Importance of Solubility Phenomena During the Separation of the Ethylene–Polyethylene Mixture in the Industrial Low Density Polyethylene Process

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SYNOPSIS

The solubility values of ethylene in polyethylene and vice versa have been evaluated for the process conditions. These results could be used in solving real problems of PE-LD process. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Phase equilibrium predictions for the ethylene–polyethylene system, at conditions that correspond to the separation step during the industrial polymerization of ethylene at high pressures, has been performed by several authors.[1–10] Most of the published articles deal with the development and choice of the adequate thermodynamic theories for such calculations, and with the exact determination of the necessary input data. Information, found in the literature, on the applicability of the predicted data for optimization on the real separation process of the ethylene–polyethylene mixture, in the pressure range of 15–30 MPa and the temperature range of 130–300°C, which are typical for the separation step in most of the commercial PE–LD processes, is extremely limited. The separation of this mixture generally depends on the process conditions and also on the geometry of the system, that is, on the size and shape of the separating vessel, construction details, etc. But since the geometry of the separating vessel is more or less similar in most of the industrial processes, it is possible, by using the phase equilibrium calculation, to obtain the exact compositions of both coexisting phases (polymer rich and monomer rich phases) for the most favorable process conditions.

Although the patent literature (e.g., see Sittig[11]) usually provides information about the conditions that should be maintained during the commercial production of PE–LD, little is known about the situations in which sudden upsets in the process occur, nor about the possible consequences of the upsets. For example, information about the behavior of the process if one or both of the basic parameters (pressure and/or temperature) are changed, is not available, so that the reliable recommendations for the corresponding practical actions cannot be provided. Hence, the purpose of this article is (a) to obtain and present the new quantitative solubility values for the ethylene and polyethylene, respectively, in each of the coexisting phases for the entire range of pressure and temperatures relevant for industrial purposes, (b) to show how the generated results could be used to establish the desired separation conditions, and (c) to point out the possibility of using the phase equilibria in analyzing real problems, which could arise during the postseparation steps of the PE–LD process.

CALCULATIONAL PROCEDURE

The Cheng free volume theory[4,12] and the computational algorithm of Bonner et al.[1] have been used to calculate the phase equilibrium for the reacting ethylene–polyethylene mixture in the pressure range 17–29 MPa and at temperatures of 130–290°C. This theory has been proved valid at the pressures of interest in the literature.[3,7] The complete information about the above calculational procedure has been presented earlier[1,3] and more details about the main concepts of the phase equilibrium computations were given in our previous work.[7] Hence, only the basic

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Journal of Applied Polymer Science, Vol. 51, 253–258 (1994)
CCC 0021-8995/94/020253-06

equations, as well as the most important information describing the computations employed, are given here briefly. Assuming that two phases (I) and (II) of the examined ethylene–polyethylene system are in equilibrium, the basic thermodynamic principles, defined by the equalities of pressure p, temperature T, and chemical potential for ethylene (μ_1) and polyethylene (μ_{2l}), where l refers to a polymer with a particular molecular weight:

$$p^{\mathrm{I}} = p^{\mathrm{II}} \qquad (1)$$

$$T^{\mathrm{I}} = T^{\mathrm{II}} \qquad (2)$$

$$\begin{aligned} \mu_1^{\mathrm{I}} &= \mu_1^{\mathrm{II}} \\ \mu_{2l}^{\mathrm{I}} &= \mu_{2l}^{\mathrm{II}} \quad l = 1, 2, \cdots \end{aligned} \qquad (3)$$

could be applied. Using the partition function for the polymer solutions,[13] at the conditions of interest for the present work and the corresponding state principle, the reduced equation of state in terms of the reduced quantities: pressure p, volume v and temperature T

$$(\tilde{p}\tilde{v})/\tilde{\mathrm{T}} = 1/(rc) + 1/(\tilde{v}^{1/3} - 1) - 1/(\tilde{v}\tilde{T}) \qquad (4)$$

was obtained.[13] Here, r and c denote number of segments per molecule and one third the number of external degrees of freedom per molecular segment, respectively.

