

Thermodynamical Study of Poly(*n*-hexyl methacrylate) with Some Solvents by Inverse Gas Chromatography

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Received 3 March 2010; accepted 26 January 2011

DOI 10.1002/app.34288

Published online 10 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The retention volume diagrams of ethyl acetate, isobutyl acetate, *tert*-butyl acetate, benzene, *n*-hexane, *n*-heptane, *n*-octane, acetone, chloroform, and acetonitrile on the poly(*n*-hexyl methacrylate) (PHMA) were plotted at temperature ranges from 333 to 393 K by inverse gas chromatography technique. Some polymer-solvent thermodynamic interaction parameters, such as weight fraction activity coefficient, Ω_1^∞ , Flory-Huggins, χ_{12}^∞ , hard-core, χ_{12}^* , and some exchange parameters such as effective energy, X_{eff} , enthalpy, X_{12} , and entropy, Q_{12} , were determined for studied solvents at infinite dilution of PHMA at tempera-

tures mentioned above. Then the partial molar heat, $\Delta\overline{H}_1^\infty$, and free energy, $\Delta\overline{G}_1^\infty$, of sorption as well as the partial molar heat, $\Delta\overline{H}_1^\infty$, and free energy, $\Delta\overline{G}_1^\infty$, of mixing at infinite dilution were determined. In addition, the solubility parameter of PHMA, δ_2 , was determined as $8.8 \text{ (cal/cm}^3)^{1/2}$ at room temperature by extrapolation of the values of solubility parameters from studied temperatures to 298 K. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1815–1822, 2011

Key words: poly (*n*-hexyl methacrylate); polymer-solvent interactions; inverse gas chromatography; solubility parameter

INTRODUCTION

Poly(alkyl methacrylate)s are most popular and well known polymers. Owing to their excellent properties such as high transparency, light weight, good mechanical and electrical properties, great resistance to high temperature, aging and chemicals, and easy formability, they are used in architecture, industry, motorization (as constructional materials and organic glasses in buildings, cars, ships, and aircrafts), in agriculture, medicine, pharmacy as well as in textile, paper, and paint industry.^{1,2} The ability of alkyl methacrylates to copolymerize with other monomers allows obtaining special copolymers and terpolymers. Since homopolymers, copolymers, and terpolymers of alkyl methacrylates are widely used to modify other commercial polymers, it is important to study their physicochemical properties to design suitable modifications.

Inverse gas chromatography (IGC) has been used for investigation of thermal behavior of polymers, interactions of various liquids and gases with polymeric materials and polymer-polymer miscibility. The method is simple, relatively rapid, and considerably accurate, with low cost, and at the same time the required equipment is available almost in all of

the laboratories. The physicochemical properties that can be obtained for polymeric systems include weight fraction activity coefficients of solvents at infinite dilution, interaction parameters of polymers with solvents and polymers, surface energies, molar heats of mixing and sorption, solubility parameter, glass transition and melting points, and crystallinity degree of polymers.^{3–5}

The exchange parameters of energy, X_{eff} , enthalpy, X_{12} , and entropy, Q_{12} , in the equation-of-state theory^{6,7} were designed to quantify the energy, enthalpy, and entropy required to exchange a polymer segment adjacent to another polymer segment with a solvent molecule. In theory, it was assumed that their magnitude depends on the chemical nature of the polymer and solvent and independent of the composition of the polymer-solvent mixture. Therefore, the X_{eff} , X_{12} , and Q_{12} values found at infinitely high polymer concentration from IGC measurements can be used to make simulations using equation of state theory in binary mixtures at lower polymer concentrations as in the case of osmotic pressure measurements.^{8–10}

It is expected that the exchange parameters of a polymer with solvents in a homologue series should be close to each other.^{11–14} It was the first time we have determined exchange enthalpy and entropy parameters of poly (dimethyl siloxane)¹⁵ and poly (methyl methacrylate)¹⁶ with some solvents directly from IGC measurements earlier. The parameters X_{12} and Q_{12} of these polymers with the studied solvents were comparable with those determined earlier by

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Contract grant sponsor: Scientific Research Projects Coordination Center, Yildiz Technical University.

other techniques at lower polymer concentrations.⁸⁻¹⁰ Therefore, it was assumed that IGC was a suitable technique to study the variation of exchange parameters of polymers with different types of solvents at several temperatures.

In this study, the retention volume diagrams of some solvents on the poly(*n*-hexyl methacrylate) (PHMA) were obtained by IGC; then, its thermodynamic interaction and exchange parameters with the studied solvents were determined. Although some studies were published on poly(alkyl methacrylates) by IGC, only one study is on PHMA in the literature in which the studied solvents are found to be poor.¹⁷ However, PHMA dissolves easily in almost all solvents in qualitative solubility tests in our laboratory. An adequate information is not found related to solubility of PHMA in the common polymer literature for instance in the *Polymer Handbook*.¹⁸ Therefore this study will supply detailed solubility data into the literature as well as some thermodynamic binary parameters.

