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A Study of the Thermodynamical Interactions of Bisphenol-A Polycarbonate With Some Solvents by Gas Chromatography

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Retentin diagrams of polycarbonate for n-nonane, ethyl acetate and n-butyl acetate were obtained using inverse gas chromatography in the temperature range 80-240 °C. The specific retention volumes, V_g° , the Flory-Huggins interaction parameters, χ_{12}^∞ , interaction parameters, χ_{12}^* , and effective exchange-energy parameters \bar{X}_{12} of the equation-of-state theory of polycarbonate for n-octane, n-nonane, n-decane, ethyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, tert-butyl acetate and isoamyl acetate were obtained in the temperature range 200-240 °C. The parameter δ_2 was estimated to be 10.7 (cal/cm³)^{1/2} at room temperature using the χ_{12}^∞ extrapolated to room temperature.

Keywords: Bisphenol-A polycarbonate, polymer-solvent interactions, inverse gas chromatography, solubility parameter.

Introduction

Inverse gas chromatography (IGC) is a technique used in the determination of certain theoretical parameters related to the interaction between a polymer and a substance lower molecular weight.¹⁻⁶ The interaction parameter, χ_{12}^∞ in the Flory-Huggins theory,^{7,8} the hardcore interaction parameter, χ_{12}^* , and the exchange-energy parameter, \bar{X}_{12} in the equation-of-state theory⁹⁻¹¹, can be obtained through IGC as well as other techniques, such as osmotic pressure, vapor sorption and viscosity.¹² The glass transition temperature, (T_g) of a polymer can also be observed using the IGC method. Sorption properties of a polymer in liquid state can be studied at temperatures at least 40 degrees higher than T_g in order to obtain useful information about thermodynamics related to the interactions between a polymer and a solvent.

The solubility parameter of a polymer, δ_2 , can be obtained from intrinsic-viscosity measurements in linear or branched polymers and by swelling experiments for cross-linked form. These procedures are time-consuming. It can also be estimated by assuming that the solubility parameter of a polymer is equal to that of a lower-molecular-weight analog with structure similar to the repeating unit of the polymer. It can also be calculated approximately by adding up the contributions of groups of repeating units. These methods involve time-consuming experiments and give approximate results. On the other hand, the solubility parameter of a polymer can be determined in a very short time and using a small amount of the substance using the IGC method.³ A disadvantage of the IGC method is that since it is necessary to study at temperatures higher

than T_g serious errors may result when extrapolating values for room temperature from values obtained at high temperatures, in comparison with values obtained with other techniques. Because IGC is a fairly new method in the determination of δ_2 , additional studies are required to scientifically justify its use.

In this study, Flory-Huggins interaction parameters, χ_{12}^∞ , were determined from the interactions of bisphenol-A polycarbonate (PC) with n-octane (O), n-nonane (N), n-decane (D), ethyl acetate (EA), isopropyl acetate (IPA), n-butyl acetate (nBA), isobutyl acetate (IBA), tert-butyl acetate (tBA) and isoamyl acetate (IAA) in the temperature range 200-240°C. The parameter χ_{12}^* and the parameter \bar{X}_{12} were also found for the polymer-solvent systems mentioned above. In addition, the solubility parameters of the polymer, δ , were estimated from the values of χ_{12}^∞ extrapolated to room temperature from the values at high temperatures.

Theoretical Background

The polymer-solvent interaction parameter, χ , gives quantitative information about the degree of interaction of a polymer-solvent system. If χ is smaller than 0.5, the solvent is good for the polymer, while, if it is higher than 0.5, it is a poor solvent. The χ parameter for a polymer-solvent system can be determined using various techniques. IGC is one of these well-known techniques. The specific retention volume, V_g° , is a quantity found experimentally from IGC measurements through the well-known equation¹⁻⁶.

$$V_g^\circ = [273.2(t_R - t_M)Q/wT]\{(3/2)[(p_i/p_o)^2 - 1]/[p_i/p_o]^3 - 1\} \quad (1)$$

where t_R and t_M are the measured retention times of the injected solvent and marker, such as air or methane; Q is the carrier-gas flow rate measured at room temperature; T is room temperature; w is the weight of the polymer in the column; and p_i and p_o are the inlet and outlet pressures of the carrier gas.

