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Thermodynamic Properties of Poly(2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) and Poly[2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate)

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Thermodynamic Properties of Poly(2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) and Poly[2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate)

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In this study, some thermodynamic properties of poly(2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) P (TMCBHEMA) and poly[2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate) P (MCBOEMA) such as the adsorption enthalpy, ΔH_a, molar evaporation enthalpy, ΔH_v, the sorption enthalpy, ΔH_1^s, sorption free energy, ΔG_1^s, sorption entropy, ΔS_1^s, the partial molar free energy, ΔG_1^∞, the partial molar heat of mixing, $\Delta \bar{H}_1^\infty$, at infinite dilution were determined for the interactions of PTMCBHEMA and PMCBOEMA with selected alcohols and alkanes by the inverse gas chromatography (IGC) method in the temperature range of 333–463 K. According to the specific retention volumes, V_g^0, the weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞, and Flory-Huggins interaction parameters, χ_{12}^∞ between PTMCBHEMA and PMCBOEMA-solvents were determined in 433–463K and 443–463K, respectively. According to Ω_1^∞ and χ_{12}^∞, selected alcohols and alkanes were found to be non-solvent for PTMCBHEMA at 433–463 K, but the same solvents (except for decane) were found to be solvent for PMCBOEMA at 443–463K. The glass transition temperature, T_g, of the PTMCBHEMA and PMCBOEMA found to be 380 and 383; 390 K and 388 K, by IGC and DSC techniques, respectively.

Keywords: poly (2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) and poly [2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate); inverse gas chromatography; polymer-solvent interactions

1 Introduction

Polymer-solute interactions of methacrylate polymers had been investigated by the IGC technique. The method had been developed by Smidsrød and Guillet and applied to many polymer-solvent and polymer-non-solvent systems. The physical-chemical properties which can be obtained for polymeric systems include the interaction parameters of polymer-solvent, polymer-non-solvent and polymer-polymer systems, solubility parameters, and weight fraction coefficients, molar heat and free energy of mixing and sorption, crystallinity degree of semi-crystalline polymers, glass transition and melting points of polymers, decomposition temperatures of polymers, and surface energy of polymers. The IGC method has been used extensively to study the structure of polymers, interactions of various liquids and gases with polymeric materials, and to investigate polymer-polymer miscibility. IGC is an extension of conventional gas chromatography in which a solid polymeric material to be investigated is immobilized within a column. Liquids of known properties are then injected into the column containing the sample. The retention times of these trace amount liquids are used in determination of their interactions with the solid in the column. Because of these properties, the method is simple, fast, and economical, and provides valuable thermodynamic information for characterization of polymeric materials (1–8).

The objective of this work was to conduct a detailed examination of the thermodynamic interactions of poly(2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) (PTMCBHEMA) and poly[2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate) (PMCBOEMA) with alcohols (polar) and alkanes (nonpolar) solvents over a temperature range from 60 to 190°C by IGC. We determined both dispersive forces between the CH_2 groups of the alcohols with substitute groups of ethyl methacrylate polymers and dipole-dipole interaction of the OH group of the alcohols with the C=O group of polymers. We also determined the solubility parameter, δ_2, of PTMCBHEMA and PMCBOEMA by using IGC techniques.

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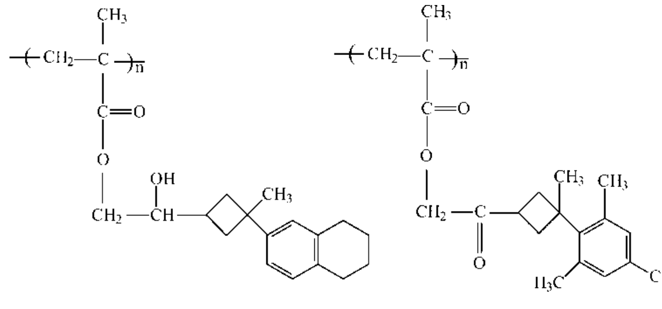
2 Experimental

