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# Determination of Polystyrene-Hydrocarbon Interaction Parameters and Solubility Parameter Using Inverse Gas Chromatography

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## ABSTRACT

The weight fraction activity coefficients $(a_1/w_1)^{\infty}$ and Flory-Huggins $\chi$ parameters have been determined by using inverse gas chromatography technique over the temperature range of 433-453 K for four hydrocarbons on polystyrene. The Hildebrand solubility parameter $\delta_2$ of polystyrene was then calculated. The values of $\delta_2$ obtained from $\overline{\Delta G}_1^{\infty}$ and $\chi$ parameters were found to agree with literature data.

## INTRODUCTION

Because of its conveince and versality, inverse gas chromatography (i.g.c) is widely used in polymer research. It provides much quantitative information on polymer solvent interactions.

Inverse gas chromatography is based on observation of retention volumes of molecular probes on the polymer which is coated onto a support. Specific retention volume $V_g^0$ is calculated from the relation[1]

$$V_g^0 = [(t_r . 273.12 . F)/(w.T)]\ 3/2\ [(P_i/P_0)^2-1]/[(P_i/P_0)^3-1] \qquad (1)$$

where $t_r$ is the net retention time, F is the flow rate of carrier gas at 273.12 K, w is the mass of polymer, T is the column temperature and $P_i$ and $P_0$ are the inlet and outlet pressure of carrier gas.

Flory-Huggins parameter X characterizing the interaction of probe with the polymer is determined from the following equation.

$$X = \ln[(273.12 . R . V_2)/(P_1^0 . V_g^0 . V_1)] - [P_1^0 (B_{11} - V_1) / R.T] - 1 \qquad (2)$$

where $V_2$ is the volume fraction of polymer, $P_1^{\circ}$ is the probe vapor pressure, $V_1$ is the molar volume of the probe and $B_{11}$ is the second virial coefficient of the probe.

The value of $B_{11}$ for the probe is calculated from

$$B_{11} / V_c = 0.430 - 0.886\, T_c/T - 0.694\,(T_c/T)^2 - 0.0375\,(T_c/T)^{4.5} \qquad (3)$$

where $V_c$ and $T_c$ are the critical volume and temparature of the probe.

Probe vapor pressure $P_1^0$ is found from the Antonie equation

$$\mathrm{Log}\, P_1^0 = A - B / t + C \qquad (4)$$

where $P_1^0$ is the probe pressure in mmHg, t is the temperature in $^0$C; A, B and C are constants taken from the standart sources.

Solubility parameter $\delta_1$ of probe is calculated from the relation

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \qquad (5)$$

where $\Delta H_v$ is the molar enthalpy of vaporization for the probe at temperature T.

Although the solubility parameter of a probe is a readily calculable quantity, the solubity parameter of polymer cannot be determined directly because most polymers cannot be vaporized without decomposing.

The Flory-Huggins X parameter is related to the solubility parameters of probe and the polymer as follows

$$X = (V_1 / RT)\,(\delta_1 - \delta_2)^2 \qquad (6)$$

where $\delta_1$ and $\delta_2$ are the solubility parameters of probe and the polymer.

The last equation can be rearranged to

$$(\delta_1^2 / RT) - X / V_1 = (2\delta_2 / RT)\,\delta_1 - (\delta_2^2 / RT) \qquad (7)$$

If the left side of this equation is plotted against $\delta_1$, a straight line having a slope of $2\delta_2$ / RT and an intercept of $\delta_2^2$ / RT is obtained.

The solubility parameters of polymer can also be obtained from the partial molar free energy $\Delta G_1^{\infty}$ of probe at infinite dilution (above the glass transition temparature of polymer). The partial molar free energy of probe is determined from the weight fraction activity coefficient $(a_1/w_1)^{\infty}$ of probe at infinite dilution. The weight fraction activity coefficient $(a_1/w_1)^{\infty}$ is measured from

$$\ln (a_1/w_1)^{\infty} = \ln [(273.12 . R)/(P_1^0 . V_g^0 . M_1)] - [(P_1^0 (B_{11} - V_1) / RT)] - 1 \quad (8)$$

The relation between $\overline{\Delta G}_1^{\infty}$ and $(a_1/w_1)^{\infty}$ at infinite dilution is

$$\overline{\Delta G}_1^{\infty} = RT \ln (a_1/w_1)^{\infty} \quad (9)$$

Assuming no pressure difference with the probe in the experiments, one obtains

$$\overline{\Delta G}_1^{\infty} = V_1 (\delta_1 - \delta_2)^2 \quad (10)$$

According to the equation10, the plot of $(\delta_1^2 - \overline{\Delta G}_1^{\infty}/V_1)$ against $\delta_1$ gives a straight line with a slope of $2\delta_2$ and the intercept of the straight line is $-\delta_1^2$

## EXPERIMENTAL

### Materials

Polystyrene (PS) having a viscosity average moleculer weight of $M_v$ = 145000 was obtained from YARPET-TURKEY. The glass transition temperature of the polymer is 373 K.