The interaction parameter, χ , is denoted by χ_{12}^∞ in the Flory-Huggins theory when the volume fraction of the polymer, ν_2 , approaches unity, as with IGC. The χ_{12}^∞ parameter is determined from the IGC measurements using the equation

$$\lim_{\nu_2 \rightarrow 1} \chi = \chi_{12}^\infty = Ln(273.2 R \nu_2 / V_g^\circ p_1^\circ V_1^\circ) - (1 - V_1^\circ / V_2^\circ) \nu_2 - p_1^\circ (B_{11} - V_1^\circ) / RT \quad (2)$$

where R is the universal gas constant; ν_2 is the specific volume of the polymer; p_1° , V_1° and B_{11} are the saturated vapour pressure, liquid molar volume and gaseous-state second virial coefficient of the solvents, respectively; V_2° is the molar volume of the polymer. The values p_1° were obtained from Reid *et al.*¹³ for O, N, D, EA, nBA, IBA; from Yaws¹⁴ for tBA; from Danner *et al.*¹⁵ for IAA; and from data of the Thermodynamical Research Center¹⁶ for IAA. The values of V_1° were obtained from Yaws¹⁴ for O, N, D; from Timmermans¹⁷ for EA; and from Reid *et al.*¹⁸ for IPA, nBA, IBA, tBA and IAA. The values of B_{11} were calculated from the related equations stated in the literature for n-alkanes and acetates¹⁹.

The interaction parameter χ , is denoted by χ_{12}^* in the equation-of-state theory. If the segment fraction of the polymer, ϕ^2 , goes to unity, as with IGC χ_{12}^* is defined as follows:

$$\lim_{\phi^2 \rightarrow 1} \chi^* = \chi_{12}^* = Ln(273.2 R \nu_2^* / V_g^\circ p_1^\circ V_1^*) - (1 - V_1^* / M_2 V_2^*) \phi^2 - p_1^\circ (B_{11} - V_1^\circ) / RT \quad (3)$$

V_1^* and V_2^* are characteristic molar volumes of the pure solvent and polymer; and M_2 is the molecular weight of the polymer.

The effective exchange-energy parameter, \bar{X}_{12} , is defined by the following equation in the theory⁹⁻¹¹:

$$RT\chi_{12}^* = p_1^*V_1^*[(3\tilde{T}_1\text{Ln}(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_1^{1/3} - 1) + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}] + \tilde{v}_2^{-1}(\bar{X}_{12}/p_1^*) \quad (4)$$

where p_1^* is characteristic pressure; \tilde{v}_1 and \tilde{T}_1 are the reduced volume and temperature of the solvent, \tilde{v}_2 is the reduced volume of the polymer.

If the Hildebrand-Scathard theory^{20,21} and Flory-Huggins theory are combined, one can write the following equation:

$$(\delta_1^2/RT - \chi_{12}^\infty/V_1^\circ) = 2\delta_2\delta_1/RT - \delta_2^2/RT \quad (5)$$

where δ_1 and δ_2 are the solubility parameters of the solvent and polymer and T is the column temperature. eq.(5) suggests tht the plot of $(\delta_1^2/RT - \chi_{12}^\infty/V_1^\circ)$ vs $1/T$ should be a straight line.

Experimental

PC is a General Electric Co. product sold commercially with the trademark Lexan. As it is a commercial product, it was purified using a suitable solvent-non solvent system before it was used, O, N, D , EA, IPA, nBA, IBA, tBA and IAA were of analytical reagent grade and were used without further purification. Studies were made in a Hewlett-Packard 5890 Model, Series II Gas Chromatograph with a thermal conductivity detector. The retention times were recorded with a Yew Model 3201 recorder. A stainless stell tubing column of 32 mm o.d. and 1m length was used. Chromosorb W-AW/DMCS were used as the support. The real percentage of the polymer in the column was determined by calcination of the support coated with polymer at 900°C. The column was mounted on the apparatus and conditioned with He gas at 260°C for one night. Since small amounts of PC can crystallize due to thermal and solvent effects, the column was reconditioned before each measurement.

Differential scanning calorimetry (DSC) was carried out with a Shimadzu, DSC 50 Model appartus with a thermal-analysis data station. A sample of 60 mg was heated to 240°C at a rate of 20°C/min.