2.1 *Materials*

Poly(2-[3-(6-tetralino)-3-methyl-1-cyclobutyl]-2-hydroxy ethyl methacrylate) and poly[2-(3-mesityl-3-methyl-1-cyclobutyl)-2-oxoethyl methacrylate) were been synthesized in dioxane solution using benzoyl peroxide (BPO) as initiator at 60°C by İ. Erol *et al.*, and the polymers had been characterized by ^{1}H-^{13}C-NMR, FT-IR, TGA, size exclusion chromatography analysis (SEC) techniques (9). Nine polar and nonpolar probes were used in this study. They were selected to provide several groups of a chemically different nature and polarity. Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, hexane, heptane, octane, decane were supplied from Merck Chemical Co. as chromatographic grade. Chromosorb W (80–100 mesh) was supplied from the Sigma Chemical Co.



PTMCBHEMA **PMCBOEMA**

2.2 *IGC Methodology*

IGC was used previously by many researchers to study the thermodynamic properties of polymers (4, 5, 10, 11). Only peak retention time data are needed and is generally expressed as retention volume (V_g^0). The specific retention volume at 0°C was determined experimentally using the following relationship (12):

$$V_g^0 = \Delta t \frac{F(273.15)}{wT} J \tag{1}$$

$$J = \frac{3}{2}\left[\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right] \tag{2}$$

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 the flow rate of the carrier gas at 273.15 K and 1 atm, T is column temperature (K), *w* is the mass of the polymeric stationary phase and J is the James-Martin correction factor for gas compressibility and P_i and P_o are the inlet and outlet pressures, respectively.

The heat of vaporization of the pure solvent are calculated as follows (13):

$$\Delta H_v = -R\partial \,\mathrm{Ln}\ P_1^0/\partial(1/T) \tag{3}$$

The sorption enthalpy (ΔH_a) of the probes adsorbed by the PTMCBHEMA and PMCBOEMA are given by the following equation:

$$\partial\,\mathrm{LnVg}^{\circ}/\partial(1/T) = -\Delta H_a/R \tag{4}$$

The values of molar heat (enthalpy), ΔH_1^s, the molar free energy, ΔG_1^s, the entropy, ΔS_1^s, of sorption of the probe absorbed by the PTMCBHEMA and PMCBOEMA and the weight fraction activity coefficient, Ω_1^{∞}, the partial molar free energy, ΔG_1^{∞} and the average partial molar enthalpy, ΔH_1^{∞} at infinite dilution of the organic solvents were calculated as in the literature (14–16). The molar heat (enthalpy), ΔH_1^s, molar free energy, ΔG_1^s, and the molar entropy, ΔS_1^s, of sorption of the probe absorbed by the PTMCBHEMA and PMCBOEMA are given by the following equations:

$$\Delta H_1^s = -R\frac{\delta(\ln V_g^0)}{\delta(1/T)} \tag{5}$$

$$\Delta G_1^s = -RT\ln\left(\frac{M_1 V_g^0}{273.15R}\right) \tag{6}$$

By incorporating Equations (5) and (6), we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \tag{7}$$

The weight fraction activity coefficient, Ω_1^{∞}, partial molar free energy, ΔG_1^{∞}, and the average partial molar enthalpy, ΔH_1^{∞} at infinite dilution of the organic solvents were calculated according to the following Equations (3):

$$\Omega_1^{\infty} = \frac{273.15R}{V_g^0 P_1^0 M_1}\exp\left(-\frac{P_1^0(B_{11} - V_1)}{RT}\right) \tag{8}$$

$$\Delta G_1^{\infty} = RT\ln\Omega_1^{\infty} \tag{9}$$

$$\Delta\bar{H}_1^{\infty} = R\frac{\delta(\ln\Omega_1^{\infty})}{\delta(1/T)} \tag{10}$$

Where B_{11} is the second virial coefficient of the organic solute in the gaseous state and P_1° is the vapor pressure of the probes at temperature, T(K) and M_1 is the molecular weight of the probe. The molar volume of the solute, V_1 was calculated using the following relation (17).

$$V_1 = V_c/\rho_r \tag{11}$$

Where V_c is the critical molar volume and ρ_r is the reduced density of the solute given as:

$$\rho_r = 1.20 + (5.565 - 11.03\,z_c)(1 - T/T_c)^{(0.8^{z}c+0.31)} \tag{12}$$

Where z_c is the critical compressibility factor and T_c is the critical temperature and these values were taken from literature (18).