Inverse gas chromatography theory

The standard application of a chromatographic column is to use it as a stationary phase to separate and thus analyze the composition of a mobile phase. In conventional IGC measurements, a known amount of a polymer is dissolved in a volatile solvent and coated on an inert support. Then, this polymer is characterized by monitoring the passage of volatile probe molecules of known properties as they are transported through the column by an inert gas.

The specific retention volume, V_g^0 , is determined experimentally from IGC measurements as follows^{14,19,20}:

$$V_g^0 = \frac{273.2Q(t_R - t_A)J}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate measured at room temperature, T_r ; t_R and t_A are retention times of the solvent and air, respectively; J is James-Martin factor used to correct the gas carrier compressibility, w is weight of polymer in the column.

The weight fraction activity coefficient of the solvents at infinite dilution, Ω_1^∞ , is defined by the following equation²¹:

$$\ln \Omega_1^\infty = \ln \left(\frac{273.2R}{V_g^0 p_1^0 M_1} \right) - p_1^0 (B_{11} - V_1^0) / RT \quad (2)$$

where R is the universal gas constant; p_1^0 , B_{11} , and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient, and molar volume of the solvent at temperature T , respectively.

The interaction parameters χ_{12}^∞ and χ_{12}^* given in the theories of Flory-Huggins and equation-of-state are defined in the following, eqs. (3) and (4), respectively:

$$\chi_{12}^\infty = \ln \left(\frac{273.2Rv_2}{p_1^0 V_g^0 V_1^0} \right) - 1 - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (3)$$

$$\chi_{12}^* = \ln \left(\frac{273.2Rv_2^*}{p_1^0 V_g^0 V_1^*} \right) - 1 - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (4)$$

where V_1^* is hard-core volume of the solvent at temperature T . v_2 and v_2^* are specific volume and specific hard-core volume of the polymer, respectively.

The effective exchange energy parameter, X_{eff} , in the equation-of-state theory is defined as follows:

$$RT\chi_{12}^* = p_1^* V_1^* \left\{ 3T_{1r} \ln \left[\frac{(v_{1r}^{1/3} - 1)}{(v_{2r}^{1/3} - 1)} \right] + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}} V_1^* v_{2r}^{-1} \right\} \quad (5)$$

where p_1^* is characteristic pressure, T_{1r} is reduced temperature of the solvent, v_{1r} and v_{2r} are reduced volumes of the solvent and polymer, respectively. Reduced quantities in above equation are defined as:

$$v_r = \frac{V}{V^*}, \quad T_r = \frac{T}{T^*}, \quad P_r = \frac{P}{P^*} \quad (6)$$

where V is actual molar volume of the liquid at actual T , temperature in K and, P , pressure. The characteristic molar volume, V^* , characteristic pressure, P^* , of the pure component can be calculated directly from the experimental values of molar volume, V , thermal expansion coefficient, α , and thermal pressure coefficient, γ , by means of the following equations:

$$v_r = \left[\frac{(\alpha T/3)}{1 + \alpha T} \right] + 1 \quad (7)$$

$$T_r = \frac{(v_r^{1/3} - 1)}{v_r^{4/3}} \quad (8)$$

$$\alpha = \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_{p=0} \quad (9)$$

$$P^* = \gamma T v_r^2 \quad (10)$$

$$\gamma = \left(\frac{\partial p}{\partial T} \right)_V \quad (11)$$

Required data to calculate α and γ values of pure components were taken from Refs. ²¹⁻²³.

The enthalpic interaction parameter χ_{12}^* can be obtained from the slope of the plot χ_{12}^* versus $1/T$ from IGC measurements according to its definition¹¹⁻¹⁴

$$\chi_{hi}^* = \frac{[\partial\chi_{12}^*/\partial(1/T)]}{T} \quad (12)$$

According to the equation-of-state theory, χ_{hi}^* is approximated under the gas chromatographic conditions:

$$\chi_{hi}^* = \left(\frac{p_1^*V_1^*}{RT}\right) \left[(v_{1r}^{-1} - v_{2r}^{-1}) + \frac{(\alpha_2 T/v_{2r})(T_{1r} - T_{2r})}{T_{2r}} + \frac{V_1^*(1 + \alpha_2 T)\chi_{12}}{v_{2r}RT} \right] \quad (11)$$

where X_{12} is exchange enthalpy parameter.