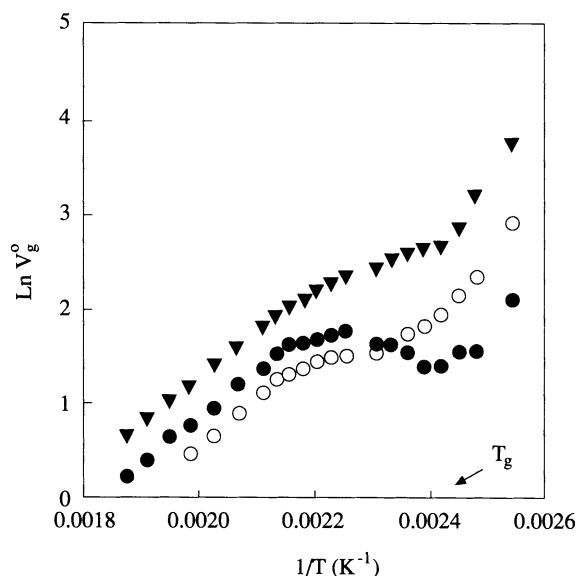


Figure 1. Variation of specific retention volume of the solvents in PC as a function of temperature. The filled circles relate to N, hollow circles to EA and the filled inverted triangles to nBA

Results and Discussion

The specific retention volumes of the solvents on the PC were determined from Eq.(1) using retention-time measurements. In Figure 1, the retention diagrams of N, EA and nBA on the PC are shown in a wide temperature range so that the region in which equilibrium sorption occurs can be observed. Figure 2 and Figure 3 exhibit the specific retention volumes, V_g° of O, D, IPA and IBA, tBA, IAA, respectively, on the PC at temperatures between 200 and 240°C in the equilibrium sorption region. In Table 1, the related numerical values are given. According to the retention diagram in Figure 1, T_g was found to be about 141°C the point from which the deviation from linearity was first seen. Furthermore, T_g was also determined to be around 140.6°C the first point in the jump of the heat capacity from Figure 4, which is a DSC thermogram of the PC. T_g of the PC was reported to be around 145°C in the literature²². However, in most other techniques, such as DSC, dynamic mechanical analysis (DMA) and dilatometry, T_g is usually taken as the point which is half the change in the property measured. Therefore, a difference of several degrees is expected in the T_g value determined with IGC and other techniques.

The χ_{12}^∞ parameters determined from Eq.(2) are given in Table 1. The results suggest that n-alkanes are poor solvents and their power to dissolve PC does not change considerably with temperature. The values of χ_{12}^∞ suggest that all the acetates given in Table 1 are good solvents of the polymer at the temperatures. This was expected in accordance with the similarity of the chemical structures of the solvents and the polymer. The χ_{12}^∞ parameter of the acetates increases with temperature, implying the existence of a lower critical solution temperature (LCST). In Table 2, the χ_{12}^∞ parameters found in this study compared with those found by the Belousov group²³ a unique study of IGC measurements of PC. It can be seen that the χ_{12}^∞ parameters found in this study were lower than those reported by Belousov *et al.*

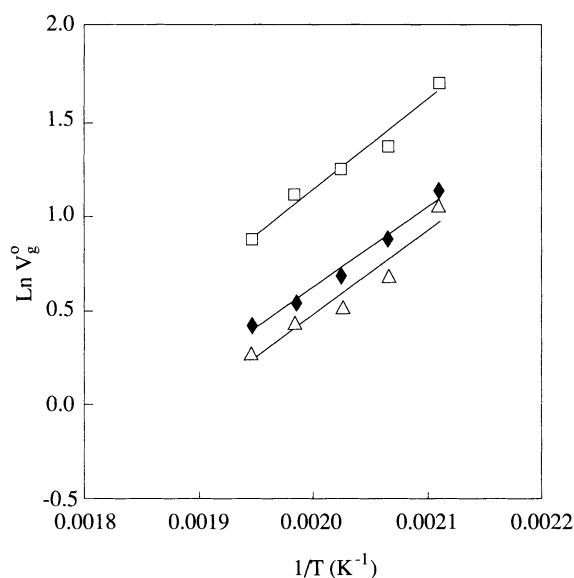


Figure 2. Variation of specific retention volume of the solvents in PC as a function of temperature. The hollow triangles belongs to O, the filled diamonds to IPA and hollow squares to D.

