

# Inversion Phenomena of Ethylene Solubility in Polyethylene

## INTRODUCTION

The experimental measurements of the ethylene solubility in polyethylene are relatively scarce, particularly at elevated and high pressures. Therefore, the thermodynamic prediction of this property is of great importance in all investigations concerning the behavior of the ethylene-polyethylene mixture.

Since the ethylene solubility in polyethylene ( $\delta$ ) is a function of pressure ( $p$ ) and temperature ( $T$ ) for a specified conversion  $\delta = \delta(p, T)$ , the following relation can be written:

$$d\delta = \left(\frac{\partial\delta}{\partial p}\right)_T dp + \left(\frac{\partial\delta}{\partial T}\right)_p dT = (K\delta)_T dp + (K\delta)_p dT \quad (1)$$

Here,  $(K\delta)_T = (\partial\delta/\partial p)_T$  represents the isothermic solubility pressure coefficient, whereas  $(K\delta)_p = (\partial\delta/\partial T)_p$  is the isobaric solubility temperature coefficient. These coefficients account for the changes of the solubility with respect to  $p$  at constant  $T$  and with respect to  $T$  at constant  $p$ , respectively. Both solubility coefficients, introduced in the above way, make the study of the solubility phenomena possible in wide ranges of pressure and temperature.

Although the ethylene solubility was studied earlier, all published data could be regarded as restricted. The data, which are concerned with the temperature inversion predictions,<sup>1-3</sup> were analyzed in the ethylene weight fraction vs. pressure diagrams. The temperature inversion was shown as the intersection of two or more isotherms. Maloney and Prausnitz<sup>1</sup> were the first to predict the temperature inversion phenomenon for the solubility of ethylene. They found the temperature inversion near 500 atm, inside the temperature range 150–300°C. Liu and Prausnitz<sup>2</sup> predicted that the two solubility lines 130 and 200°C cross at ca. 800 atm, assuming monodispersed LDPE ( $M = 17,000$ ). Wohlfarth and Ratzsch<sup>3</sup> reported the prediction of the cross of solubility isotherms 403 and 493 K at ca. 65 MPa. They also discussed the shifting tendency of such crosses at various temperatures and pressures.

Having in mind eq. (1), all previously mentioned results, presenting the solubility as a function of pressure at constant temperature, could be discussed only in light of the coefficient  $(K\delta)_T$ ; namely, the  $(K\delta)_T$  is always positive. Further, by comparing two isotherms ( $T_1$  and  $T_2$ ,  $T_1 > T_2$ ), which by crossing determine the temperature inversion point (for which  $(K\delta)_{T_1} \neq (K\delta)_{T_2}$ ), one can conclude that for pressures below and above this point the inequalities  $(\delta)_{T_2} > (\delta)_{T_1}$  and  $(\delta)_{T_1} > (\delta)_{T_2}$ , respectively, are valid. Contrary to other authors, in the present work, the ethylene solubility in polyethylene is represented in a completely different way, i.e., by the solubility-temperature diagram. The solubility phenomena in wide temperature and pressure ranges of 20–100 MPa and 383.15–583.15 K, respectively, will be discussed in accordance to both the isobaric solubility temperature coefficient  $(K\delta)_p$  and the inversion curve, defined below. The above-mentioned  $p$  and  $T$  ranges are of both theoretical and practical interest. The theoretical aspects deal with the unexpected phenomena concerning the solubility inversion, whereas the practical are connected with some of the major steps of low-density polyethylene (LDPE) manufacture.

## CALCULATIONAL PROCEDURE

The Prigogine-Flory theory of polymer solution<sup>4</sup> that fits well with the experiments up to 100 MPa, as was shown recently,<sup>5</sup> was used here to calculate the ethylene solubility in polyethylene. The calculational procedure was based on the work of Bonner et al.<sup>6</sup> and was presented in detail elsewhere.<sup>1,4,6-10</sup> Hence, only the main equations and most important information, describing the computations used, are given here.

Assuming that two phases (I) and (II) of the examined ethylene-polyethylene system are in equilibrium, the basic thermodynamic principles, defined by equalities of pressure, temperature, and chemical potential  $\mu_i$  for each component  $i$ ,

$$p^I = p^{II} \quad (2a)$$

$$T^I = T^{II} \quad (2b)$$

and

$$\mu_i^I = \mu_i^{II}, \quad i = 1, 2 \quad (2c)$$

could be applied.

Using the partition function for polymer solutions at the conditions of interest for the present work,<sup>11</sup> and the corresponding state principle, the reduced equation of state

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (3)$$

was obtained.<sup>4,11</sup> Here,  $\tilde{p}$ ,  $\tilde{v}$ , and  $\tilde{T}$  denote the reduced pressure, volume, and temperature, respectively.