The PTMCBHEMA and PMCBOEMA–solute interaction parameters, χ_{12}^{∞} at infinite dilution of different solutes used in this study are defined by the following equation:

$$\chi_{12}^{\infty} = \ln(273.2\,R\,\nu_2/Vg^{\circ}\,V_1\,P_1^{\circ}) - 1 - P_1^{\circ}/RT(B_{11} - V_1) \tag{13}$$

Where R is the gas constant, ν_2 is the specific volume of the polymer. The solubility parameter of the probe is calculated from the relation (19–21).

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \tag{14}$$

The vapor pressure P_1^0 was calculated from the Antonie equation as follows:

$$\log P_1^0 = A - B/(t + C) \tag{15}$$

Where t is the temperature (in °C) and A, B and C are constants (18). The second virial coefficients B_{11} were computed using the following Equation (15):

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375\,(n-1)(T_c/T)^{4.5} \tag{16}$$

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 as in the literature (19).

The molar evaporation enthalpy (ΔH_v) of the probes adsorbed by the PTMCBHEMA and PMCBOEMA are given by the following Equation (17):

$$\Delta H_v = \Delta H_1^{\infty} - \Delta H_1{}^{s} \tag{17}$$

The solubility parameter of the polymer, δ_2 can be calculated by using the following relation:

$$[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1] = (2\delta_2/RT)\delta_1 - \delta_2{}^2/RT \tag{18}$$

If the left hand side of this equation is plotted against δ_1, a straight line having a slope of $2\delta_2/RT$ and an intercept of $(-\delta_2^2/RT)$ is obtained. The solubility parameter of polymer, δ_2 can be determined from both the slope and intercept of the straight line (14).

2.3 Instrumentation and Procedure

A Packard 430 model gas chromatography equipped with a dual flame ionization detector was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a non-interacting marker to correct dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and the probe molecule at each temperature. Pressures at inlet of the column, read from a mercury manometer 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 15 $cm^3\ min^{-1}$ was used throughout our experiment. The copper (3.2 mm I.D. × 1 m.) tubing was washed with acetone and annealed prior to use. A column packing material was prepared by coating 80-100 mesh size Chromosorb W treated with PTMCBHEMA and PMCBOEMA. 0.300 g of PTMCBHEMA and PMCBOEMA were dissolved in 25 ml of 1, 4-dioxane, and 3.000 g of the solid supporting materials were 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 spiral glass tubing. The column was conditioned at temperature above the glass transition temperature and fast carrier gas (N_2) flow rate for 24 h prior to use. The probes were injected onto the column with 1 μL Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume was selected at 0.2 μL. The retention times of the probes were measured by using a Shimadzu CR2A Chromatopac model integrator. Methane was synthesized in the

Table 1. The variation of specific retention volumes, V_g^0 (cm^3/g) of selected some alcohols and alkanes with temperature using PTMCBHEMA as stationary phase

T(K)/Probe	Hexane	Heptane	Octane	Decane	MeOH	EtOH	1-Propanol	1-Butanol	1-Pentanol
333	5.398	5.604	6.222	11.167	7.211	6.099	6.428	7.170	8.695
343	4.992	5.224	5.727	8.474	6.462	5.998	6.075	6.656	8.242
353	4.665	4.812	5.179	7.126	6.097	5.950	5.693	6.134	7.236
363	4.364	4.468	4.745	5.958	5.785	5.300	5.126	5.577	6.235
373	4.080	4.178	4.341	5.157	5.059	4.896	4.798	5.157	5.549
383	3.150	3.397	3.490	3.768	3.737	3.706	3.675	3.861	4.200
393	3.583	3.670	3.729	4.165	4.107	4.136	4.107	4.340	4.777
403	3.333	3.416	3.471	3.830	3.664	3.692	3.802	4.022	4.435
413	3.151	3.203	3.281	3.515	3.359	3.437	3.541	3.750	4.140
423	2.958	2.983	3.082	3.303	3.082	3.131	3.254	3.476	3.870
433	2.762	2.786	2.903	3.113	2.856	2.926	3.020	3.230	3.558
443	2.543	2.565	2.631	2.830	2.587	2.631	2.720	2.875	3.140
453	2.371	2.392	2.413	2.602	2.476	2.539	2.560	2.686	2.854
463	2.314	2.334	2.355	2.516	2.535	2.435	2.475	2.596	2.737

