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# Pressure–volume–temperature behaviour of molten polymers

## Solubility parameters in the view of Prigogine-Flory and Sanchez-Lacombe EOS-theories

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## SUMMARY

The solubility parameter theory of *Hildebrand* and *Scott* extended for polymer blends originally has accounted for dissimilarities only between contact energies of the blend components, neglecting free volume effects which are predicted by the corresponding states theories. Biroš et al., however, have shown that using expressions of the *Prigogine-Flory* corresponding state theories for energy and volume, effects of free volume will be implicitly included in the solubility parameter approach too. The results are similar then to those derived by the corresponding state theories. In addition, it is shown that in this case the temperature and pressure dependencies of the solubility parameters are predicted qualitatively correct.

We performed this procedure with the *Sanchez- Lacombe* EOS theory instead of the Prigogine-Flory approach. Formally, identical expressions result, and the calculated solubility parameters evaluated according to the two EOS theories are in good agreement. However, because Sanchez-Lacombe's approach is not a corresponding state theory, it is able to predict additionally qualitatively correct the dependence of the solubility parameters on chain length.

## INTRODUCTION

A simple way of predicting miscibility has been suggested for small molecules by *Hildebrand* and *Scott* (1). According to this theory the interaction parameter, $\chi$, of a binary system, in the supposition of identical molar volume, is related to the difference between the solubility parameters of the two components

$$\chi_{12} = V_m(\delta_1 - \delta_2)^2/RT \qquad (1)$$

The solubility parameters are defined as

$$\delta_i = (\Delta E_{vi}/V_{mi})^{1/2} \qquad (2)$$

$\Delta E_{vi} = N_A z w_{ii}/2$ is the molar energy of vaporization, and $V_{mi}$ the molar volume. $N_A$ is Avogadro's number, and $w_{ii}$ the interaction energy between binary contacts. For polymer systems sometimes an empirical constant is added to $\chi_{12}$.

The difference between the solubility parameters in equ. (1) reflects the difference between the interaction energy of the mean of the homo-contacts (1-1) and (2-2) and the binary hetero-contacts (1-2)

$$\Delta w_{12} = [(w_{11} + w_{22})/2] - w_{12} \qquad (3)$$

In order to avoid troublesome experimental determinations for blends, Berthelot's rule is used for the evaluation of $w_{12}$

$$w_{12} = (w_{11} w_{22})^{1/2} \qquad (4)$$

That means, the difference between the interaction energy of the mean of the homo-contacts and of the hetero-contact, ho-c and he-c, is attributed to the difference between the arithmetical and geometrical means of the interaction energy of the ho-c's. Therefore, the interaction energy of the he-c will be always smaller than the mean of the ho-c's. As a consequence any interaction in favour of he-c formation is neglected. In addition, according to this presentation, the solubility parameter theory apparently is not accounting for free volume effects and thus for possible differences in the thermal expansion of the two components. Biroš et al.(2) have demonstrated, however, that the solubility parameter defined by equ. (2), depends in fact on the free volume through both, $\Delta E_v$ and $V_m$.

The energy of vaporization, unfortunately, is not accesible for polymers, but it can be substituted by the negative of the respective configurational energy, which can be deduced for polymers using the corresponding relations of the EOS theories.

In both the *Prigogine-Flory* and *Sanchez-Lacombe* EOS theory the configurational energy can be expressed as

$$U = -p^* V^* / \tilde{v} \qquad (5)$$

where $p^*$ is the reduction presure, $V^*$ the reduction volume, i. e. the 'hard core volume' of the system and $\tilde{v}$ the reduced volume. The reduction parameters, $p^*$, $V^*$ and $T^*$ can be used to evaluate the reduced pressure, $\tilde{p}$, volume, $\tilde{v}$, and temperature, $\tilde{T}$.

$$\tilde{p} = p/p^* \qquad \tilde{v} = V/V^* \qquad \tilde{T} = T/T^*$$

They are interconnected by the respective equations of state.

The EOS of the *Prigogine-Flory* theory is of the form

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1//\tilde{v}\tilde{T} \qquad (6PF)$$

whereas the EOS of the *Sanchez-Lacombe* theory is given by the expression

$$(1/\tilde{v}^2)+\tilde{p}+\tilde{T}[\ln\{1-(1/\tilde{v})\}+\{1-(1/r)\}(1/\tilde{v})]=0 \qquad (6SL)$$

where $r$ is the number of segments per polymer chain. Using the above expression (5) for the configurational energy, relation (2) for the solubility parameter can be reformulated as follows

$$\delta=(-U/V)^{1/2}=p^{*1/2}/\tilde{v} \qquad (7)$$

Starting with this last expression of the solubility parameter, the temperature and pressure dependencies are given by the expressions

$$(\partial\ln\delta/\partial T)_p=-\alpha \qquad (\partial\ln\delta/\partial p)_T=\kappa \qquad (8)$$

The reduction parameters are accessible via expansion coefficient, $\alpha$, compressibility, $\kappa$ and specific volume at $p=0$, by using the respective equation of states.

