Estimation of Thermodynamic Parameters of Polystyrene-n_Hydrocarbons Systems Using Inverse Gas Chromatography

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ESTIMATION OF THERMODYNAMIC PARAMETERS OF POLYSTYRENE-n_HYDROCARBONS SYSTEMS USING INVERSE GAS CHROMATOGRAPHY.

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SUMMARY

Thermodynamic parameters like partial molar free energy, Flory-Huggins interaction parameter, weight fraction activity coefficient and molar heats of polystyrene- n_hydrocarbons systems were determined by using inverse gas chromatography technique. The results obtained showed similarity with that of polymer-non solvent systems.

INTRODUCTION

Inverse gas chromatography (IGC, also called the molecular probe technique) which was developed by Smidsrod and Guillet[1] is used in the study of the organic polymers and their interactions with the probes.

The method consists of coating an inert material such as Chromosorb W with the polymer to be studied and recording the retention diagram[2]. Such a diagram obtained for a selected solvent is used to measure surface areas and adsorbtion isotherms[3,4], glass and other solid phase transitions in polymer[5,6], degree of crystallinity[7,8], and diffusion constants for small molecules in polymeric materials[9] as well as thermodynamic parameters of small molecules with polymers in the solid phase[10,11].

Gas chromatography is based on the distribution of a compound between two phases. The injected compound is carried by the gas through a column filled with solid phase and partitioning occurs via the sorption-desorption of the compound as it travels through the solid. The net volume required to move the probe molecules through the column is V_g'.

the total volume of gas needed minus the dead volume in the column. This is determined by injecting an inert probe such as methane or air into the column

The specific retention volume V_g is calculated as,

$$V_g = [(t_r \cdot 273.2 \cdot F)/(w.T)] \cdot 3/2 \cdot [(P_i/P_0)^2-1]/[(P_i/P_0)^3-1] \qquad (1)$$

where t_r is the net retention time, w is the weight of polymer, F is the flow rate of carrier gas at 273.2 K, T is the column temperature, P_i and P_0 are the inlet and outlet carrier gas pressures, respectively.

Information from a molecular probe experiment is usually presented in the form of a retention diagram, that is, a plot of ln V_g against 1/T.

Estimation of thermodynamic parameters:

The partial molar free energy of sorption ΔG_1^s is calculated from the relation,

$$\Delta G_1^s = -RT \ln (M_1 V_g / 273 \cdot R) \qquad (2)$$

where M_1, is molar mass of the probe and R is the gas constant.

The molar enthalpy of sorption ΔH_1^s is of the form,

$$\Delta H_1^s = -R (\ln V_g / (1/T)) \qquad (3)$$

The entropy is calculated as

$$\Delta S_1^s = (\Delta H_1^s - \Delta G_1^s) / T \qquad (4)$$

The probe vapour pressure P_1^0 is estimated using the Antonie equation[12]

$$\log P_1^0 = A - (B / t + C) \qquad (5)$$

where A, B and C are constants.

The weight fraction activity coefficient of probes at infinite dilution (40°C above T_g) is calculated from the expression:

$$\ln (a_1/w_1)^\infty = \ln [(273.2 \cdot R)/(P_1^0 \cdot V_g M_1)] - [P_i^0 (B_{11} - V_1) / R.T] \qquad (6)$$

where V_1 is the volume of the probe and B_{11} is the second virial coefficient of the probe. The value of B_{11} is evaluated from the following equation[2],

$$B_{11}/V_c = 0.430 - 0.886\, T_c/ - 0.694\,(T_c/T)^2 - 0.0375\,(n-1)(T_c/T)^{4.5} \quad (7)$$

where V_c and T_c are the critical volume and temparature of the probe, and n is the number of carbon atoms in the probe molecule.

The Flory-Huggins parameter X is calculated from

$$X = \ln\left[(273.2 \cdot R \cdot V_2)/(P_1^0 \cdot V_g \cdot M_1)\right] - \left[P_1^0\,(B_{11} - V_1)/R.T\right] \quad (8)$$

where V_2 is the volume fraction of the polymer.

The partial molar heat of mixing ΔH_1^∞ at infinite dilution is given by

$$\Delta H_1^\infty = R \ln (a_1 / w_1)^\infty / (1/T) \quad (9)$$

Consequently, the partial molar free energy of mixing ΔG_1^∞ is

$$\Delta G_1^\infty = RT \ln (a_1 / w_1)^\infty \quad (10)$$

This paper describes some thermodynamic parameters of polystyrene by using the inverse gas chromatography.

EXPERIMENTAL

Materials

Amorphous polystyrene (PS) having a viscosity average molecular weight of $M_v =$ 145000 was obtained from YARPET-TURKEY.

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.

Chromatography

The gas chromatography used was a Packard 430 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 1μL 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

The specific retention volumes of for each probe molecular on polystyrene were determined at a series of temperature. The results are shown in Fig. 1.
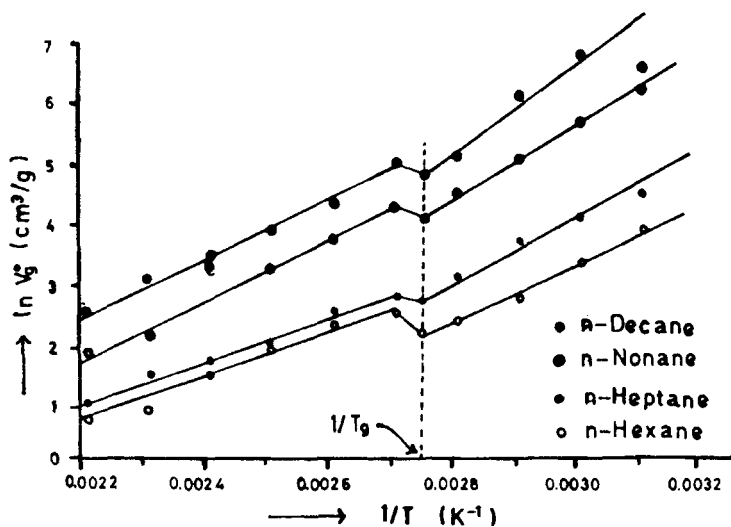