Employing eqs. (2c) and (3), and using the Prigogine-Flory theory for dense fluids,<sup>4,11,12</sup> the basic expression

$$\begin{aligned} \frac{\mu_1 - \mu_1^0}{kT} = \ln \psi_1 + \left(1 - \frac{r_1}{r_2}\right) \psi_2 + \frac{r_1 v_1^*}{k} \left[ \frac{3p_1^*}{T_1^*} \ln \left( \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right) + \frac{p}{T} (\tilde{v} - \tilde{v}_1) \right] \\ + \frac{r_1 v_1^*}{k} \frac{p_1^*}{T} \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) + \frac{r_1 v_1^*}{k} \frac{X_{12}}{T} \frac{\theta_2^2}{\tilde{v}} \quad (4) \end{aligned}$$

was obtained.<sup>4,6</sup> In this equation,  $\psi$  and  $\theta$  represent the segment and site fractions, respectively;  $r$  is the number of segments per molecule; and  $k$  denotes the Boltzmann's constant.  $p^*$ ,  $v^*$ , and  $T^*$  are the characteristic parameters, whereas  $X$  is the binary interaction parameter for the mixture; all these parameters are accounted for as the temperature-dependent quantities, as proposed previously.<sup>6</sup> Subscripts 1, 2, and 12 refer to the ethylene, polyethylene, and their mixture, respectively. Superscript 0 designates the property in the standard state.

Starting from the input data  $p^*$ ,  $v^*$ ,  $T^*$ , and  $X_{12}$ , the segment fraction  $\psi_1$ , i.e., the solubility of ethylene, can be computed for the operating conditions  $p$  and  $T$  and for the specified conversion of ethylene.

## RESULTS AND DISCUSSION

Our results are presented in Table I and in Figure 1. Figure 1 shows that at lower temperatures the ethylene solubility decreases along the isobars, whereas at higher temperatures, this quantity increases. The  $(K\delta)_p$  represents a measure of the trend of solubility variation during its increase or decrease. The negative sign of  $(K\delta)_p$  is characteristic for the initial part of each isobar in the lower temperature region. With a further increase in temperature, this coefficient becomes equal to zero at the certain temperatures called the inversion points. Beyond these points, the ethylene solubility starts to increase, i.e., its  $(K\delta)_p$  changes its sign.

The points corresponding to the solubility minima, at each specified isobar, constitute the solubility inversion curve—the dashed line in Figure 1, which obviously divides the whole solubility region into two parts. In the region below the inversion curve, the solubility of ethylene decreases with the increase in temperature [ $(K\delta)_p < 0$ ], whereas above it, this property increases [ $(K\delta)_p > 0$ ]. For the inversion curve, the isobaric solubility-temperature coefficient is equal to zero, indicating that in this case it does not increase or decrease along the inversion curve. In other words, from the condition

TABLE I  
Influence of Pressure and Temperature on the Ethylene Content  
in Polyethylene (wt %) for 12% Conversion<sup>a</sup>

Pressure (MPa)	Temperature (K)										
	383.15	403.15	423.15	443.15	463.15	483.15	503.15	523.15	543.15	563.15	583.15
20.27	12.7	11.3	10.2	9.3	8.6	8.0	7.6	7.3	7.1	6.9	6.8
25.33	15.7	14.4	13.3	12.3	11.6	10.9	10.4	10.0	9.7	9.5	9.4
30.40	18.1	17.0	16.0	15.1	14.4	13.7	13.2	12.8	12.5	12.3	12.2
35.46	20.4	19.4	18.6	17.8	17.0	16.6	16.1	15.8	15.5	15.4	15.4
40.53	22.5	21.7	21.0	20.4	19.9	19.4	19.1	18.9	18.7	<u>18.7</u>	<u>18.7</u>
45.60	24.7	24.0	23.4	22.9	22.6	22.3	22.1	<u>22.0</u>	<u>22.0</u>	22.1	22.4
50.66	26.8	26.2	25.8	25.5	25.3	<u>25.2</u>	<u>25.2</u>	25.3	25.5	25.8	26.2
55.73	28.9	28.4	28.2	<u>28.1</u>	<u>28.1</u>	28.2	28.4	28.7	29.1	29.7	30.4
60.80	30.9	<u>30.7</u>	<u>30.6</u>	<u>30.7</u>	30.9	31.3	31.8	32.4	33.1	34.0	35.0
65.86	<u>33.1</u>	<u>33.0</u>	33.1	33.4	33.9	34.5	35.3	36.2	37.3	38.5	39.9
70.93	35.2	35.3	35.6	36.2	36.9	37.9	39.0	40.3	41.8	43.5	45.3
75.99	37.3	37.6	38.2	39.0	40.1	41.4	43.0	44.7	46.7	48.9	51.3
81.06	39.5	40.0	40.9	42.0	43.4	45.2	47.2	49.5	52.0	54.8	57.9
86.13	41.7	42.4	43.6	45.1	47.0	49.2	51.8	54.7	57.9	61.4	65.2
91.19	43.9	44.9	47.4	48.3	50.7	53.5	56.7	60.4	64.4	68.8	73.6
96.26	46.2	47.5	49.3	51.7	54.6	58.1	62.1	66.6	71.7	—	—
101.33	48.5	50.1	52.3	55.2	58.8	63.1	68.0	73.6	—	—	—