In both EOS theories the reduction pressure is related via the ratio between expansion coefficient and compressibility with the reduced volume of the polymer

$$p^*=\alpha\tilde{v}^2T/\kappa \qquad (9)$$

The reduced volume and temperature, however, are determined differently in the two models.

The *Prigogine-Flory* EOS theory (3) assumes all lattice sites to be occupied by polymer-segments. The reduced volume is given accordingly by the ratio between the volume and the 'hard core volume', the latter being correlated to the coordinate of the minimum of the Lennard- Jones potential of the system. The reduced volume can be evaluated from the expansion coefficient for $p=0$, using the expression

$$\tilde{v}^{1/3}-1=\alpha T/3(1+\alpha T) \qquad (10)$$

Knowing the reduced volume, the reduced temperature, $\tilde{T}$, can be calculated using the EOS for $p=0$

$$\tilde{T}=(\tilde{v}^{1/3}-1)/\tilde{v}^{4/3} \qquad (10a)$$

With these reduced quantities the corresponding reduction parameters can be determined. The Prigogine-Flory EOS theory predicts, that the polymer characteristics, i.e. expansion coefficient, compressibility, and specific volume do not depend on chain length. Experimentally, however, it has been shown that higher molecular weight polymers pack denser (i.e. exhibit smaller specific volume) and show smaller values of $\alpha$ and $\kappa$.

Conversely, if the reduction parameters of a series of homologues are evaluated from the respective pVT-data using the appropriate expressions of the EOS, they turn out to vary with chain length. In addition, because of varying free volumes, nonvanishing values are obtained for the difference between the solubility parameters $(\delta_1-\delta_2)^2$. Furthermore, since the different molecular weight polymers show different coefficients of expansion, the decreases of the solubility parameters with temperature might also be different. This can lead to phase separation with increasing temperature, i.e. LCST-behaviour, a phenomenon which is not predicted by the original Hildebrand solubility parameter theory.

The *Sanchez-Lacombe* EOS theory is a lattice theory too, where the underlaying lattice comprises vacant sites. Thus, the reduced volume is defined by the ratio between the overall volume and the volume occupied by the mers of the polymer

$$\tilde{v} = (N_0 + rN)/rN \qquad (11)$$

$N_o$ is the number of vacant lattice sites and rN the number of lattice sites occupied by the segments of the N polymer chains containing r segments, respectively. Since this theory is not a corresponding states theory, the state parameters are predicted to vary with chain length. Calculations have shown(5) that expansion coefficients, compressibilities and free volumes are predicted by the Sanchez-Lacombe EOS to decrease with increasing degree of polymerization, in accordance with the experiment. The decrease of the free volume with increasing molecular weight is supported by the observation that the glass temperature increases with increasing molecular weight (6).

For the evaluation of the reduction parameters from pVT-data the equation of state (6SL) for p=0 and infinite molecular weight $(r \rightarrow \infty)$ are used

$$(1/\tilde{v}^2) + \tilde{p} + \tilde{T}[\ln\{1-(1/\tilde{v})\} + (1/\tilde{v})] = 0 \qquad (12)$$

as well as the corresponding expression for the expansion coefficient

$$\alpha T = 1/\left[\tilde{T}/(1-1/\tilde{v})-2)\right] \qquad (13)$$

Starting with these two expressions the reduced quantities $\tilde{v}$ and $\tilde{T}$ can be calculated numerically, and from them v* and T*, respectively.

As the theory assumes a dependence of the volume on chain length, expressed by r, beside the expansion coefficient and compressibility, the solubility parameter depends on the chain length too

$$(\partial \ln \delta/\partial r)_{p,T} = -(1/\tilde{v})\partial\tilde{v}/\partial r \qquad (14)$$

Since the free volume decreases with increasing degree of polymerization, the solubility parameter will increase with increasing chain length.

Taking into account, that the Sanchez-Lacombe theory predicts a dependence of the polymer characteristics on chain length, in principle it is possible to evaluate the EOS parameters for polymers of any molecular weight of a homologous series, starting with the corresponding data of a polymer of any given molecular weight. The effects predicted by theory are, however, too small. Thus, in reality the parameters for polymers of different chain lengths have to be determined separately, similar as in the Prigogine-Flory EOS theory.