Employing eqs. (3) and (4), and the Cheng free volume theory, the equations for chemical potentials of both ethylene and polyethylene can be obtained:

$$\begin{aligned} (\mu_1 - \mu_1^0)/(kT) &= \ln \psi_1 + [1 - (r_1/r_2)]\psi_2 \\ &+ (v_1^0 * r_1^*/k)\{(3p_1^*/T_1^*)\ln[(\tilde{v}_1^{1/3} - 1)/ \\ &(\tilde{v}^{1/3} - 1)] + (p/T)(\tilde{v}^{4/3} - \tilde{v}_1^{4/3}) + (1/T) \\ &\times [(p^*/\tilde{v}^{2/3}) - (p_1^*/\tilde{v}_1^{2/3})] + (p_1^*/T_1^*) \\ &- (p^*/T^*)\} + [(p_1^* v_1^* r_1^*)/(kT_1^*) - 1] \\ &\times \ln(\tilde{v}/\tilde{v}_1) - 1 - (r_1/r)(\tilde{v}^{1/3} - 1) \\ &+ [r_1 v_1^*/(kT)]\{(x_{12}\theta_2^2/\tilde{v}) - p_1^*[(1/\tilde{v}) \\ &- (1/\tilde{v}_1)] + (p_1^*/\tilde{v}_1) - (p^*/\tilde{\mathrm{v}})\} + \tilde{v}_1^{1/3} \end{aligned} \qquad (5)$$

$$\begin{aligned} (\mu_{2l} - \mu_{2l}^0)/(kT) &= \ln \psi_{2l} - [(r_{2l}/r_1) - 1] \\ &+ \psi_2(r_{2l}/r_1)[1 - r_1/(r_2)_n] + (v_1^* r_{2l}/k) \\ &\times \{(3p_2^*/T_2^*)\ln[(\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \\ &+ (p/T)(\tilde{v}^{4/3} - \tilde{v}_2^{4/3}) + (1/T)[(p^*/\tilde{v}^{2/3}) \\ &- (p_2^*/\tilde{v}_2^{2/3})] + (p_2^*/T_2^*) - (p^*/T^*)\} \\ &+ [(p_2^* v_1^* r_{2l})/(kT_2^*) - 1]\ln(\tilde{v}/\tilde{v}_2) - 1 \\ &- (r_{2l}/r)(\tilde{v}^{1/3} - 1) + [r_{2l}v_1^*/(kT)] \\ &\times \{(x_{21}\theta_1^2/\tilde{\mathrm{v}}) - p_2^*[(1/\tilde{v}) - (1/\tilde{v}_2)] \\ &+ (p_2^*/\tilde{v}_2) - (p_2^*/\tilde{v})\} + \tilde{v}_2^{1/3}. \end{aligned} \qquad (6)$$

In the above equations, T, p, and k are temperature, pressure, and Boltzmann's constant, respectively. p_i^*, T_i^* and p^*, T^* are characteristic pressure and temperature of species i and of mixture. The reduced volume of species i and of mixture are denoted by $\tilde{v}_i$ and v, respectively. ψ_i and θ_i stand for segment and site fractions for species i, respectively. Finally, x is the Flory–Huggins binary interaction parameter, and r represents the number of segments per corresponding molecules. Subscript $i = 1, 2$. Starting from the input data (characteristic parameters for pure components and for the mixture, as well as for the segment fraction of ethylene) the solubility of the constituents can be computed for the operating conditions and also for the specified conversion of ethylene. The numerical values of all input data are presented in our previous work (Table I. of Ref. 7).

RESULTS AND DISCUSSION

Using the calculational method mentioned above, the detailed results about the composition of the phases at equilibrium, are obtained here for the conversion of 16%. They are summarized in Tables I and II. Table I presents the solubility of ethylene in the polyethylene-rich phase for the pressure and temperature ranges 130–290°C and 17–29 MPa, respectively. Table II summarizes the solubility of polyethylene in the ethylene-rich phase for the same ranges of pressure and temperature.

