperature range of interest.

Characteristic Pressure, p^*

The thermal pressure coefficient is given by

$$\gamma = p^*/\tilde{\nu}^2 T + p/T \tag{A2}$$

Using the previously determined value of v_{sp}^*, we can determine the characteristic pressure p^* from Equation (A2) using nonlinear least-squares regression.

Characteristic Temperature, T^*

The following expression is given for the temperature T:

$$T = \frac{\tilde{p}\tilde{\nu}^2 + 1}{\dfrac{RT^*\tilde{\nu}}{p^* v_{sp}^* M} + \dfrac{\tilde{\nu}}{\tilde{\nu}^{1/3} - 1}} T^* \tag{A3}$$

Using the previously determined values of v_{sp}^* and p^*, we can determine the characteristic temperature T^* from Equation (A3) using nonlinear least-squares regression.

Characteristic Parameters for Gases

An alternate procedure is used to determine the characteristic parameters for gases composed of simple molecules. The value of rc is assumed to be unity, which is equivalent to the assumption of three external degrees of freedom. With $rc = 1$, the equation for α becomes

$$\alpha = \frac{1}{T} \frac{3}{3 - 6\dfrac{\gamma T - p}{\gamma T} + \dfrac{1}{\tilde{\nu}^{1/3} - 1}} \tag{A4}$$

The specific hard core volume v_{sp}^* can be determined from Equation (A4) using nonlinear least-squares regression.

The equation for the thermal pressure coefficient with $rc = 1$ is the same as Equation (A2). The characteristic pressure p^* can be determined from Equation (A2) using nonlinear least-squares regression.

With the value of rc fixed at unity, the value of the characteristic temperature T^* is fixed by Equation (7), the relationship between characteristic parameters.

Binary Interaction Parameter, p_{12}^*

The characteristic interaction parameter p_{12}^* is determined from binary phase equilibrium data using Equation (16) for the ethylene chemical potential. Nonlinear least-squares regression is used to determine the value of p_{12}^* which minimizes the sum of the squares of the differences between the calculated ethylene chemical potentials in the two phases. The standard state value of μ_1^0 is that of pure ethylene at mixture temperature and pressure. The ethylene chemical potential μ_1^0 was determined from the data of Benzler and Köch (1955). The data of Cheng (1977a) for sorption of pure ethylene in low-density polyethylene (for which $\mu_1 = \mu_1^0$) were used to determine segment fraction ethylene sorbed as a function of temperature and ethylene partial pressure.

Manuscript received March 7, 1977; revision received May 16, and accepted May 27, 1977.