X_{eff} combines the exchange parameters of enthalpy, X_{12} , and entropy, Q_{12} , as follows^{6,7}:

$$X_{\text{eff}} = X_{12} - Tv_{2r}Q_{12} \quad (14)$$

The partial molar heat of sorption, $\Delta\bar{H}_1^s$, of the solvent sorbed by the polymer is given as:

$$\Delta\bar{H}_1^s = -R \left[\frac{\partial(\ln V_1^s)}{\partial(1/T)} \right] \quad (15)$$

where T , is column temperature in K.

The partial molar heat of mixing, $\Delta\bar{H}_1^\infty$, at infinite dilution of the solvent is given as:

$$\Delta\bar{H}_1^\infty = R \left[\frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)} \right] \quad (16)$$

Molar heat of vaporization, ΔH_v , of the solvent is related to $\Delta\bar{H}_1^s$ and $\Delta\bar{H}_1^\infty$ as follows:

$$\Delta H_v = \Delta\bar{H}_1^\infty - \Delta\bar{H}_1^s \quad (17)$$

The partial molar free energy, $\Delta\bar{G}_1^s$, and entropy, $\Delta\bar{S}_1^s$, of sorption at infinite dilution of solvent were determined with the following equations:

$$\Delta\bar{G}_1^s = -RT \ln \left(\frac{M_1 V_1^s}{273.2R} \right) \quad (18)$$

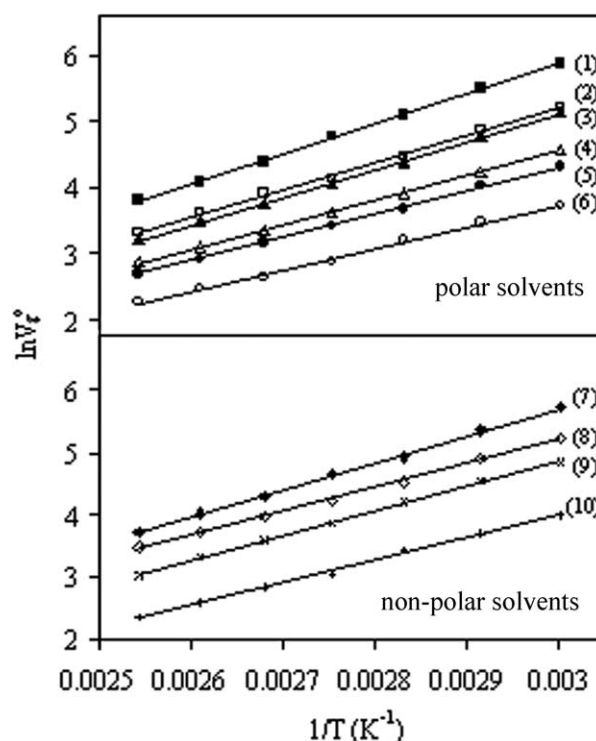


Figure 1 The retention volume diagrams of IBA (1), Ch (2), tBA (3), EA (4), AcN (5), and Ac (6) as polar solvents, and O (7), B (8), Hp (9), and Hx (10) as nonpolar solvents on PHMA.

$$\Delta\bar{G}_1^s = \Delta\bar{H}_1^s - T\Delta\bar{S}_1^s \quad (19)$$

The partial molar free energy, $\Delta\bar{G}_1^\infty$, of mixing at infinite dilution of the solvent was obtained according to the following equation:

$$\Delta\bar{G}_1^\infty = RT \ln \Omega_1^\infty \quad (20)$$

The solubility parameter of the polymer, δ_2 , is found by combining the theories of Flory-Huggins and Hildebrand-Scatchard^{4,5}:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1^0} \right) = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \left(\frac{\delta_2^2}{RT} \right) \quad (21)$$

where δ_1 is the solubility parameter of the solvent.

TABLE I
The Weight Fraction Activity Coefficient at Infinite Dilution of the Solvents Ω_1^∞ with PHMA

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	AcN
333	4.99	4.26	4.32	3.07	6.67	6.41	6.21	8.53	1.11	15.3
343	4.81	4.16	4.25	3.01	6.64	6.14	6.06	8.01	1.15	14.3
353	4.95	4.25	4.45	3.25	6.37	6.24	6.27	7.85	1.31	14.9
363	4.76	4.12	4.33	3.27	7.09	6.40	5.77	8.48	1.39	13.9
373	4.84	4.29	4.29	3.24	7.01	6.26	6.07	8.15	1.35	13.5
383	4.82	4.22	4.19	3.21	7.02	6.27	5.91	7.72	1.43	13.5
393	4.76	4.18	4.14	3.26	7.13	6.60	5.82	7.49	1.56	13.3

TABLE II
Flory-Huggins Polymer-Solvent Interaction Parameters χ_{12}^{∞} of PHMA with the Solvents (Ref. 17)