Published solubility information is fragmentary, mostly for a limited number of isobars or isotherms.[1–3,5,8,9,14]

In our previous work,[8] solubility of ethylene in polyethylene was investigated, in view of the temperature inversion phenomena, in a wide range of pressures (20.27–101.33 MPa). Also, in the same article, the position of the solubility inversion curve was given. In the present investigation, however, the solubility results are extended toward lower pressures, corresponding to the separation and post-separation steps of the process. In this pressure range (17–29 MPa), solubilities are tabulated in sufficient detail, enabling in this way the investigation

Table I Solubility (wt %) of Ethylene in the Polyethylene Rich Phase for the Ranges of Temperature and Pressure 130–290°C and 17–29 MPa, Respectively[a]

Temperature (°C)	Pressure (MPa)												
	17	18	19	20	21	22	23	24	25	26	27	28	29
130	5.50	6.09	6.68	7.27	7.85	8.43	9.00	9.56	10.12	10.67	11.21	11.73	12.25
140	4.86	5.38	5.91	6.45	6.98	7.51	8.03	8.55	9.07	9.59	10.09	10.59	11.08
150	4.32	4.79	5.27	5.75	6.23	6.72	7.20	7.69	8.17	8.65	9.13	9.60	10.06
160	3.86	4.29	4.72	5.16	5.60	6.05	6.50	6.95	7.40	7.85	8.29	8.73	9.17
170	3.48	3.87	4.26	4.66	5.07	5.48	5.89	6.31	6.73	7.15	7.57	7.98	8.40
180	3.17	3.52	3.88	4.24	4.62	5.00	5.38	5.77	6.16	6.55	6.94	7.33	7.72
190	2.90	3.22	3.55	3.89	4.23	4.58	4.94	5.30	5.66	6.03	6.40	6.77	7.13
200	2.67	2.97	3.27	3.58	3.90	4.23	4.56	4.90	5.24	5.58	5.92	6.27	6.62
210	2.48	2.75	3.03	3.32	3.62	3.92	4.23	4.55	4.86	5.19	5.51	5.83	6.16
220	2.31	2.57	2.83	3.10	3.38	3.66	3.95	4.24	4.54	4.84	5.14	5.45	5.76
230	2.16	2.40	2.65	2.90	3.16	3.42	3.69	3.97	4.25	4.53	4.82	5.11	5.40
240	2.03	2.25	2.48	2.72	2.97	3.22	3.47	3.73	3.99	4.26	4.53	4.81	5.09
250	1.91	2.12	2.34	2.56	2.79	3.03	3.27	3.51	3.76	4.02	4.28	4.54	4.80
260	1.80	2.00	2.20	2.41	2.63	2.85	3.08	3.32	3.56	3.80	4.05	4.30	4.55
270	1.71	1.89	2.08	2.28	2.48	2.70	2.92	3.14	3.38	3.61	3.84	4.08	4.32
280	1.62	1.79	1.95	2.15	2.35	2.56	2.77	2.99	3.21	3.44	3.67	3.89	4.11
290	1.56	1.70	1.86	2.04	2.23	2.43	2.64	2.85	3.07	3.29	3.51	3.73	3.93

[a] Data correspond to the conversion of 16%.

of the p–T–S behavior of the ethylene–polyethylene system. In addition, the solubility inversion curve is located out of the present temperature range, at pressures of 17–29 MPa.

Graphical representation of the results of Tables I and II could be considered useful for the practical work. These tabulations of variable solubilities have been converted into the values of constant solubilities, in order to prepare Figures 1 and 2.