Table 2. The variation of specific retention volumes, V_g^0 (cm^3/g) of selected some alcohols and alkanes with temperature using PMCBOEMA as stationary phase

T(K)/Probe	Hexane	Heptane	Octane	Decane	MeOH	EtOH	1-Propanol	1-Butanol	1-Pentanol
333	13.837	14.495	16.209	27.893	16.911	16.209	15.857	17.087	21.304
343	12.894	13.679	14.464	21.076	15.539	14.836	14.547	15.497	17.109
353	12.191	12.463	13.281	17.098	13.982	13.710	13.710	14.333	15.462
363	11.518	11.592	12.254	14.977	12.843	12.806	12.990	13.027	14.462
373	11.028	11.132	11.515	13.602	11.932	12.002	12.245	12.384	13.219
383	10.494	10.461	10.562	12.681	10.999	11.066	11.201	11.571	12.479
393	9.120	9.598	9.725	11.033	9.725	9.757	9.821	10.523	11.734
403	9.634	9.816	10.028	11.694	10.028	10.209	10.331	11.421	12.512
413	9.358	9.473	9.704	11.201	9.646	9.790	9.991	10.999	12.237
423	9.056	9.138	9.356	10.830	9.302	9.384	9.575	10.311	11.457
433	8.697	8.957	9.060	10.488	8.905	9.034	9.320	9.865	10.982
443	8.616	8.814	8.962	10.077	8.467	8.740	8.962	9.532	10.398
453	8.524	8.547	8.784	9.681	8.547	8.595	8.784	9.161	9.917
463	8.145	8.235	8.506	9.047	8.190	8.235	8.467	8.822	9.476

laboratory by the reaction of sodium acetate with sodium hydroxide (22).

3 Results and Discussion

3.1 Thermodynamic Properties

Thermodynamic properties of nine solvents in PTMCBHEMA and PMCBOEMA were determined by inverse gas chromatography from 333 to 463 K. The values of specific retention volumes, V_g^0 of these PTMCBHEMA and PMCBOEMA-probes were calculated according to Equation (1), and are given in Tables 1 and 2, respectively. Generally, V_g^0 of the probes decreased with increasing

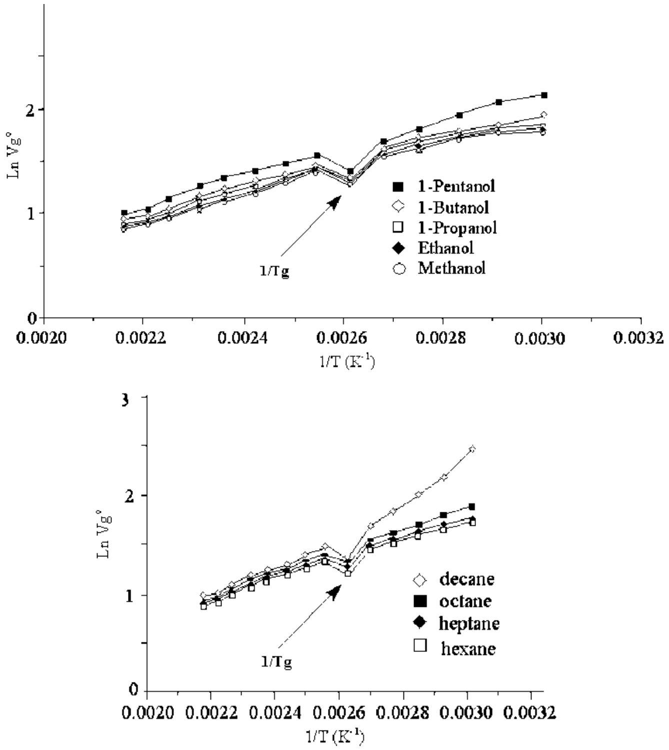


Fig. 1. Changes in the specific retention volumes of the PTMCBHEMA-probes as a function of the inverse of temperature.