The probes (n-hexane, n-heptane, n-nonane and n-decane) were analytical or chromatography grade solvents and were used without any purification. The following abbreviations were used for the probes:

n-hexane : n-$C_6$

n-heptane : n-$C_7$

n-nonane : n-$C_9$

n-decane : n-$C_{10}$

### Columns

Polystyrene was dissolved in methylene chloride ($CH_2Cl_2$) and deposited onto an inert chromatographic support Chromosorb W by slow evaporation of methylene chloride with gentle stirring. After vacum drying for 48 h. with slight heating, the chromatographic support was packed with the aid of a mechanical vibrator into 3.25 mm i.d. copper column which is 1 m. long

Table I. Specific Retention Volumes of Probes as a Function of Temperature (433-453 K) on Polystyrene

| T (K) | $V_g^0$ cm$^3$/g n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ |
|---|---|---|---|---|
| 433 | 1.980 | 1.980 | 5.180 | 6.800 |
| 443 | 1.390 | 1.960 | 5.220 | 5.820 |
| 453 | 1.190 | 1.690 | 3.730 | 3.600 |

Table II. Probe Parameters as a Function of Temperature.

| | $P_1^0$ mmHg | | | | $V_1$ cm$^3$/mol | | | | $\delta_1$ (cal/cm$^3$)$^{1/2}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T (K) | n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ | n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ | n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ |
| 433 | 6739 | 3432 | 959 | 520 | 168 | 181 | 209 | 231 | 4.9 | 5.4 | 6.1 | 6.2 |
| 443 | 8053 | 4192 | 1225 | 680 | 173 | 185 | 213 | 234 | 4.6 | 5.2 | 5.9 | 6.1 |
| 453 | 9359 | 5069 | 1545 | 877 | 177 | 189 | 217 | 238 | 4.4 | 5.0 | 5.8 | 5.9 |

Table III. Flory-Huggins Parameters X of Probes on Polystyrene

| T (K) | X n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ |
|---|---|---|---|---|
| 433 | 1.8972 | 1.7206 | 1.8132 | 1.9154 |
| 443 | 1.3709 | 1.5303 | 1.5574 | 1.9154 |
| 453 | 1.3586 | 1.4887 | 1.6589 | 2.1382 |

Table IV. Weight Fraction Activity Coefficients $(a_1/w_1)^\infty$ of Probes on Polystyrene

| T (K) | $(a_1/w_1)^\infty$ n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ |
|---|---|---|---|---|
| 433 | 2923 | 2899 | 2826 | 3028 |
| 443 | 2526 | 2799 | 2669 | 2999 |
| 453 | 2571 | 2825 | 2823 | 3271 |

## Chromatography

The gas chromatography used was a Packard 436 with a flame ionization detector. The retention times were measured with a Shimadzu integrator. Methane was used as the internal marker and nitrogen as the carrier gas. The carrier gas flow rate was measured by a soap-bubble flow meter. Probe injections were done with a 1 µL Hamilton syringe. Pressures at inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes.

## RESULTS AND DISCUSSION



Specific retention volumes (above $T_g$) as a function of temperature for four probes on polystyrene were measured. The values are shown in Table I.

As can be seen from Table 1, the specific retention volumes of probes on polystyrene are temperature dependent and decrease with the increasing of temperature for each probe. Similar results had been obtained for the other (polymer-probe) systems [2,3].

The probe parameters including the vapor pressures $P_1^0$, the molar volume $V_1$ and solubility parameters $\delta_1$ at different temperatures were not found in the literature sources over the temperature range of433-453 K, so the values of $P_1^0$ and $\delta_1$ for each probe were computed from the equations 4 and 5 respectively. The molar volumes $V_1$ of probes at different temperatures (Table II) were computed with the help of some constants taken from literature sources[4,5].

Flory-Huggins X parameters calculated as a function of temperature for each probe from the equation 2 are tabulated in Table III.

Flory-Huggins X parameter characterizes the interactions between the chain segments of probe and the chain segments of polymer. A consequence from theoretical considerations is that X has to be smaller than 0.5 for the solvents and larger than 0.5 for the nonsolvents of polymer[6]. X values which we have obtained are in good agreement with this theoretical considerations.

Weight fraction activity coefficients $(a_1/w_1)^\infty$ at infinite dilution for each probe were determined as a function of temperature by using the specific retention volumes and probe parameters over the temperature range 433-453 K Table IV. shows the results.