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	AcN
333	0.48	0.21	0.29	-0.05	0.45	0.43	0.43	0.84	-0.55	1.41
343	0.43	0.18	0.27	-0.07	0.44	0.38	0.39	0.77	-0.52	1.34
353	0.45	0.19	0.30	-0.06	0.38	0.38	0.42	0.73	-0.40	1.37
363	0.40	0.16	0.27	-0.08	0.48	0.40	0.33	0.80	-0.35	1.28
373	0.40	0.18	0.25	-0.02	0.45	0.37	0.37	0.76	-0.39	1.24
383	0.39	0.16	0.21	-0.05	0.44	0.36	0.36	0.67	-0.34	1.22
393	0.36	0.14	0.19	-0.04	0.44	0.40	0.31	0.63	-0.26	1.19
393*	0.90*				0.91*			1.2*	0.22*	1.47*

EXPERIMENTAL

PHMA was purchased from Sigma-Aldrich ($M_w = 400,000$ g/mol, $T_g = -5^{\circ}\text{C}$, $d = 1.007$ g/cm³). Studied solvents such as *n*-hexane (Hx), *n*-heptane (Hp), *n*-octane (O), chloroform (Ch), acetone (Ac), ethyl acetate (EA), isobutyl acetate (iBA), *tert*-butyl acetate (tBA), acetonitrile (AcN), and benzene (B) were used without further purification. The solvents and support materials being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG, Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc., respectively.

A Hewlett-Packard 6890 Model series II gas chromatograph with a thermal conductivity detector was used to measure the retention time of the solvents in this study. The column was stainless steel tubing with 3.2 mm od and 1 m in length. The polymer was coated on the support by slow evaporation of chloroform by stirring the Chromosorb W in the polymer solution. The amount of coated polymer on the support was determined as 8% by calcination. Trace amount of solvent was injected into the chromatograph. The column was conditioned at 393 K for 24 h under helium atmosphere.

RESULTS AND DISCUSSION

The specific retention volumes, V_g^o , of the studied solvents were obtained experimentally from IGC measurements using eq. (1) The maximum standard error in V_g^o was calculated as ± 1.6 by assuming that the errors resulted only from three sequential reten-

tion time measurements of each datum. Their variations with reciprocal of absolute column temperature were given in Figure 1 for polar and nonpolar solvents between 333 and 393 K.

The linearity of the plots indicates that the polymer is in thermodynamic equilibrium at the studied temperature range.

The weight fraction activity coefficients of the studied solvents at infinite dilution, Ω_1^{∞} , were determined from eq. (2) with a maximum ± 0.2 standard error calculated by the assumption that the only source of error are retention time measurements of each datum; then the results were given in Table I. The parameter Ω_1^{∞} derived from fundamental relations of physicochemistry does not include any uncertainty coming from theoretical assumptions.

According to Guillet⁴, the solvent is good if $\Omega_1^{\infty} < 5$ but it is poor if $\Omega_1^{\infty} > 10$. The values between 5 and 10 indicate moderately good solubility. The values of Ω_1^{∞} found in this study suggest that Ch, B, EA, IBA, tBA are good, whereas Hx, Hp, O, and Ac are moderately good but AcN is a poor solvent for PHMA. In the qualitative macroscopic solubility tests at room temperature in our laboratory, the polymer dissolved immediately in Ch and B without shaking although it dissolved with shaking in tBA, iBA, EA, O, Hp, Hx, and Ac for approximately 20–90 s. In the case of AcN, PHMA did not dissolve even at high temperatures. These qualitative tests are consistent with the results reported in this study. *n*-Alkanes are nonsolvent for poly (alkyl methacrylate)s with small pendant groups, like poly(methyl methacrylate). However, PHMA with a long aliphatic group and ester group dissolve easily in *n*-alkanes

TABLE III
The Hard-Core Polymer-Solvent Interaction Parameters χ_{12}^* of PHMA with the Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	AcN
333	0.63	0.34	0.43	0.09	0.63	0.57	0.55	1.03	-0.42	1.60
343	0.61	0.31	0.42	0.07	0.62	0.53	0.53	0.99	-0.37	1.52
353	0.64	0.34	0.47	0.14	0.57	0.55	0.56	0.93	-0.26	1.57
363	0.60	0.31	0.44	0.15	0.70	0.58	0.48	1.02	-0.19	1.49
373	0.61	0.35	0.43	0.14	0.70	0.56	0.52	0.98	-0.23	1.48
383	0.61	0.33	0.42	0.13	0.68	0.58	0.50	0.92	-0.17	1.44
393	0.60	0.32	0.40	0.14	0.69	0.61	0.48	0.89	-0.06	1.44

