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THERMODYNAMIC PARAMETERS AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE) WITH SOME PROBES USING INVERSE GAS CHROMATOGRAPHY

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ABSTRACT

Activity coefficient Ω_1^r , Flory-Huggins interaction parameters χ_{12} and partial molar free energy of mixing at infinite dilution ΔG_1^∞ , for solutions of poly (methyl methacrylate) (PMMA) with alkanes, ketones, acetates, aromatic and alcohol at temperatures ranging from 433K to 473K have been obtained from inverse gas chromatography retention data. Five different families with different chemical nature and polarity were used to obtain some insights about PMMA-solvent interactions. The PMMA-solvent interaction parameters and the free energy of mixing were found at a series of temperature. The glass transition temperature and melting point of PMMA is found 110 °C and 170 °C, respectively. The thermodynamic sorption functions for the sorption process of the different chemical nature of probes into PMMA solution were obtained and discussed in terms of their interactions with PMMA. Furthermore, the contributions of CH₂, C=O, C=O-OR, aromatic and OH functional groups in the five series to the sorption process were also obtained. Acetates, ketones and methanol were found to be good solvents for PMMA, and alkanes and o-xylene were found to be non-solvents of PMMA.

INTRODUCTION

The i.g.c. method was developed by Smidsrod and Guillet¹ and was applied to many polymeric systems. Recently, the i.g.c. method has been used extensively by many workers and applied to amorphous and semicrystalline polymers and polymer blends¹⁻¹⁰. It has been shown that the i.g.c. method yields information on polymer-solvent and polymer-polymer systems such as solubility parameters, interaction parameters, diffusion coefficients, enthalpies of mixing, surface energies and areas, adsorption isotherms, glass transition temperatures, melting point temperatures and degree of crystallinity. Furthermore, the i.g.c. method is capable of obtaining physicochemical properties, the structure and chemical interactions of macromolecules.

Recently, Al-Saigh et al. demonstrated that the inverse gas chromatography (i.g.c.) method can yield, after careful analysis, a wealth of information on polymeric systems¹¹⁻¹⁵. The term "inverse" indicates that the polymeric stationary phase of the chromatographic column is of interest in contrast to conventional gas chromatography. The chromatographic column in this work contains the polymer under study. Because of the high viscosity of polymers, the existing methods for the characterization of polymers are best by a number of technical difficulties. The i.g.c. method is a fast method to obtain thermodynamic quantities on polymers and polymer blend systems.

In this paper, we have examined the application of the i.g.c. method to an semicrystalline poly (methyl methacrylate) (PMMA) in the temperature range of 323 K to 473 K.

Data reductions

The probe specific retention volumes, V_g° corrected to 0°C were calculated from the standard chromatographic relation:¹⁶

$$V_g^\circ = \Delta t F J 273.2 / w T_r \quad (1)$$

Where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe, t_p , and the methane t_g , F is the flow rate of the carrier gas measured at room temperature T_r , w is the mass of the polymeric stationary phase and J is a correction factor for gas compressibility, defined by the following relation:

$$J = 3/2 [(P_1/P_0)^2 - 1 / (P_1/P_0)^3 - 1] \tag{2}$$

Where P_1 and P_0 are the inlet and outlet pressures, respectively.

Flory-Huggins χ_{12} parameters characterizing the interactions of the vapour-phase probe with polymer are determined by the following equation:

$$\chi_{12} = \text{Ln} (273.2R v_2 / Vg^\circ V_1 P_1^\circ) - 1 - P_1^\circ / RT (B_{11} - V_1) \tag{3}$$

where R is the gas constant, v_2 and V_1 the molar volume (ml/g) of PMMA and the solutes, respectively, P_1° is the vapour pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. V_1 , P_1° and B_{11} were calculated at the column temperature. The vapour pressure P_1° was calculated from the Antoine equation¹⁷.

Second virial coefficients B_{11} values of hydrocarbons were computed using the following equation:¹⁸

$$B_{11} / V_c = 0.430 - 0.886 (T_c/T) - 0.694 (T_c/T)^2 - 0.0375 (n - 1) (T_c/T)^{4.5} \tag{4}$$

Where V_c and T_c are the critical molar volume and the critical temperature of the solute, respectively, and n is the number of carbon atoms in the solute. The molar volumes of the solutes V_1 , were calculated using equations given in the literature.¹⁷

The molar heat (enthalpy) of sorption of probe absorbed by the PMMA (ΔH_1^s) is given by the following equation:

$$\Delta H_1^s = -R \partial \ln V_g^\circ / \partial (1/T) \tag{5}$$

Where V_g° is the probe specific retention volumes and T is the column temperature.

