

# The Relationship Between the Permeation Rate and the Solubility Parameter for Polyethylene-n-Hexane-Benzene System in Pervaporation

Ji-Won Rhim

Dept. of Chem. Eng., Hannam Univ.,  
Daedeok-Gu, Ojung-Dong 133, Daejeon 300-791, Korea  
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폴리에틸렌-n-헥산-벤젠계에 대한 투과속도와 용해도 파라메타 사이의 관계

임 지원

한남대학교 화학공학과, 대전시 대덕구 오정동 133, 300-791  
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## 1. Introduction

It is well known that the membrane permeation in pervaporation is governed by both the chemical nature of the membrane material and the physical structure of the membrane and also the separation can be achieved by differences in either solubility, size or shape. The solubility of the penetrant in the polymeric membrane can be described qualitatively by applying the Hildebrand relation [1] which relates the energy of mixing of the penetrant and the polymer material. Froehling et al. have tried to predict the swelling behavior of polymers for the systems of polyvinylchloride(PVC)-toluene-methanol, PVC-trichloroethylene-nitromethane and PVC-n-butylacetate-nitromethane[2]. The former two systems which do not show the donor/acceptor interactions upon mixing showed the successful results[2]. In addition to this technique, there are several other possible approaches to predict the

swelling behaviors of polymers, such as the surface thermodynamic approach[3, 4], the comparison of the membrane polarity with the solvent polarity in terms of Dimroth's solvent polarity value[5].

However, there has not been studied for the relation of the permeation rate and the solubility parameter in pervaporation area. This can provide the membrane material selection eventually. In this note, the study was focused on the connection of the solubility parameter to the permeation rate for polyethylene-n-hexane-benzene system at 25°C.

## 2. Theory

According to Hildebrand theory[1], the solubility parameter can be described in terms of the energy of mixing of two components and their individual energies of vaporization :

$$\frac{\Delta E_{\text{mix}}}{\Phi_1 \Phi_2} = V(\delta_1 - \delta_2)^2 \quad (1)$$

$$\delta = [\text{C. E. D.}]^{1/2} = \left[ \frac{\Delta E_{\text{mix}}}{V_m} \right]^{1/2} \quad (2)$$

where  $\Delta E_{\text{mix}}$  is the energy of mixing;  $\Phi_1$  and  $\Phi_2$ , the volume fractions of the components;  $V$ , the total volume of the mole of the mixture;  $\delta_1$ ,  $\delta_2$ , the Hildebrand solubility parameters; C. E. D., the cohesive energy density;  $\Delta E_{\text{vap}}$ , the energy of vaporization, and  $V_m$ , the molar volume. Eq. (1) illustrates that a smaller difference in  $\delta$  between a penetrant and a polymeric membrane material results in reducing the energy of mixing. And a decrease in the energy of mixing causes a higher degree of swelling and eventually complete solubility may be given. The Hildebrand solubility parameters,  $\delta$ 's, in Eq. (1) are defined by Eq. (2). Hansen [6] extended the solubility parameter in Eq. (1) into three components, disperse contribution ( $\delta_d$ ), dipole contribution ( $\delta_p$ ) and hydrogen bonding (or donor/acceptor) contribution ( $\delta_h$ ) as followings :

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

These three components lie as vectors along orthogonal axes in 3-dimensional space. The end-point of the vector represents the solubility parameter. Froehling et al. [2] used the expression of each of the solubility parameter components for a mixture of two solvents as :

$$\delta_{m,i} = \Phi_1 \delta_{1,i} + \Phi_2 \delta_{2,i}; \quad i = d, p, h \quad (4)$$

where  $\Phi_1$  and  $\Phi_2$  are the volume fractions of the components.

This relation should be used in the system which has no specific interactions upon mixing each other because these interactions, e. g., donor/acceptor interactions, do not obey the geometric mean rule. In the case of the donor/acceptor mixtures system, there should be considered the correction term in the above equation.

Finally, each mixed solvent and each polymer can be located by the three coordinates ( $\delta_d$ ,

$\delta_p$ ,  $\delta_h$ ). The distance  $\Delta$  between the end-points of the vectors representing polymer and solvent mixture is given by

$$\Delta = [(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2]^{1/2} \quad (5)$$

where the subscripts S and P refer to solvent mixture and polymer, respectively.