TABLE IV
The Effective Exchange Energy Parameters X_{eff} (J/cm³) of PHMA with the Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	AcN
333	5.5	-4.6	-1.0	-15.6	1.8	2.8	3.1	24.9	-37.9	74.2
343	0.6	-4.4	-3.5	-16.3	2.1	1.5	2.4	21.3	-38.9	74.2
353	1.7	-5.6	-2.2	-13.5	1.0	0.9	3.1	23.2	-31.5	77.3
363	-0.2	-7.0	-3.1	-11.9	2.7	1.9	0.8	26.3	-30.6	76.6
373	1.0	-5.8	-4.6	-13.8	4.6	0.7	2.2	24.9	-31.5	69.6
383	-0.4	-6.4	-6.3	-15.5	3.7	1.3	0.7	21.9	-29.7	79.2
393	-1.5	-7.8	-7.5	-13.2	4.4	2.2	0.5	20.8	-27.9	75.1

and esters since similar chemicals solve similar ones. Considerably low values in chloroform should arise from some specific attractive forces, stronger than van der Waals, between the polymer and solvent. In the case of Ch, the Ω_1^∞ values increase slightly with temperature, suggesting an exothermic solubility with lower critical solution temperature; however, in the case of Ac and AcN, the Ω_1^∞ values increase slightly with temperature, suggesting an endothermic solubility with upper critical solution temperature. In other solvents, it did not change considerably suggesting almost athermal solubility. It is known that exothermic solubility indicates a specific favorable interaction between the components of a mixture.

The solution properties of PHMA were studied by determination of its intrinsic viscosity in homologous series of normal *n*-alkanes from *n*-heptane to *n*-hexadecane by Aqeel et al.²⁴ In that study, the intrinsic viscosities of PHMA are close to each other in the heptane and octane with a slight increase with temperature. This suggests that normal *n*-alkanes are good solvents for PHMA.

The polymer-solvent interaction parameters, χ_{12}^∞ and χ_{12}^* , were determined from eqs. (3) and (4) and were given in Tables II and III, respectively. The standard errors in the values of χ_{12}^∞ and χ_{12}^* were less than ± 0.04 .

The values of χ_{12}^∞ confirm the evaluations on the values of Ω_1^∞ since $\chi_{12}^\infty < 0.5$ indicates good but $\chi_{12}^\infty > 0.5$ indicates poor solubility. In Table II, the values of χ_{12}^∞ found in this study are compared with data at 393 K reported by Walsh and McKeown.¹⁷ With the exclusion of chloroform, the literature values are considerably higher, i.e., suggest poor solubility. As

mentioned above, in the qualitative solubility tests in our laboratory, PHMA exhibits good solubility in the studied solvents except AcN. Therefore, the values given in this study are reasonable quantitative data. In the case of chloroform, considerably lower χ values can be attributed to the favorable specific interaction between the polymer and solvent. The exothermic solution of PHMA in chloroform, i.e., the lower critical solution temperature behavior also indicates a specific favorable interaction between the polymer and solvent. In the literature especially in the case of chlorinated hydrocarbons such as chloroform, negative χ -parameters are encountered.^{17,25,26} For example, in the study of oligomeric polyether-urethane system by IGC, χ_{12}^∞ parameters were reported as -0.2387 and -0.2769 for CH₂Cl₂ and CHCl₃, respectively, at 403 K.²⁵ And also, in the oligomer polyether-urethane, χ_{12}^∞ parameter was reported as -0.3215 for CHCl₃ at 363 K.²⁶ In the literature, for the poly(ethyl methacrylate), χ_{12}^∞ was given as -0.25 at 120°C.¹⁷

Walsh and McKeown¹⁷ stated that this type of interaction was known to exist in many similar systems and they interpreted these low χ parameters in terms of the hydrogen bonding of the proton of chloroform to the ester group. Actually, the low glass transition temperature of the polymer can contribute to the lower χ parameters of PHMA than other poly(alkyl methacrylate)s.

The effective exchange energy parameters, X_{eff} in the equation of state theory were obtained from eq. (5) and results were given in Table IV.

The magnitudes of X_{eff} are considerably high in the case of AcN and highly low in the case of Ch

TABLE V
The Exchange Enthalpy Parameter X_{12} (J/cm³) of PHMA with the Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	AcN
333	15.2	5.9	10.1	-7.9	-8.9	-2.2	13.1	50.1	-85.3	98.3
343	18.0	5.7	11.6	-7.6	-8.6	-1.6	13.6	51.7	-84.4	95.9
353	19.3	7.1	12.2	-6.8	-8.0	-0.8	14.0	50.0	-83.6	100.5
363	20.0	7.7	12.7	-7.0	-5.4	-0.3	14.4	53.9	-82.7	97.3
373	20.8	8.2	14.0	-5.8	-5.3	0.7	14.7	54.4	-82.1	108.2
383	23.2	8.6	15.3	-4.6	-4.4	1.7	15.6	56.3	-81.0	97.6
393	24.8	9.8	16.3	-5.0	-3.3	0.2	15.8	56.9	-79.1	106.5