The average partial molar heat of mixing at infinite dilution of the probe was calculated as following:

$$\Delta H_1^m = R \partial \ln (\Omega_1^m) / \partial (1/T) \tag{6}$$

Where (Ω_1^m) is the weight fraction activity coefficient of the solute probe at infinite dilution which is calculated according to the following equation:¹⁹

$$\Omega_1^m = 273.2 R / V_g^\circ P_1^\circ M_1 \exp [- P_1^\circ (B_{11} - V_1) / RT] \tag{7}$$

Where P_1° and V_1 were defined as in literature (17), (18), respectively, and M_1 is the molecular weight of the probe.

The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient of the solute as follows :

$$\Delta G_1^m = RT \ln \Omega_1^m \quad (8)$$

The partial molar free energy of sorption at infinite dilution is calculated from the following equation:

$$\Delta G_1^s = -RT \ln (M_1 V_g^\circ / 273.2 R) \quad (9)$$

By incorporating equations (5) and (9) we calculated the entropy of sorption of solutes as :

$$\Delta G_1^s = \Delta H_1^s - T \Delta S_1^s \quad (10)$$

EXPERIMENTAL

Materials

Eleven polar and non-polar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. n-Octane, n-nonane, n-decane, n-undecane and n-dodecane were supplied from Aldrich Chemical Co. and methanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate and o-xylene were supplied from Merck Chemical Co. as chromatographic grade. Poly(methyl methacrylate) was supplied by Aldrich Chemical Co. in powder form. Its average molecular weight was 120,000. Chromosorb W (45-60 mesh) was supplied from Sigma Chemical Co.

Instrumentation and procedure

A Shimadzu GC-14A model gas chromatography equipped with a dual flame ionization detectors, FID was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time was determined from the positions of

the peak maxima for methane and for the probe molecule at each temperature. Pressures at inlet and outlet of the column, read from a mercury manometer (mmHg) were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. A flow rate of about 20 ml/ min^{-1} was used throughout our experiment. The spiral glass tubing was washed with methylene chloride and was annealed prior to use. A column packing material was prepared by coating 45-60 mesh size Chromosorb w with PMMA. 0.53600 g was dissolved in 50 ml of benzene (Merck) and 6.15731 g of the solid supporting material was then added to this solution and stirred. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a Rotary evaporator. The prepared material was packed into a spiral glass tubing (3.2mm I.D. x 2.1m.). Column was conditioned at 80°C and fast carrier gas (N_2) flow rate for 24h prior to use. Probes were injected onto the column with $1\mu\text{l}$ Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume was selected $0.3\mu\text{l}$. The retention times of the probes were measured by using chromatopac CR6A, Shimadzu. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide.

RESULTS AND DISCUSSION

The specific retention volumes (V_g° of 11 probes) were obtained by using one loading PMMA and at a series of temperature. Different chemical nature and polarity (n-alkanes, n-acetates, n-ketones, aromatic and alcohol) were selected for this study. The V_g° values of these probes were calculated according to equation (1). The specific retention volume data are essential in the determination of physicochemical or thermodynamic properties of a polymer by i.g.c. In order to obtain these data, it is necessary to know the amount of the polymer that has been coated onto the support, the gas flow rate, column pressures and temperature. The amount of injected sample also affects the retention volume¹⁵. The specific retention volumes (V_g°) are given in Table 1. Data in Table 1. for each probe is demonstrated such as in Figure 1.

As can be seen from Figure 1, the specific retention volumes of probes on PMMA are temperature dependent and decrease with the increase of temperature. The glass transition temperature of PMMA is found 110°C , which is in agreement with the previous literature data.²⁰

TABLE 1

Changes in specific retention volumes as a function of temperature (cm^3/g polymer)