Figure 1. Variation of ln V_g° against 1/T

Table I. Molar enthalpy of probes on polystyrene

Probe	ΔH_1^S Cal / mol
n_Hexane	- 7520
n_Heptane	- 12066
n_Nonane	- 12713
n_Decane	- 12622

Table II. ΔG_1^S and ΔS_1^S values of probes on polystyrene for sorption

T (K)	ΔG_1^S (Cal/mol)				ΔS_1^S (Cal/mol)			
	C_6	C_7	C_9	C_{10}	C_6	C_7	C_9	C_{10}
373	2472	2189	1122	617	-26,17	-38,31	-37,08	-35,49
383	2819	2663	1529	961	-26,96	-38,66	-37,17	-35,46
393	3195	2898	1408	1294	-27,24	-38,22	-35,91	-35,47
403	3264	3685	2836	1759	-27,62	-39,28	-37,36	-35,67

As can be seen from Fig. I, the specific retention volumes of probes on polystyrene are temperature dependent and decrease with the increasing of temperature. The glass transtition temperature of polystyrene is found 363 K, which is in agreement with the previous literature data.[13]

The thermodynamic parameters of sorption (between 373-403 K) calculated for the polymer include contributions from the process of the transfer of a polymer molecule to the adsorbed phase and of its penetration inside the polymer. The values of molar enthalpy of sorption ΔH_1^S for each probe on polystyrene are given in Table I.

It is seen that ΔH_1^S values of probes increased with the molecular weight of probe molecules.

The values of ΔG_1^S and ΔS_1^S calculated according to the equations (2) and (4) are given in Table II.

The values ΔG_1^S for sorption are positive and ΔS_1^S values are negative. They agree well with the (polymer-nonsolvent) systems[14].

Table III. Weight Fraction Activity Coefficients $(a_1/w_1)^\infty$ of n-Hydrobons on Polystyrene as a Function of Temperature

T (K)	$(a_1/w_1)^\infty$			
	n_C$_6$	n_C$_7$	n_C$_9$	n_C$_{10}$
413	16.31	76.50	37.76	29.45
423	14.18	30.60	41.06	38.15
433	29.85	25.09	26.92	33.45
443	17.40	20.74	20.78	30.25
453	17.40	19.76	23.01	37.92

Table IV. X Parameters of n-Hydrocarbons on Polystyrene as a Function of Temperature

T (K)	X			
	n_C$_6$	n_C$_7$	n_C$_9$	n_C$_{10}$
413	1.2868	2.5399	2.0129	1.9025
423	1.1515	1.9076	1.8834	2.0933
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

The weight fraction activity coefficient at infinite dilution (between 403-453 K) may be regarded as a measure of the interaction between the polymer and probes. The following rules have been formulated by Guillet[15],

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

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

$(a_1/w_1)^\infty > 10$ bad solvents

Table III. shows that the measured values of $(a_1/w_1)^\infty$ are bigger than 10 similar to the values of $(a_1/w_1)^\infty$ whic have been found by Baranyi at al for the system polystyrene - n_hexadecane[16]. Also the values of $(a_1/w_1)^\infty$ decrease with increasing temperature for all probes. This suggests that solubility of the hydrocarbons in the polymer increases with temperature[17].

The dependence of the Flory-Huggins X parameter on the temperature has been found to be similar to that for $(a_1/w_1)^\infty$. The dependence of X on the temperature is shown in Table IV.

As a free Hehmholtz energy the parameter X characterizes the interaction of the probes with the chain segments of polymer. A consequence from theoretical considerations is that X has to be larger than 0.5 for the (polymer-nonsolvent) systems and smaller than 0.5 for the (polymer-solvent) system [18]. The values of X found in this experiment are high, as usual for polymer-nonsolvent systems.

Table V. The values of ΔH_1^{∞} of hydrocarbons on polystyrene

Probe	ΔH_1^{∞} Cal / mol
n_Hexane	100
n_Heptane	1116
n_Nonane	3377
n_Decane	3629

The partial molar heats of mixing ΔH_1^s at infinite dilution were determined by means of equation (9). For this purpose, the values of $\ln(a_1/w_1)^{\infty}$ were plotted against $1/T$ between 403-453 K. The values of ΔH_1^{∞} calculated from the slopes of straight lines are shown in Table V.

According to DiPaola-Baranyi at al endothermic heats of mixing are characteristics of polymer-nonsolvent systems while for the polymer -solvent systems are exothermic[16]. In view of the weak polymer-probe interactions, a positive heat of mixing would have been expected. The positive ΔH_1^{∞} values obtained in these experiments is of the order of magnitude which might be expected for the systems of this type; reported values fall in the range of 0 to 4000 cal/mol[19,20].

CONCLUSIONS

Inverse gas chromatography technique was successfully applied to determine the glass transition temperature of polystyrene, the weight fraction activity coefficients, X Flory Huggins parameters and molar heats of n_hydrocarbons on polystyrene. The results obtained are in good agreement with that of polymer-nonsolvent systems. The technique is relatively uncomplicated and the data reduction is carried out by a moderate-size minicomputer.

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