Figures 1 and 2 present the solubilities for the

Table II Solubility (wt %) of Polyethylene in the Ethylene Rich Phase for the Ranges of Temperature and Pressure 130–290°C and 17–29 MPa, Respectively[a]

Temperature (°C)	Pressure (MPa)												
	17	18	19	20	21	22	23	24	25	26	27	28	29
130	0.0017	0.0019	0.0022	0.0026	0.0030	0.0035	0.0040	0.0046	0.0052	0.0059	0.0066	0.0073	0.0081
140	0.0017	0.0019	0.0022	0.0026	0.0029	0.0034	0.0039	0.0044	0.0050	0.0057	0.0063	0.0071	0.0079
150	0.0018	0.0020	0.0023	0.0026	0.0030	0.0034	0.0039	0.0044	0.0050	0.0056	0.0063	0.0070	0.0078
160	0.0020	0.0022	0.0025	0.0028	0.0032	0.0036	0.0040	0.0045	0.0051	0.0057	0.0064	0.0071	0.0079
170	0.0022	0.0024	0.0027	0.0030	0.0034	0.0038	0.0043	0.0047	0.0053	0.0059	0.0066	0.0073	0.0081
180	0.0025	0.0027	0.0030	0.0033	0.0037	0.0041	0.0045	0.0050	0.0056	0.0062	0.0069	0.0076	0.0084
190	0.0028	0.0030	0.0033	0.0037	0.0040	0.0044	0.0049	0.0054	0.0060	0.0066	0.0073	0.0080	0.0088
200	0.0032	0.0034	0.0037	0.0040	0.0044	0.0048	0.0053	0.0058	0.0064	0.0071	0.0078	0.0085	0.0093
210	0.0036	0.0039	0.0042	0.0045	0.0049	0.0053	0.0058	0.0064	0.0070	0.0077	0.0084	0.0092	0.0100
220	0.0041	0.0044	0.0047	0.0051	0.0055	0.0060	0.0065	0.0071	0.0077	0.0084	0.0092	0.0100	0.0109
230	0.0048	0.0051	0.0054	0.0058	0.0062	0.0067	0.0073	0.0079	0.0086	0.0094	0.0102	0.0111	0.0120
240	0.0056	0.0059	0.0063	0.0067	0.0072	0.0077	0.0083	0.0090	0.0098	0.0106	0.0115	0.0124	0.0135
250	0.0067	0.0070	0.0074	0.0079	0.0084	0.0090	0.0097	0.0104	0.0112	0.0121	0.0131	0.0141	0.0153
260	0.0081	0.0084	0.0089	0.0094	0.0099	0.0106	0.0113	0.0121	0.0130	0.0140	0.0151	0.0163	0.0176
270	0.0098	0.0102	0.0107	0.0113	0.0119	0.0126	0.0134	0.0143	0.0153	0.0165	0.0177	0.0190	0.0205
280	0.0120	0.0125	0.0130	0.0136	0.0143	0.0152	0.0161	0.0171	0.0182	0.0195	0.0209	0.0224	0.0241
290	0.0148	0.0153	0.0159	0.0166	0.0174	0.0183	0.0193	0.0205	0.0218	0.0232	0.0248	0.0266	0.0285

[a] Data correspond to the conversion of 16%.

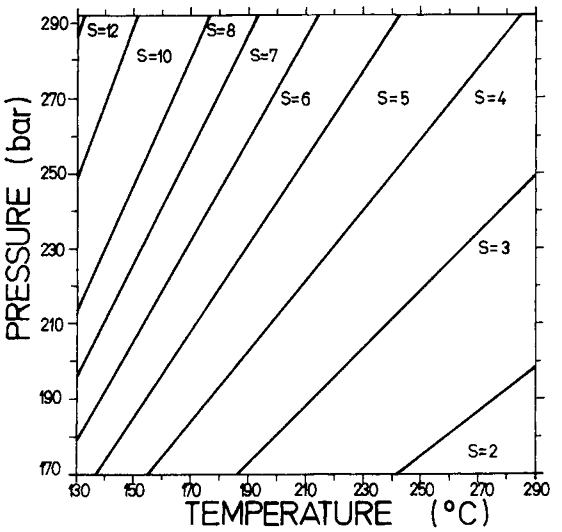

Figure 1 Solubility S (wt %) of ethylene in polyethylene for the temperatures 130–290°C and the pressures 17–29 MPa (conversion 16%).