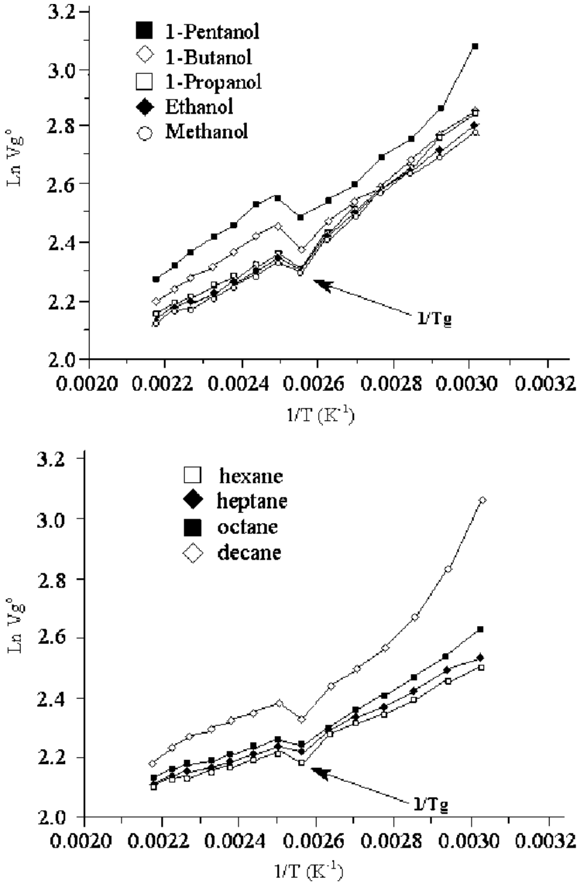


Fig. 2. Changes in the specific retention volumes of the PMCBOEMA-probes as a function of the inverse of temperature.

Table 3. The partial molar sorption free energies, ΔG_1^s (cal/mol), the partial molar sorption enthalpy, ΔH_1^s (cal/mol), adsorption enthalpy ΔH_a (cal/mol) and sorption entropy, ΔS_1^s (cal/mol) of PTMCBHEMA with selected some alcohols and alkanes systems

	ΔG_1^s (cal/mol)				ΔH_1^s (cal/mol)	ΔH_a (cal/mol)	ΔS_1^s (cal/mol)			
Probe/T(K)	393	403	413	423	393–423	333–383	393	403	413	423
Methanol	4011	4205	4380	4559	−3135	−6523	−18.18	−18.21	−18.20	−18.19
Ethanol	3722	3908	4063	4240	−2996	−7953	−17.10	−17.13	−17.10	−17.11
1-Propanol	3520	3671	3821	3984	−2541	−7725	−15.42	−15.42	−15.40	−15.43
1-Butanol	3313	3458	3602	3753	−2429	−8275	−14.61	−14.61	−14.60	−14.61
1-Pentanol	3103	3241	3378	3517	−2317	−7743	−13.79	−13.79	−13.79	−13.79
Hexane	3345	3488	3621	3761	−2076	−5144	−13.79	−13.81	−13.79	−13.80
Heptane	3209	3348	3484	3628	−2268	−5884	−13.92	−13.92	−13.92	−13.93
Octane	3094	3230	3356	3490	−2079	−6372	−13.16	−13.17	−13.16	−13.17
Decane	2836	2975	3120	3247	−2580	−5710	−13.78	−13.79	−13.80	−13.78