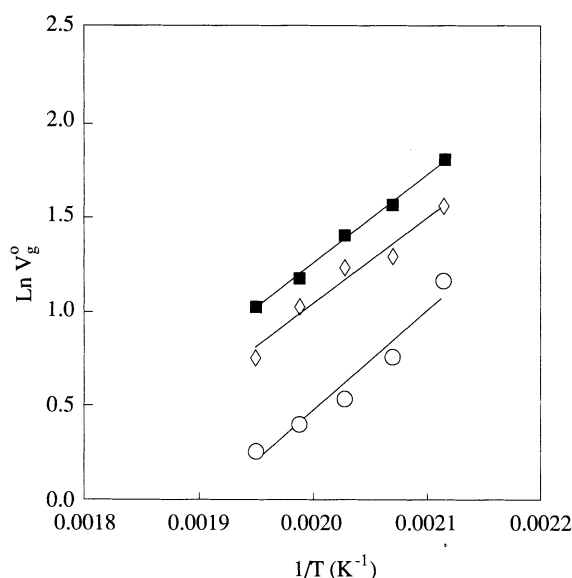


Figure 3. Variation of specific retention volume of the solvents in PC as a function of temperature. The dotted hollow circles relate to tBA, the hollow diamonds to IBA and filled squares to IAA.

The interaction parameters, χ_{12}^* , and effective exchange-energy parameters, \bar{X}_{12} , of the equation-of-state theory were obtained from Eq.(3) and Eq.(4), respectively. They are shown Table 1. The \bar{X}_{12} parameters of the PC-tBA pair have a negative value at 200°C but sharply increase with temperature and

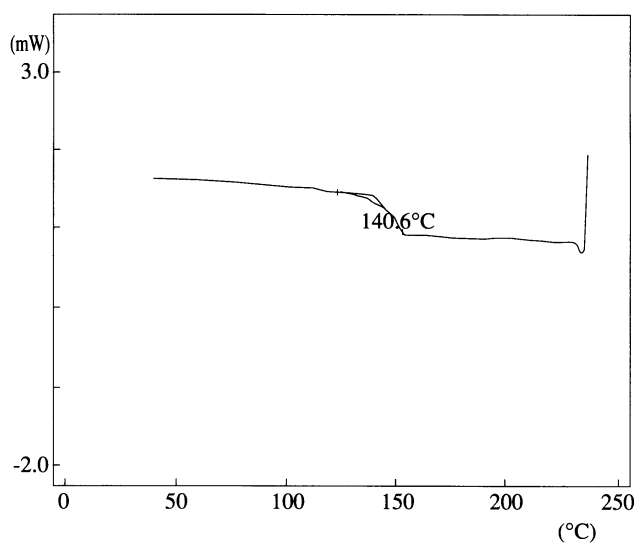
approach the values of butyl acetate-PC pairs at 240° C. The \bar{X}_{12} of EA and IPA increase very rapidly with temperature. These results suggest that an exothermic solution may exist between the acetates and the PC. The \bar{X}_{12} values of the n-alkanes are and, generally, increase slowly with temperature.

Table 1. Specific retention volume (V_g°), Flory-Huggins interaction parameters (χ_{12}^∞), total interaction parameters (χ_g^*) and effective exchange-energy parameters \bar{X}_{12} of O, N, D, EA, IPA, nBA, IBA, tBA and IAA with polycarbonate at various column temperatures

Solvents	Column temp. (°C)	V_g° cm ³ /g pol	χ_{12}^∞	χ_{12}^*	\bar{X}_{12} J/cm ³
O	200	2.80	0.99	1.26	27.4
	210	1.94	1.18	1.48	36.4
	220	1.65	1.17	1.48	38.0
	230	1.51	1.10	1.42	37.2
	240	1.29	1.10	1.45	39.6
N	200	3.91	1.09	1.33	27.4
	210	3.31	1.06	1.31	27.7
	220	2.59	1.12	1.39	31.0
	230	2.15	1.12	1.41	32.3
	240	1.93	1.07	1.36	32.3
D	200	5.42	1.19	1.40	27.9
	210	3.88	1.31	1.53	32.7
	220	3.45	1.22	1.46	30.9
	230	3.01	1.16	1.41	30.3
	240	2.36	1.22	1.49	33.7
EA	200	3.04	0.32	0.71	8.2
	210	2.45	0.37	0.79	16.3
	220	1.94	0.44	0.90	26.8
	230	1.61	0.46	0.96	35.9
IPA	200	3.04	0.33	0.69	6.6
	210	2.37	0.41	0.79	13.8
	220	1.94	0.44	0.86	19.5
	230	1.69	0.42	0.86	23.0
	240	1.50	0.37	0.85	27.0
nBA	200	6.08	0.36	0.63	4.8
	210	4.80	0.42	0.70	8.1
	220	4.10	0.40	0.70	8.4
	230	3.23	0.46	0.78	13.7
	240	2.79	0.45	0.79	15.0