ethylene and polyethylene, respectively, at the process conditions of interest. The lines of constant solubility, appearing in these graphs, have been obtained by applying the bisection method to the equilibrium values from Tables I and II. Figures 1 and 2 enable the solubility of polyethylene in ethylene, or vice versa, to be predicted for any pair of pressure and temperature. In order to achieve a particular solubility value, which is necessary in the process, these graphs enable one to select properly the process pressure and temperature, accounting for various reacting requirements. Namely, most of the information in the literature indicates that approximately 5 wt % of retained ethylene should be expected in the polymer-rich phase[15,16] and that the polyethylene content in the ethylene-rich phase is in the range of 0.0040–0.01 wt %.[1,17] Since the shapes and the trends of the lines of constant solubility in Figures 1 and 2 are different, they should be discussed separately. Figure 1 shows that the gradient $(\partial p/\partial T)_S$ is positive and is practically constant; also, in the range of $S = 2$–12, the $(\partial p/\partial T)_S$ values rise if the solubility is increased. From Figure 2, which is valid for the solubility of polyethylene, one can note that the gradients $(\partial p/\partial T)_S$ remain mainly negative and variable (they decrease with the lowering of temperature). Graph 2 can be divided into two solubility regions: one above and the other below the solubility line 0.010 wt % of polyethylene. In the region $S = 0.01$–0.02, the gradient, $(\partial p/\partial T)_S$, is always negative and decreases with the increase of S. In the region with $S = 0.004$–0.008, the gradient $(\partial p/\partial T)_S$ is negative, becoming approximately zero for the temperatures 130°–160°C. This is true for the entire pressure range of interest. In this temperature range, any solubility could be maintained practically constant without changing the pressure. Figures 1 and 2 could also be useful in all cases, which occur more or less frequently in the industrial practice, when sudden changes of one or both of the basic parameters (pressure and/or temperature) take place, and, accordingly, when proper decisions for the corrective actions should be made immediately. In most cases, if the upsets occur in commercial production, the whole polymerization process is stopped, or at least the capacity of the unit must be significantly reduced. By using the graphs presented, the consequences could be predicted, and most of the sudden unfavorable phenomena could be compensated and/or prevented. The additional advantage of using Figures 1 and 2 could be expressed fully when optimum separation conditions have to be identified, not only from the point of view of ease of polymerization reaction and energy savings, but also in view of the content of retained polyethylene in ethylene and vice versa, after the separation step.

The above general remarks could be discussed in more detail in order to show how the phase equilibrium results, in Figures 1 and 2, could be applied to the operation of an actual industrial process. Thus, if one considers the solubility of ethylene in polyethylene at a typical pressure value (approx. 27 MPa) and temperatures (e.g., 270°C), it could be seen from Figure 1 that the expected solubility for

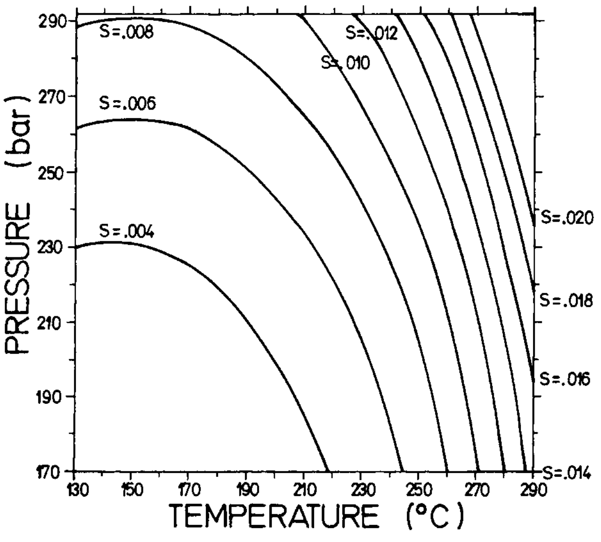

Figure 2 Solubility S (wt %) of polyethylene in ethylene for the temperatures 130–290°C and the pressures 17–29 MPa (conversion 16%).

these conditions is approximately 4. However, in some cases, when the reduced capacity of the whole unit is required, either due to upsets in the process or because of a shortage in the ethylene supply, the pressure of the secondary compressor and, consequently, the working pressure in the separation section, shown in Figure 3, should be reduced up to 20 MPa.