Table 4. The partial molar sorption free energies, ΔG_1^s (cal/mol), the partial molar sorption enthalpy, ΔH_1^s (cal/mol), adsorption enthalpy ΔH_a (cal/mol) and sorption entropy, ΔS_1^s (cal/mol) of PMCBOEMA with selected some alcohols and alkanes systems

	ΔG_1^s (cal/mol)				ΔH_1^s (cal/mol)	ΔH_a (cal/mol)	ΔS_1^s (cal/mol)			
Probe/T(K)	393	403	413	423	393–423	333–373	393	403	413	423
Methanol	3398	3514	3630	3753	−1354	−6334	−11.79	−11.79	−11.78	−11.79
Ethanol	3093	3204	3318	3429	−1416	−7353	−11.19	−11.19	−11.19	−11.19
1-Propanol	2871	2970	3077	3173	−1224	−7804	−10.16	−10.15	−10.17	−10.15
1-Butanol	2623	2719	2839	2944	−1745	−8243	−10.84	−10.80	−10.84	−10.83
1-Pentanol	2410	2489	2604	2702	−1586	−7939	−9.92	−9.87	−9.91	−9.90
Hexane	2638	2727	2821	2923	−1172	−5408	−9.45	−9.44	−9.44	−9.46
Heptane	2502	2594	2687	2767	−1088	−5970	−8.91	−8.91	−8.92	−8.90
Octane	2380	2466	2557	2645	−1176	−6431	−8.82	−8.82	−8.82	−8.82
Decane	2081	2168	2249	2330	−1255	−6371	−8.28	−8.29	−8.28	−8.28

temperature for each group solvents. This behavior showed that this temperature range was in the equilibrium sorption. The T_g values of PTMCBHEMA and PMCBOEMA were found about 380 K and 390 K by inverse gas chromatography, respectively. The V_g^0 values of PMCBOEMA-probes systems were found to be higher than PTMCBHEMA-probes systems. The reason for this may be strong hydrogen bonding between probes with PMCBOEMA.

ΔH_a and ΔH_1^s values of PTMCBHEMA and PMCBOEMA-probe systems were calculated by plotting ln Vg° against 1/T (K^{-1}) (Figures 1 and 2). Tables 3 and 4 shows the experimentally obtained adsorption enthalpy, ΔH_a, sorption heats, ΔH_1^s,

Table 5. The weight fraction activity coefficients, Ω_1^∞ and Flory-Huggins interaction parameters, χ_{12}^∞, of PTMCBHEMA with selected some alcohols and alkanes systems

	Ω_1^∞				χ_{12}^∞			
Probe/T(K)	433	443	453	463	433	443	453	463
Methanol	14.04	12.41	10.49	8.37	1.1853	1.0578	0.8873	0.6609
Ethanol	12.88	11.24	9.25	7.74	1.1453	1.0104	0.8192	0.6480
1-Propanol	17.79	15.43	12.97	10.75	1.4740	1.3294	1.1557	0.9692
1-Butanol	25.07	21.59	17.98	14.67	1.8311	1.6793	1.4954	1.2928
1-Pentanol	36.72	31.66	26.93	22.03	2.2246	2.0712	1.9051	1.7007
Hexane	10.61	9.65	8.73	7.62	0.8603	0.7661	0.6685	0.5338
Heptane	17.77	15.80	14.01	11.99	1.3846	1.2673	1.1478	0.9928
Octane	28.54	25.20	22.25	18.65	1.8616	1.7359	1.6104	1.4340
Decane	73.80	62.10	52.42	42.63	2.8138	2.6266	2.4631	2.2531

Table 6. The weight fraction activity coefficients, Ω_1^∞ and Flory-Huggins interaction parameters, χ_{12}^∞, of PMCBOEMA with selected some alcohols and alkanes systems