TABLE VI
The Exchange Entropy Parameter $Q_{12} \cdot 10^2$ (J cm⁻³ K⁻¹) of PHMA with the Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	can
333	2.5	2.7	2.8	2.0	-2.7	-1.3	2.5	6.4	-12	6.1
343	4.3	2.5	3.7	2.1	-2.6	-0.8	2.8	7.5	-11	5.4
353	4.2	3.0	3.4	1.6	-2.2	-0.4	2.6	6.4	-12	5.6
363	4.6	3.4	3.6	1.1	-1.9	-0.5	3.2	6.4	-12	4.8
373	4.4	3.1	4.2	1.8	-2.2	0.0	2.8	6.6	-11	8.7
383	5.1	3.3	4.7	2.4	-1.8	0.1	3.2	7.5	-11	4.0
393	5.6	3.7	5.0	1.7	-1.6	-0.4	3.2	7.6	-11	6.6

than those of *n*-alkanes and aliphatic esters. Therefore, the higher values of X_{eff} indicate poor solubility or vice versa. Small positive and small negative values were obtained in the case of *n*-alkanes and aliphatic esters, respectively. The values of X_{eff} can be accepted as close to each other in the homologous series such as *n*-alkanes or butyl acetates. In addition, it can be accepted roughly that X_{eff} is independent on temperature.

The exchange enthalpy parameters X_{12} were obtained by means of the eq. (13) using χ_h^* found from slopes of the plots according to eq. (12) and results were given in Table V at studied column temperatures.

The magnitude of the parameters X_{12} changes with the quality of the solvent for PHMA. Its value is highly low for good solvents but high for poor solvents. In addition it increases with temperature. X_{12} increases from negative to fairly positive with increasing molecular weight of *n*-alkanes. This suggests that the value of X_{12} is proportional to the dispersive interaction between polymer segments and solvent molecules. It was stated that the value of X_{12} should be around 8 J/cm³ if the chemical structure of a polymer and a solvent were similar.²⁷ The values of IBA and tBA verify this statement. It can be stated from the values of X_{12} in Table V that favorable Lewis acid–base interaction, e.g., in Ch, creates considerably low values; however unfavorable Lewis base–base interaction, e.g., AcN, creates considerably high values. The results of the parameters Q_{12} obtained from eq. (14) are given in Table VI.

It is seen from the values in Table VI that the parameters of Q_{12} do not change considerably with the molecular weight of esters but increase slightly with molecular weight of *n*-alkanes. The lowest Q_{12} belongs to Ch whereas the highest Q_{12} s belong to AcN and Ac in this study. The temperature dependence of Q_{12} can be ignored for all of the studied solvents. It can be expected contrary to these results that the value of Q_{12} should be higher in better solvents and lower in poorer solvents by increasing with temperature because it is an entropy parameter. However, Q_{12} is not just an entropy parameter but it includes all of the uncertainties as well as it is small

which can be ignored. As a matter of fact, Flory was obliged to present Q_{12} as an empirical parameter of uncertain origin in his studies in which X_{12} and Q_{12} were used as adjustable parameters to reproduce the experimental results by theory. Q_{12} values estimated are -0.038 for polystyrene-methyl ethyl ketone⁸ and 0.023 for polystyrene-cyclohexane¹⁰ which exhibit poor solubility while -0.029 for polystyrene-ethyl benzene⁹ exhibits good solubility. This suggests that the sign of Q_{12} do not reflect a change in entropy.

The partial molar heats of sorption of the solvents, $\Delta\bar{H}_1^s$, on the PHMA were found from the slopes of the straight lines of $\ln V_g^0$ versus $1/T$ using eq. (15) at the temperature ranges from 333 to 393 K and given in Table VII.

It can be seen from Table VII that the sorption of the studied solvents are an exothermic phenomenon as expected. In the aliphatic ester and aliphatic hydrocarbon series, the sorption heats become slightly more exothermic as the number of CH₂ groups increases. This implies that dispersive forces take part in the sorption. The partial molar heat of mixing, $\Delta\bar{H}_1^\infty$, were calculated from the slopes of the plots of $\ln \Omega_1^\infty$ versus $1/T$ in the temperature ranges from 333 to 393 K using eq. (16) Results for all of the studied solvents were given in Table VII. The partial

TABLE VII
The Partial Molar Heat of Sorption, $\Delta\bar{H}_1^s$ (kJ/mol), the Partial Molar Heat of Mixing, $\Delta\bar{H}_1^\infty$ (kJ/mol), Molar Heat of Vaporization, ΔH_V (kJ/mol) Obtained by eq. (18) in the Temperature Ranges from 333 to 393 K and Molar Heat of Vaporization, ΔH_V [28] (kJ/mol), the Boiling Temperatures of Solvents, T_b (K)