Table V. The Partial Molar Free Energies of Probes of Polystyrene.

| T (K) | $\Delta\bar{G}_1^{\infty}$ cal / mol n-$C_6$ | n-$C_7$ | n-$C_9$ | n-$C_{10}$ |
|---|---|---|---|---|
| 433 | 2923.71 | 2899.23 | 2826.27 | 3028.43 |
| 443 | 2526.81 | 2799.50 | 2669.23 | 2999.65 |
| 453 | 2571.31 | 2827.59 | 2823.15 | 3271.59 |

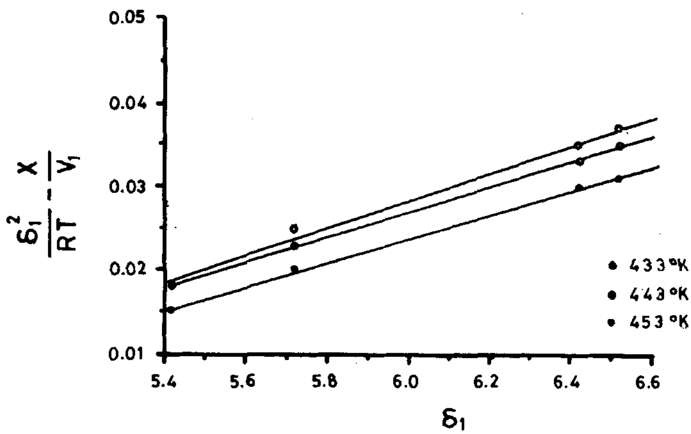


Figure I. Estimation of the Solubility Parameter $\delta_2$ of Polystyrene from Flory-Huggins X Parameters

The weight fraction activity coefficient $(a_1/w_1)^{\infty}$ at infinite dilution may be regarded as a measure of the interaction between the polymer and probes. Table IV shows that the values of $(a_1/w_1)^{\infty}$ decrease with increasing temperature for all probes. This means that the solubility of probes in the polymer increases with the increasing temperature[7].

According to the values of $(a_1/w_1)^{\infty}$, the following rules for (polymer-solvent) system have been formulated by Guillet[8],

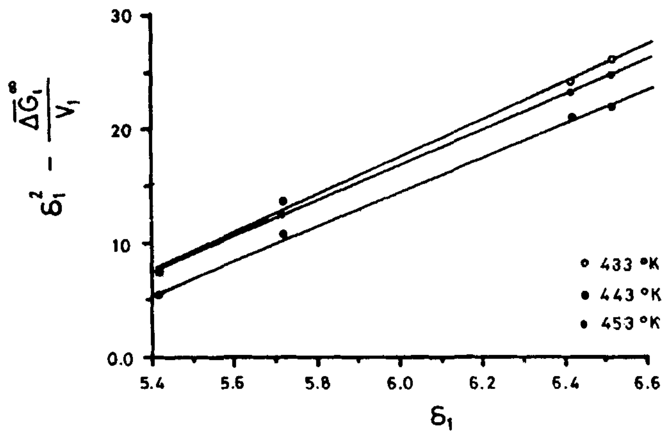


**Figure II. Estimation of the Solubility Parameter $\delta_2$ of Polystyrene from the Partial Molar Free Energy of mixing $\overline{\Delta G}_1^\infty$**

Table VI. $\delta_2$ Values of Polystyrene at Different Temperatures.

| T(K) | $\delta_2$ from X Slope | $\delta_2$ from X Intercept | $\delta_2$ from $\Delta G_1^\infty$ Slope | $\delta_2$ from $\Delta G_1^\infty$ Intercept |
|---|---|---|---|---|
| 433 | 8.18 | 8.18 | 7.91 | 7.90 |
| 443 | 7.63 | 7.62 | 7.20 | 7.20 |
| 453 | 6.64 | 6.76 | 6.70 | 6.80 |

$(a_1/w_1)^\infty < 5$ for good solvents

$5 < (a_1/w_1)^\infty < 10$ for moderate solvents

and $(a_1/w_1)^\infty > 10$ for non-solvents

Table IV indicates that the values of $(a_1/w_1)^\infty$ are all of the magnitude expected for (polymer-nonsolvent) systems.

The solubility parameter $\delta_2$ for polystyrene was evaluated from the equations 7 and 9 over the temperature range of 433-453 K. To eliminate the solubility parameter $\delta_2$ from equation 10, the partial molar free energies $\overline{\Delta G}_1^\infty$ of probes on polystyrene at infinite dilution were calculated by using equation 9. These values are shown in Table V.

Using the solubility parameters $\delta_1$ of probes at the same temperature from Table II, values of $\delta_2$ for the polystyrene were obtained from the slopes and intercepts of the plots of ( $\delta_1^2/RT - X/V_1$) againts $\delta_1$ (Fig. I) and ( $\delta_1^2 - \overline{\Delta G}_1^\infty/V_1$) againts $\delta_1$ (Fig.II). The values are shown in Table VI.

It is seen that solubility parameters obtained from the slopes and intercepts of plots are in good agreement with each other. These values seem to be most convenient with the $\delta_2$ values obtained by DiPaola Baranyi and Guillet[9].

In comparing the $\delta_1$ and $\delta_2$ values of probes and polymer at different temperatures it was seen that both $\delta_1$ and $\delta_2$ solubility parameters decreased with increasing temperature.

## CONCLUSIONS

Using the inverse gas chromatography technique, we have obtained Flory-Huggins X parameters and weight fraction activity coifficients $(a_1/w_1)^\infty$ for polystyrene-probes systems and also solubilitiy parameter $\delta_2$ of polystyrene. The results are in good agreement with the literature data. Our experience with this apparatus indicates that it can be used to estimate thermodynamic parameters of (polymer-probe) systems.

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