T(K)	Meth.	Acet.	Met.Act.	Et.Act.	E.M.K	o-xyl.	n-oct.	n-non.	n-dec.	n-undec	n-dodec.
323	18.86	6.85	5.48	6.88	6.90	29.82	6.81	21.21	42.15	82.97	115.20
333	17.22	5.18	5.03	5.21	6.05	15.79	5.96	14.88	31.23	58.70	89.52
343	16.74	5.06	5.01	5.20	5.68	13.84	5.30	11.62	24.57	44.46	70.08
353	15.13	5.00	4.95	5.17	5.58	10.84	4.78	8.94	17.85	34.04	65.47
363	11.25	4.99	4.94	5.16	5.52	9.40	4.65	8.67	13.79	22.78	42.49
373	8.84	4.92	4.88	5.06	5.41	7.43	4.41	7.72	11.19	17.56	29.18
383	6.82	4.88	4.86	4.96	5.37	7.07	4.34	7.26	7.36	11.59	15.51
393	6.84	5.78	5.70	5.80	6.34	11.46	4.57	7.32	9.94	13.52	18.74
403	6.52	6.27	5.96	6.30	7.21	15.00	5.65	7.57	9.96	11.99	14.13
413	6.21	6.33	6.46	6.83	7.62	17.46	8.01	8.73	13.03	16.74	14.88
423	5.99	6.31	6.22	6.62	7.31	16.25	7.51	8.40	10.65	15.17	13.89
433	5.78	5.64	5.96	6.35	6.98	15.10	7.09	7.46	9.86	9.80	13.04
443	5.22	5.48	5.59	5.90	6.41	13.52	6.64	6.43	7.62	9.20	11.92
453	5.45	5.50	5.55	5.62	5.89	11.96	6.13	6.57	8.79	11.24	10.48
463	5.21	5.26	5.30	5.38	5.63	9.12	5.28	5.85	7.14	10.10	9.44
473	4.98	5.06	5.07	5.10	5.37	8.46	5.05	5.55	6.19	7.05	8.25

Meth : Methanol, Acet: Acetone, Met Act: Methyl Acetate, Et.Act: Ethyl Acetate, E.M.K.: Ethyl methyl ketone, O-xyl: O-xylene, n-Oct: n-Octane, n-Non: n-Nonane, n-Dec: n-Decane, n-Undec: n-Undecane, n-dodec: n-Dodecane.

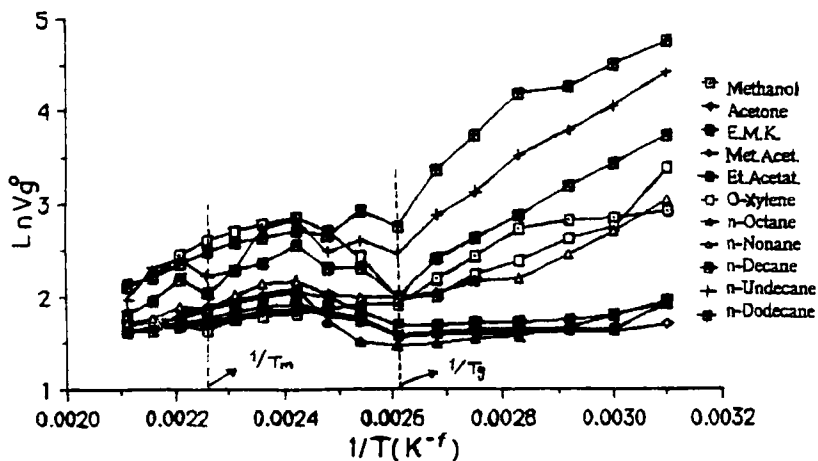


Figure 1. Changes in the specific retention volumes of the probes as a function of the inverse of emperature.

PMMA-solvent interaction parameters, such as Flory-Huggins interaction parameter χ_{12} at infinite dilution of the probe, were calculated according to equation (3) in between 433K to 473K Generally, χ_{12} showed considerable dependence with change in the number of carbons and temperature at alkanes, ketones and acetates (Table 2). A consequence from theoretical considerations is that χ_{12} has to be larger than 0.5 for the (polymer-nonsolvent) systems and smaller than 0.5 for the (polymer-solvent) systems.²¹ The values of χ_{12} found in this experiment are high for alkanes and o-xylene, as usual for polymer-nonsolvent systems but are low for acetates , ketones, benzene, THF and methanol as usual for polymer-solvent systems. Similar results were obtained for the weight fraction activity coefficients (Ω_{12}^w) and results listed in Table 2. We calculated the partial molar free energy of mixing (ΔG_1^m) and partial molar free energies of sorption (ΔG_1^s) of probes according to equation (8), (9) and results listed in Table 3.

According to data in Table 2 it shows that alkanes and o-xylene are nonsolvents but acetates, ketones, are good solvents and methanol is moderate solvent for PMMA for the following rules which have been formulated by Guillet.²²

TABLE 2

PMMA-solute interaction coefficients χ_{12} and weight fraction activity coefficient Ω_1^w of alkanes, acetates, ketones, o-xylene and methanol at 433-473K.