### 3. Results

Three dimensional solubility parameters for n-hexane, benzene and polyethylene (PE) considered in this note are shown in Table 1.

**Table 1.** Solubility Parameters in (cal/cm<sup>3</sup>)<sup>1/2</sup> for n-Hexane, Benzene and PE

Compound	$\delta_d$	$\delta_p$	$\delta_h$	References
n-hexane(1)	7.23	0	0	7
	7.27	0	0	3
benzene(2)	8.95	0.5	1.0	7
PE(3)	8.047	0	0	8
	8.61	0	0	3

As can be seen in Table 1, there is a little difference along with the reference sources particularly for PE. 8.047 value for PE was calculated from the group contribution theory which has been commonly used for various polymeric materials. And the permeation rates cited in the next sentences should be referred to ref. 9.

The two sets of the calculated  $\Delta$  values by using the solubility parameter shown in Table 1 from Eq. (5) are plotted in Fig. 1. The curve 1 used the values of n-hexane 7.23, benzene 8.95 and PE 8.047, and the curve 2 the values of n-hexane 7.27, benzene 8.95 and PE 8.61. It is well known that a smaller value in  $\Delta$  values results in a more swelling behavior or a more permeation rate. Two minimum points at 0.45 and 0.67 of the n-hexane volume fraction for the curves 1 and 2, respectively, and the maximum permeation rate could be observed at the

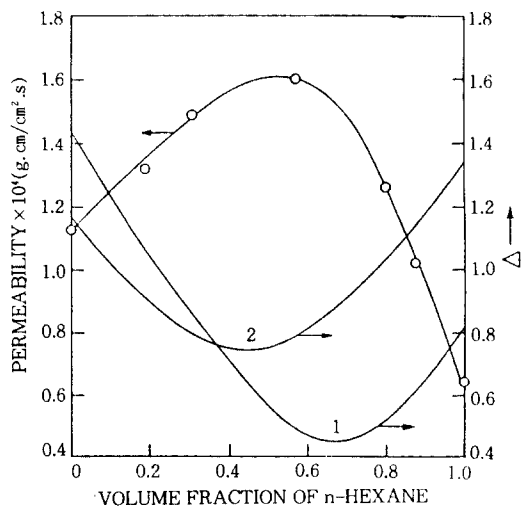


Fig. 1. The relationship between the permeation rate and the solubility parameters taken from the different source for n-hexane-benzene-PE system at 25°C.

former value rather than the latter value.

However, when comparing the pure permeation rates with the  $\Delta$  values of each pure component of the curves 1 and 2, the results are contrary each other. In other words, in the case of the curve 1 the relationship between the pure permeation rates and the  $\Delta$  values does not follow the rule mentioned above, which is that a smaller difference in  $\Delta$  values results in a more swelling behavior. However, the curve 2 obeys this rule. Therefore, from this results, the proper choice of solubility parameters is also very important for the prediction of the permeation rate for the ternary system.

Another thing to be pointed out from Fig. 1 is that this figure provides a good guideline for the membrane material selection. When the  $\Delta$  values at both axes (the volume fraction of n-hexane=0 and 1) are defined by  $\Delta_{B/PE}$  and  $\Delta_{H/PE}$ , respectively, there is a small difference between  $\Delta_{B/PE}$  and  $\Delta_{H/PE}$ . It is well known, in general, that a larger difference of these value

results in a higher selectivity. In fact, the selectivity for the system in question varies only from 1.0 to 1.82[9].

In conclusion, the relation between the permeation rate and the solubility parameter for the system of n-hexane(1)-benzene(2)-PE(3) was simulated. The minimum point in the  $\Delta$  values coincided with the maximum in the permeation rate curve at 0.45 volume fraction of n-hexane. However, the selection of the solubility parameter values was very important, otherwise the wrong value of the feed concentration at which showed the maximum permeation rate could be obtained. Therefore, caution should be exercised for using the calculated solubility parameters for the polymers which their values are not available in the literatures. And finally, this would provide a good guideline for the membrane material selection for the solvent pairs to be separated by pervaporation technique which do not show the donor/acceptor interactions.

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