Solvents	$-\Delta H_{1,\text{sorp}}$	$\Delta\bar{H}_1^\infty$	ΔH_V	ΔH_V [19]	T_b
EA	31	0.6	31.6	32.2	350.3
tBA	34	0.7	34.7	33.4	370.2
IBA	38	0.1	38.1	35.8	390.2
B	32	-0.6	31.4	30.7	353.3
Hx	30	-1.6	28.4	28.8	341.9
Hp	33	-0.5	32.5	31.7	371.6
O	36	1.1	34.9	34.4	398.8
Ac	27	1.6	25.4	29.1	329.4
Ch	34	-5.9	28.1	29.7	334.3
AcN	29	2.5	31.5	31.4	354.2

TABLE VIII
The Molar Free Energy of Sorption $\Delta\bar{G}_1^s$ (kJ mol⁻¹) of PHMA with Studied Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	can
333	7.6	12.0	9.9	9.1	6.0	8.8	11.6	4.2	10.3	4.8
343	6.9	11.3	9.2	8.5	5.3	8.1	10.8	3.6	9.6	4.2
353	6.1	10.4	8.3	7.6	4.7	7.4	9.9	2.9	8.7	3.2
363	5.5	9.7	7.6	6.9	3.7	6.5	9.4	1.9	7.9	2.6
373	4.7	8.8	6.9	6.3	3.1	5.9	8.5	1.3	7.5	1.9
383	4.1	8.1	6.2	5.7	2.4	5.2	7.8	0.8	6.7	1.1
393	3.4	7.4	5.6	5.0	1.7	4.3	7.1	0.2	5.9	0.4

molar heats of mixing, $\Delta\bar{H}_1^\infty$, have positive sign for EA, IBA, tBA, O, Ac, and AcN, which reflect endothermic mixing; however, the signs were negative for B, Hx, Hp, and Ch that reflect exothermic mixing. In comparison with the value in Table V, it can be seen that the negative sign of the parameter X_{12} refers to exothermic solubility behavior. $\Delta\bar{H}_1^\infty$ has highest negative value for Ch but highest positive for AcN, suggesting that PHMA is a Lewis base. The values of ΔH_v obtained from eq. (17) were also compared to the values of ΔH_v calculated according to an empirical relationship given in the reference.²⁸ The maximum standard error in the heat of vaporization across the different solvents was found as ± 0.2 . It is shown that the agreement is good between the values of ΔH_v found in this study and calculated from the relation given in literature.

The molar free energies of sorption, $\Delta\bar{G}_1^s$, obtained from eq. (18) are given in Table VIII.

It can be seen from the negative sign that the sorption of the solvents on PHMA is spontaneous. The values higher than -40 kJ mol⁻¹ suggest that the sorption is physical. It can be stated that the dispersive forces are dominant in sorption since the negativity of $\Delta\bar{G}_1^s$ increase with molecular weight in homologous series. Again decreasing negativity with temperature exhibits that the sorption becomes more willing as decreasing temperature as expected. From the values in Table VIII, it is not seen as a distinguishing difference related to specific favorable interaction of PHMA with Ch and unfavorable interaction with AcN.

The partial molar free energies of mixing, $\Delta\bar{G}_1^\infty$, at infinite dilution of solvents were calculated using eq. (20) and are given in Table IX. It was expected that the signs of $\Delta\bar{G}_1^\infty$ should be negative since PHMA dissolves easily in them except AcN. However, $\Delta\bar{G}_1^\infty$ should be lower than 4.5 for good solvents and should be higher than 6.4 at 333 K; in addition its value increases with temperature according to eq. (20). Therefore it can be stated that the sign of $\Delta\bar{G}_1^\infty$ does not reflect the spontaneous solubility and their change with temperature also do not reflect the change of solubility. However their magnitudes reflect the quality of the solvent, e.g., the smallest and highest values belong to Ch and AcN, respectively. However, the negative sign of the Gibbs free energy must indicate the spontaneous phenomenon. It can be concluded that the values of $\Delta\bar{G}_1^\infty$ is not a good criterion to catch on spontaneous solubility.

The solubility parameter of PHMA, δ_2 , was determined from the slope and intercept of the straight lines plotted according to eq. (21). The plot at 393 K was given as an example in Figure 2.

The magnitude of δ_2 was found as averaging of the values obtained from the slope and intercept at studied temperatures. In Figure 3, δ_2 at room temperature was approximately estimated as 8.8 (cal/cm³)^{1/2} with a maximum ± 0.2 standard error by extrapolating the average values of the δ_2 obtained at temperatures studied up to 298 K.