<sup>a</sup> The underlined numerical values of ethylene content at the adjacent isotherms indicate the neighborhood of points of inversion.

$$(K\delta)_p = \left( \frac{\partial \delta}{\partial T} \right)_p = 0 \quad (5)$$

it follows that for each point of the inversion curve  $\delta$  does not depend on  $T$ . Hence, the analytical expression for solubility can be given in the form  $\delta = \delta(p)$ . Also, inspection of Table I shows that for small changes of temperature in the vicinity of each point of the inversion curve the consequences of  $(K\delta)_p = 0$  are almost valid. It could be also seen from Figure 1 that the slope of the inversion curve increases permanently with the rise of temperature and with the decrease of pressure. Also, the shifting of the solubility, corresponding to the individual inversion points, toward the lower values is evident with the rise of temperature.

Determination of the solubility ( $\delta_2$ ) for each selected state (2) can be performed by integrating eq. (1)

$$\delta_2 - \delta_1 = \Delta\delta_p + \Delta\delta_T = \int_1^2 (K\delta)_p dT + \int_1^2 (K\delta)_T dp \quad (6)$$

where ( $\delta_1$ ) should be known. Eq. (6) can be used in all regions, particularly in those that are of interest for industrial purposes where experimental data are scarce.

Information about the isobaric solubility-temperature coefficient and the existence of the solubility inversion curve, under studied conditions, have not been reported up to now. Therefore, the present work contributes to the quantitative description of solubility phenomena, i.e., to introducing the quantities  $K\delta$  and the concept of the inversion curve. Also, our results make possible the discussion of the location of this curve as well as its shape and trend.

## CONCLUSION

Solubility phenomena are complex and include some unexpected effects treated in this work. The following conclusions can be drawn:

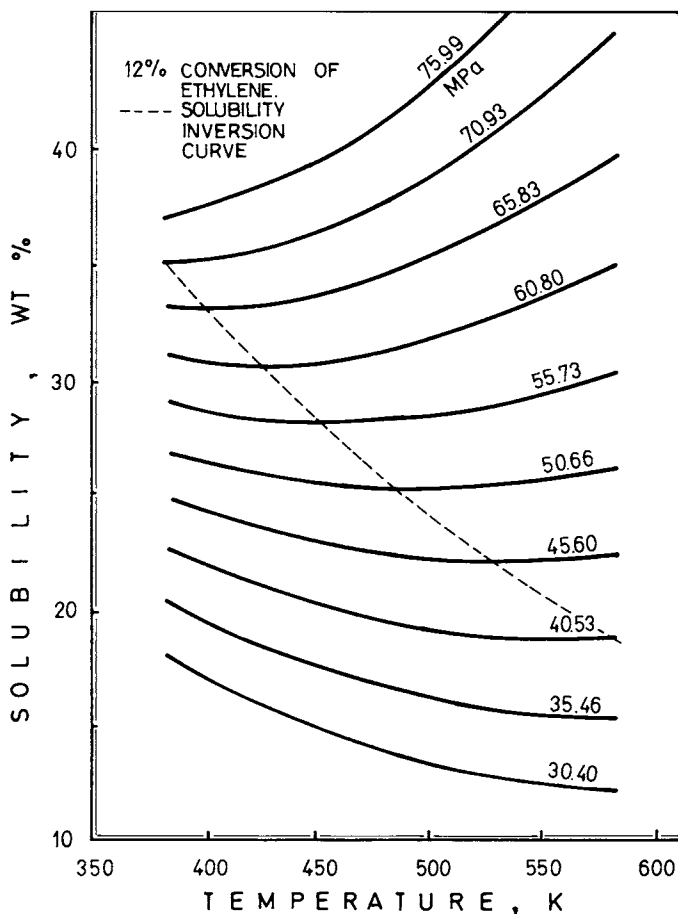


Fig. 1. Dependence of ethylene solubility on temperature and pressure.

- Investigations of the solubility phenomena in wide ranges of temperature and pressure could be treated employing the isothermic solubility-pressure coefficient  $(K\delta)_T$  and the isobaric solubility-temperature coefficient  $(K\delta)_p$ . Then, the results, given in the solubility-pressure diagram, can be analyzed using  $(K\delta)_T$ , whereas for the analysis of the solubility-temperature diagram,  $(K\delta)_p$  can be employed.
- Existence of the solubility inversion curve is a new unexpected phenomenon, which is visible if presentation is carried out via a solubility-temperature plot. The basic characteristic of this curve is  $(K\delta)_p = 0$ .
- On the basis of the previous articles cited above, it can be concluded that the temperature inversion point, as the feature of the solubility-pressure diagram only, can be obtained as an intersection of isotherms of interest.
- Eq. (6) makes it possible to account for the temperature and pressure variations of the solubility simultaneously.

Finally, the presented results and their analysis contribute to both the quantitative and the qualitative description of solubility phenomena, which are important for further theoretical and practical purposes.

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