This is one of the easiest manners for achieving the reduction of the total capacity. However, during this action, the solubility of ethylene in polyethylene is also significantly reduced (solubility about 2.3) with further consequences. Namely, since lower content of ethylene is expected in the polymer phase, the next separation step (low pressure separation) is facilitated. In addition, the quality of the final product is improved (less ethylene will be present in the polymer phase, avoiding in this way possible bubble formation). Moreover, the losses of ethylene are decreased in the later stages of the process (low pressure separation and silo manipulation). It can also be concluded from Figure 1 that high solubility of ethylene should be expected at low temperatures (below 200°C at operating pressures of approx. 27 MPa). These temperatures are not normally applied, but during some upsets of the process, they may become realistic with possible consequences, such as material loss and quality deterioration due to increased ethylene content in the main process stream.

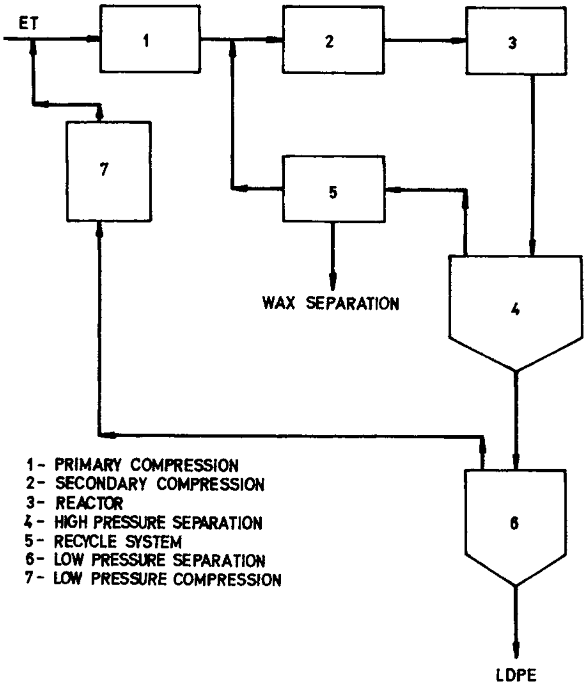

Figure 3 Simplified scheme of the PE–LD process.

As shown in Figure 2, if the same conditions (pressures of 27 and 20 MPa, alternatively, and a temperature of 270°C) are considered, the significant decrease of the polyethylene solubility in ethylene is to be expected at lower pressures. This means that less polymer is entrained with the gas phase and should be easily removed in the wax separation units that are shown in Figure 3. Successful removal of waxes is an extremely important step in the process, since its improper work causes partial or complete shut down of the whole plant. Therefore, the quantity of the waxes removed, which represents the undesirable by-product of the process, is decreased, causing, at the same time, material savings up to a level at which the product quality is not affected.

It can be concluded that the detailed phase equilibrium data, presented in Tables I and II, and the solubility curves, shown in Figures 1 and 2, could be employed to yield useful information on various aspects that can occur during the industrial separation process of the ethylene–polyethylene mixture. This information enables the process engineer to have better insight into the complex behavior of the separation step, choosing the most favorable process conditions, including energy requirements, and predicting the solubilities of both components of interest at different combinations of temperature and pressure, which are typical for the investigated step of the PE–LD process.

SUMMARY

In this work, the detailed quantitative solubility results of ethylene in polyethylene and the new solubility values of polyethylene in ethylene have been predicted. The results have been tabulated for the temperature and pressure ranges of 130°–290°C and 17–29 MPa, respectively, and for the conversion of 16%. These conditions are typical for the separation step in most of the industrial, low-density polyethylene processes. The above results have been used as a basis for generating the graphs, containing lines for which specific solubility values appear as constant parameters. Use of the graphs has been discussed from the practical point of view, that is, in selecting the most favorable separation conditions, in obtaining better insight into the possible energy savings during the recycling of unreacted ethylene, and in solving other real problems arising often during the postseparation steps of the process (fouling, quality of the final product, etc.).

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Received March 11, 1993
Accepted May 20, 1993