The solubility parameter obtained in this study agrees very well with the values of 8.6 (cal/cm³)^{1/2} given in Ref. 17 and 8.5 (cal/cm³)^{1/2} calculated by group contribution method.²⁹

TABLE IX
The Partial Molar Free Energies of Mixing $\Delta\bar{G}_1^\infty$ (kJ mol⁻¹) of PHMA with Studied Solvents

T(K)	EA	IBA	tBA	B	Hx	Hp	O	Ac	Ch	can
333	4.5	4.0	4.1	3.1	5.3	5.2	5.1	6.0	0.3	7.6
343	4.5	4.1	4.1	3.2	5.4	5.2	5.2	6.0	0.4	7.6
353	4.7	4.3	4.4	3.5	5.5	5.4	5.4	6.1	0.8	8.0
363	4.7	4.3	4.4	3.6	5.9	5.6	5.3	6.5	1.0	8.0
373	4.9	4.5	4.5	3.7	6.1	5.7	5.6	6.5	0.9	8.1
383	5.0	4.6	4.6	3.7	6.2	5.9	5.7	6.5	1.1	8.3
393	5.1	4.7	4.7	3.9	6.4	6.2	5.8	6.6	1.5	8.5

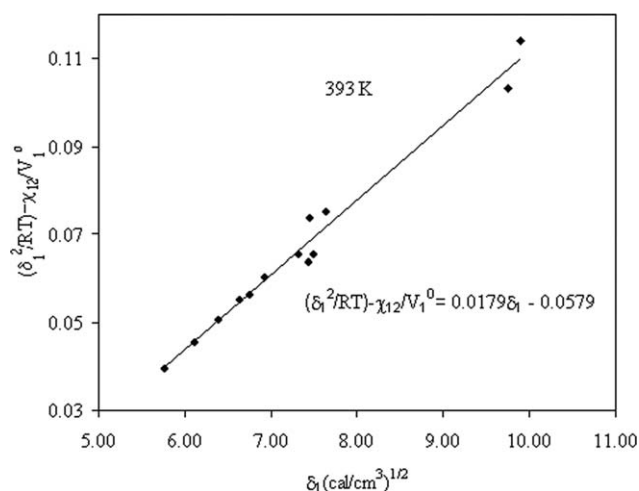


Figure 2 Estimation of solubility parameter δ_2 of PHMA from solubility parameter of the solvents (δ_1) and Flory-Huggins interaction parameters. χ_{12}^∞ at 393 K [see eq. (21)].

CONCLUSIONS

IGC technique was applied on determination of some thermodynamic solubility parameters of PHMA. The results are used to evaluate its thermodynamic interactions with some solvents. The results suggest that Ch is very good, B, IBA, tBA, and EA are good, Hx, Hp, O, and Ac are moderately good, and AcN is a poor solvent for the polymer. The study indicates that PHMA behaves as a Lewis base against the studied solvents. This study verifies the equation-of-state theory since the parameter X_{12} is close to 8 J cm^{-3} for solvents in which the chemical structure is similar, and temperature dependence is negligible. It seems that a more pronounced differ-

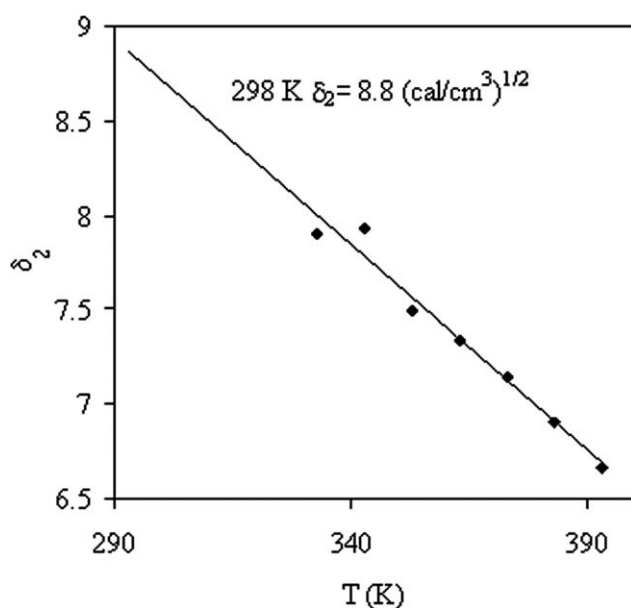


Figure 3 Extrapolation of the solubility parameter δ_2 of PHMA from studied temperatures to 298 K.

ence appears in the values of exchange parameters of equation-of-state theory, e.g., X_{eff} and X_{12} than the values of molar free energy terms, e.g., ΔG_1^s and ΔG_1^∞ to see favorable and unfavorable interactions between polymer and solvents. The solubility parameter of PHMA was determined to be $8.8 (\text{cal/cm}^3)^{1/2}$ at 298 K.

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