Table 1. Continued

Solvents	Column temp. (°C)	V_g° cm ³ /g pol	χ_{12}^∞	χ_{12}^*	\bar{X}_{12} J/cm ³
IBA	200	4.77	0.35	0.65	2.9
	210	3.66	0.44	0.75	7.9
	220	3.45	0.32	0.66	4.7
	230	2.80	0.36	0.72	8.9
	240	2.14	0.48	0.85	16.4
tBA	200	3.25	0.02	0.36	-9.8
	210	2.15	0.21	0.57	1.1
	220	1.72	0.27	0.66	6.7
	230	1.50	0.28	0.69	10.4
	240	1.29	0.32	0.76	16.8
IAA	200	7.58	0.32	0.57	2.6
	210	5.83	0.38	0.64	6.1
	220	4.74	0.40	0.67	7.4
	230	4.30	0.31	0.59	5.0
	240	3.22	0.43	0.73	11.4

**Figure 4.** Differential scanning calorimetry (DSC) thermogram of PC

The χ_{12}^∞ parameters vary linearly with the reciprocal of the absolute temperature. The value of χ_{12}^∞ at room temperature was found by extrapolation of the χ_{12}^∞ parameters of each solvent from temperatures studied up to 25°C, using the plot of χ_{12}^∞ vs the reciprocal of absolute column temperature. By plotting the left-hand side of Eq.(5) against the solubility parameters of the solvents, δ_1 , it was found that δ_2 is 10.70 (cal/cm³)^{1/2} at 25°C from the slope and intercept (Figure 5). The solubility parameters of PC vary between 9.5 and 10.6 (cal/cm³)^{1/2} according to the literature²².

Table 2. Comparison of Flory-Huggins Interaction parameters (χ_{12}^{∞}) estimated in this study with values found in the literature

Solvents	This study		Literature*	
	Column temp.(°C)	χ_{12}^{∞}	Column temp.(°C)	χ_{12}^{∞}
O	200	0.98	198	1.53
	220	1.17	220	1.42
	240	1.10	238	1.36
N	200	1.09	198	1.26
	220	1.12	198	1.36
	240	1.07	238	1.26
D	200	1.19	198	1.33
	220	1.22	220	1.31
	240	1.22	238	1.26

*Ref. (23)

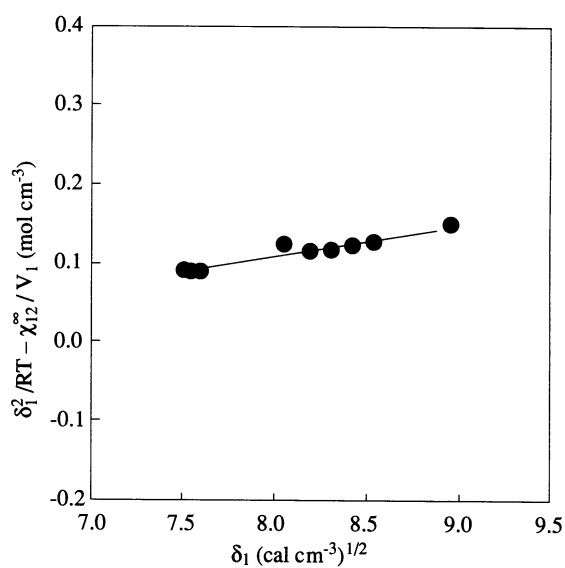


Figure 5. Variation of the left-hand side of Equation (5) with the solubility parameters of the solvents at 25° C

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