An empirical way for the evaluation of the solubility parameters has been suggested by *Small* (7). According to Small, the solubility parameter can be calculated knowing the density, $\rho$, and the molecular weight, M, of the repeating unit and using molar attraction constants, $F_i$, of the chemical structural units included in the polymer repeating unit

$$\delta = \rho \sum (F_i/M) \qquad (15)$$

The attraction constants have been evaluated and tabulated using molar energies of vaporization of corresponding low molecular model compounds.

The method of Small accounts thus only for the different interactions between the chemical units of the polymer. Effects of the free volume, which can be predicted by the EOS theories, are not considered.

Solubility parameters of different polymers were calculated starting with experimental pVT-data and using the respective expressions of the two above discussed EOS theories. They are subsequently compared with the values obtained by Small's method of the attraction constants.

## EXPERIMENTAL

Using the GNOMIX pVT-apparatus, measurements have been performed for several polymers, in order to determine their expansion coefficients, compressibilities and specific volumes at various tem-

| polymer | $M_n$ (g/mol) | $M_w/M_n$ |
|---|---|---|
| polystyrene 2.1 | 2117 | 1.08 |
| polystyrene 6 | 5966 | 1.12 |
| polystyrene 102 | 102000 | 1.05 |
| polyisoprene 2.6 [a] | 2594 | 1.08 |
| poly(methylphenylsiloxane) 1.7 | 1682 [b] | 1.35 [b] |
| poly(cyclohexylmethacrylate) 114[c] | 80740<br>114000 [d] | 1.26 |
| poly(vinylmethylether) 48 | 48140 | 1.62 |

[a] anionic polymerization in cyclohexane, initiator sec-butyllithium, 90% cis 1,4 -content

[b] Aldrich [c] anionic polymerization in THF, initiator 1,1-diphenyl-3-methylpentyllithium

[d] from membrane osmosis

Table I: *Characteristics of the polymers used for pVT-measurements* peratures. The measurements were carried out in the isothermal mode, in steps of 10° C, for the polymer melts above their glass transition temperature.

Starting with these pVT-data the reduction parameters have been evaluated using the expressions of the Prigogine-Flory and of the Sanchez-Lacombe theory, respectively. The expansion coefficients were averaged over the whole temperature range. Compressibilities and specific volumes were determined for each temperature separately and then used to evaluate the corresponding reduction parameters. Since the parameters resulted temperature dependent, they were finally averaged over the respective temperature ranges of interest. The characteristics of the polymers used for the pVT-studies are shown in table I. Unless otherwise stated $M_n$ and $M_w/M_n$ were determined by GPC, calibrated with standard polystyrenes.

## RESULTS AND DISCUSSION

The reduction parameters evaluated using the respective expressions of the two EOS theories employed, are presented in table IIa for the Prigogine-Flory and in table IIb for the Sanchez-Lacombe theory. For the reduction volume the corresponding specific volumes are listed.

| | $p^*$ (MPa) | $v_s^*$ (cm$^3$/g) | $T^*$ (K) |
|---|---|---|---|
| PS 2.1 | 559.1 | 0.8141 | 7090 |
| PS 6 | 566.8 | 0.8436 | 7728 |
| PS 102 | 574.8 | 0.8194 | 7913 |
| PI 2.6 | 469.7 | 0.9396 | 6713 |
| PMPS 1.7 | 519.3 | 0.7583 | 6459 |
| PCHMA 114 | 511.4 | 0.7791 | 8115 |
| PVME 48 | 450.8 | 0.8295 | 7395 |

*Table IIa: Reduction parameters of the Prigogine-Flory theory*

| | $p^*$ (MPa) | $v_s^*$ (cm$^3$/g) | $T^*$ (K) |
|---|---|---|---|
| PS 2.1 | 464.5 | 0.8996 | 661.4 |
| PS 6 | 468.0 | 0.9282 | 715.2 |
| PS 102 | 474.0 | 0.9028 | 729.9 |
| PI 2.6 | 383.0 | 1.0405 | 631.2 |
| PMPS 1.7 | 427.6 | 0.8389 | 606.7 |
| PCHMA 114 | 417.6 | 0.8620 | 760.8 |
| PVME 48 | 369.5 | 0.9165 | 699.7 |

*Table IIb: Reduction parameters of the Sanchez-Lacombe theory*

Except of the reduction temperatures, the obtained values of the reduction parameters are quite similar. Especially the trends in the observed changes of the reduction pressures and specific volumes are the same. Taking into account that the SL-theory admits holes, the corresponding specific reduction volumes are by a factor of about 10% larger than those of the PF-theory. Accordingly the reduction pressures are the smaller.