Probes/ T(K)	Ω_1^w					χ_{12}				
	433	443	453	463	473	433	443	453	463	473
Meth.	7.85	7.13	5.67	4.95	4.42	0.644	0.504	0.213	0.032	-0.144
Ace.	5.99	5.27	4.54	4.13	3.79	0.254	0.079	-0.119	-0.274	-0.413
Met Act.	5.76	5.24	4.70	4.23	3.89	0.261	0.123	-0.033	-0.197	-0.330
Et.Act.	6.83	6.22	5.77	5.18	4.69	0.463	0.327	0.211	0.051	-0.099
E.M.K.	4.58	4.22	3.68	3.38	3.10	-0.037	-0.164	-0.354	-0.496	-0.642
O-Xyl.	10.03	8.99	8.33	8.82	4.90	1.001	0.871	0.767	0.799	0.659
n-Oct.	12.98	11.30	10.12	9.82	8.93	1.170	0.999	0.849	0.777	0.610
n-Non.	19.91	18.41	14.54	13.33	11.59	1.668	1.563	1.297	1.176	1.000
n-Dec.	25.00	24.59	16.66	16.34	15.20	1.919	1.907	1.491	1.446	1.343
n-Undec.	40.08	32.20	20.30	17.61	19.89	2.447	2.212	1.733	1.569	1.666
n-Dodec.	49.32	39.81	33.78	28.57	25.43	2.676	2.450	2.272	2.088	1.954

$(\Omega_1^w) < 5$ good solvents

$5 < (\Omega_1^w) < 10$ moderate solvents

$(\Omega_1^w) > 10$ non-solvents

Partial molar heats of probes into PMMA solution were calculated by using equation (5). Table 4. shows the calculated sorption values for the temperature range of 393-443 K. Since the chemical nature and number of carbons of each probe are different, the values of sorption heat increases as more CH₂ groups are added to these three families of probes. The attraction forces between PMMA and acetates and ketones are actually a combination of two types; dispersive forces between the CH₂ groups of the acetates, ketones and the methyl group of PMMA, and the interaction of the C=O groups of the acetates and ketones with the C=O groups of PMMA via dipole-dipole interactions. We

TABLE 3

The partial molar free energies of mixing ΔG_1^m (kcal mol⁻¹) and partial molar free energies of sorption ΔG_1^s (kcal mol⁻¹) alkanes, acetates, ketones, o-xylene and methanol at a series temperature by using PMMA as stationary phase.

Probes/T(K)	ΔG_1^m					ΔG_1^s					
	433	443	453	463	473	393	403	413	423	433	443
Methanol	1.77	1.73	1.56	1.47	1.40	3.61	3.74	3.88	4.00	4.13	4.31
Acetone	1.54	1.46	1.36	1.31	1.25	3.28	3.30	3.37	3.46	3.64	3.74
Methyl Acet.	1.51	1.46	1.40	1.33	1.28	2.95	2.96	2.97	3.07	3.17	3.31
Ethyl Acet.	1.65	1.61	1.58	1.51	1.45	3.04	3.01	3.04	3.15	3.27	3.42
E.M.K.	1.31	1.27	1.17	1.12	1.06	3.10	3.14	3.16	3.26	3.38	3.51
O-xylene	1.98	1.93	1.91	2.00	1.94	2.27	2.12	2.05	2.16	2.27	2.42
n-Octane	2.21	2.13	2.08	2.10	2.06	2.94	2.84	2.62	2.74	2.86	2.98
n-Nonane	2.57	2.56	2.41	2.38	2.30	2.48	2.51	2.46	2.55	2.71	2.91
n-Decane	2.77	2.82	2.53	2.57	2.56	2.16	2.21	2.04	2.26	2.38	2.67
n-Undecane	3.18	3.06	2.71	2.64	2.61	1.84	1.99	1.76	1.89	2.31	2.42
n-Dodecane	3.35	3.24	3.17	3.08	3.04	1.52	1.79	1.79	1.89	1.99	2.11

TABLE 4

Partial molar heats of sorption ΔH_1^s (kcal mol⁻¹) of alkanes, acetates, ketones, o-xylene and methanol at temperature range 393-443K

Methanol	Acetone	Methyl Acetate	Ethyl Acetate	Ethyl Methyl Ketone	O-xylene	n-C8	n-C9	n-C10	n-C11	n-C12
-2.05	-2.03	-1.77	-1.79	-2.09	-3.14	-2.34	-3.84	-6.31	-8.32	-9.78

calculated the contribution of the C=O groups of the acetates, ketones and the -OH group of the methanol to the sorption functions, by subtracting the contribution of alkanes and o-xylene sorption functions from that of the acetates, ketones and methanol (Table 3-4). The dipole-dipole interactions in PMMA-acetates systems are weaker than ketones. On the other hand, the dipole-dipole interactions in PMMA-ketones and acetates systems are weaker than the hydrogen-bond interactions in PMMA-methanol system.

According to GC analysis the glass transition temperature, T_g and melting point, T_m of PMMA has been found 110 °C and 170 °C, respectively.

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