The solubility parameters were then evaluated by equ. (7) for 25°C and p=0. In table III the obtained δ are compared with the values calculated according to Small's rule using the respective attraction constants. They are of about 10-15% smaller than the values obtained by the two EOS-theories. While the Small solubility parameter data for the polystyrenes of different molecular mass are constant, they show a slight molecular weight dependence in both EOS theories used.

| | $\delta_{\text{Prigogine-Flory}}$ ((J/cm$^3$)$^{1/2}$) | $\delta_{\text{Sanchez-Lacombe}}$ ((J/cm$^3$)$^{1/2}$) | $\delta_{\text{Small}}$ ((J/cm$^3$)$^{1/2}$) |
|---|---|---|---|
| PS 2.1 | 20.34 | 20.40 | 18.52 |
| PS 6 | 20.78 | 20.71 | 18.52 |
| PS 102 | 21.02 | 20.90 | 18.52 |
| PI 2.6 | 18.45 | 18.38 | 16.76 |
| PMPS 1.7 | 19.25 | 19.27 | - |
| PCHMA 114 | 19.90 | 19.71 | 18.45 |
| PVME 48 | 18.41 | 18.35 | 16.65 |

*Table III: Solubility parameters from EOS-theories and Small's table*

The dependence of the solubility parameter on the reciprocal chain length as predicted by SL is shown in Fig. 1 (full lines). The calculations were performed by using the parameters of the three different PS. The calculated chain length influence is much smaller than that predicted using reduction parameters of PS of different chain lengths. For comparison, the values obtained for the respective PS are shown as well, for both the SL- (full circles) and the PF-theory (full triangles). It is evident, that the dependence on molecular mass $M_n$ as predicted by the SL-theory is too small. Thus, it is impossible to evaluate the $M_n$ dependence of the parameters starting with the respective EOS-parameters computed from pVT-data of a single polymer.

The pVT-behavior is described better by PF than by SL. For higher pressures the compressibility $\kappa$ is predicted too low by both models, with higher deviation from experimental data in the SL-theory$^{(5)}$. Thus, it is expected, that the pressure dependence of the parameters predicted by the PF-theory is the more realistic one.

The pressure dependence of the PS solubility parameters as calculated with the two theories is illustrated in Figure 2. Since $\kappa$ is predicted to be lower for SL, the predicted pressure influence is lower too. PF, however, also predicts too low κ. Thus, the pressure dependence given by this theory might be too small too.

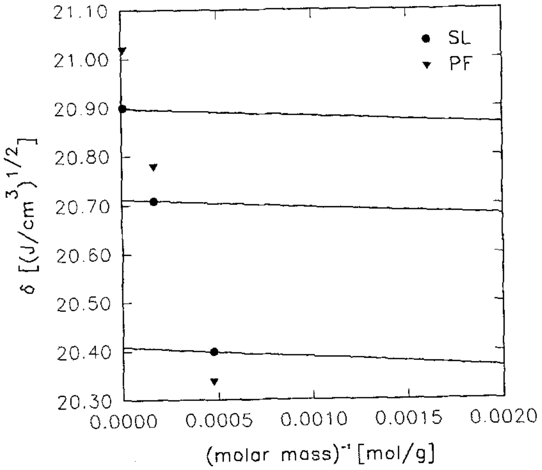

*Figure 1:* Solubility parameter of polystyrene vs. inverse chain length
- full lines SL-theory
- points experimental

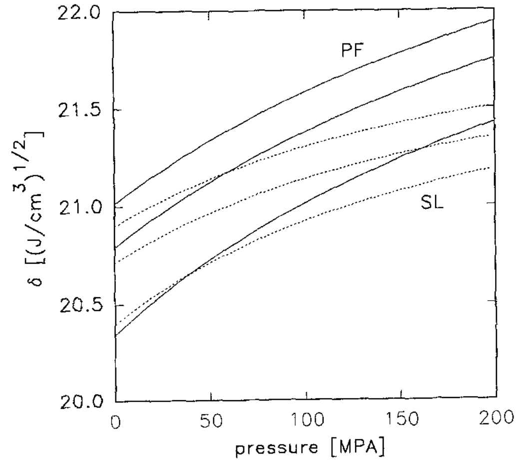

*Figure 2:* Solubility parameter of polystyrene vs. pressure
- dotted lines SL-theory
- full lines PF-theory

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