	Ω_1^∞			χ_{12}^∞		
Probe/T(K)	443	453	463	443	453	463
Methanol	3.79	3.04	2.59	−0.1279	−0.3516	−0.5118
Ethanol	3.38	2.73	2.29	−0.1901	−0.4002	−0.5704
1-Propanol	4.68	3.78	3.14	0.1370	−0.0772	−0.2607
1-Butanol	6.51	5.27	4.32	0.4807	0.2685	0.0695
1-Pentanol	9.56	7.75	6.36	0.8738	0.6596	0.4588
Hexane	2.85	2.43	2.16	−0.4542	−0.6111	−0.7247
Heptane	4.60	3.92	3.40	0.0329	−0.1257	−0.2680
Octane	7.40	6.11	5.16	0.5103	0.3184	0.1498
Decane	17.44	14.09	11.86	1.3666	1.1492	0.9733

for PTMCBHEMA and PMCBOEMA-probe systems in temperatures ranges 333–373 and 393–423 K; 333–383 and 393–423 K, respectively. ΔH_a values of selected probes have changed for PTMCBHEMA and PMCBOEMA-probe systems as follows: Methanol< ethanol < 1-propanol < 1-butanol < 1-pentanol < hexane < heptane < octane < decane. The ΔG_1^s and ΔS_1^s values of PTMCBHEMA and PMCBOEMA-probe systems were calculated according to the literature (23) and are given in Tables 3 and 4. The sorption values ΔH_1^s and ΔS_1^s and average partial molar heats of mixing, $\Delta\bar{H}_1^\infty$, were found to be negative and positive, respectively. Chen *et al.* had been used to three loading of PEMA (3–12%, w/w) and they had been determined ΔH_1^s, ΔG_1^s and ΔS_1^s values of alkanes, acetates and alcohols-PEMA. ΔH_1^s and ΔS_1^s and ΔG_1^s values of alkanes, acetates and alcohols had been found to be negative and positive, respectively, for PEMA at 458K (24). The two series showed an exothermic heat of sorption and negative entropy of sorption, which is responsible for the endothermic free energy of sorption. The enthalpy change of the sorption process is dependent on interaction between the PTMCBHEMA-probe and PMCBOEMA-probe. Because of the chemical nature, and the number of carbons of each probe are different from each other, the heat of sorption becomes more exothermic as more CH_2 groups are added to the two families of probes. This is an indication that the individual CH_2 group, regardless of the chemical nature of the probe, has a significant interaction with the PTMCBHEMA and PMCBOEMA. Alcohols showed more exothermic values than alkanes. While alcohols have two contributions to the sorption process interaction with PTMCBHEMA and PMCBOEMA via OH and CH_2, alkanes have only one contribution, which is the interaction of CH_2 groups with PTMCBHEMA and PMCBOEMA. Our interpretation is that alcohols form stronger attraction forces with PTMCBHEMA and PMCBOEMA than do alkanes. The attraction forces between PTMCBHEMA and PMCBOEMA and alcohols are actually a combination of two types. The first of these dispersive forces between the CH_2 groups of the alcohols and the 6-tetralino)-3-methyl-1-cyclobutyl and 3-mesityl-3-methyl-1-cyclobutyl groups of PTMCBHEMA and PMCBOEMA, the second is dipole-dipole interaction of the OH group of the alcohols with the C=O group of PTMCBHEMA and PMCBOEMA.

It has been proposed that the values of Ω_1^∞ greater than 5 are indicative of poor polymer-solute systems, while lower values characterize good solubility for such a system (25). The values of χ_{12}^∞ greater than 0.5 represent unfavorable polymer-solvent interactions, while the values lower than 0.5 indicate favorable interactions in dilute polymer solutions (26). The values of Ω_1^∞ and χ_{12}^∞ calculated by the Equations (8) and (13) for PTMCBHEMA and PMCBOEMA-probe systems and also collected in Table 5 and 6, respectively. According to these Ω_1^∞ and χ_{12}^∞ values, selected alcohols and alkanes found to be non-solvent for PTMCBHEMA. While methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, hexane, heptane and octane are good solvents, decane is a non-solvent for PMCBOEMA. These values increased with increasing the number of carbons in the alcohols and alkanes. To be dependent on change in the number of carbons in selected alcohols and alkanes of the Flory-Huggins interaction

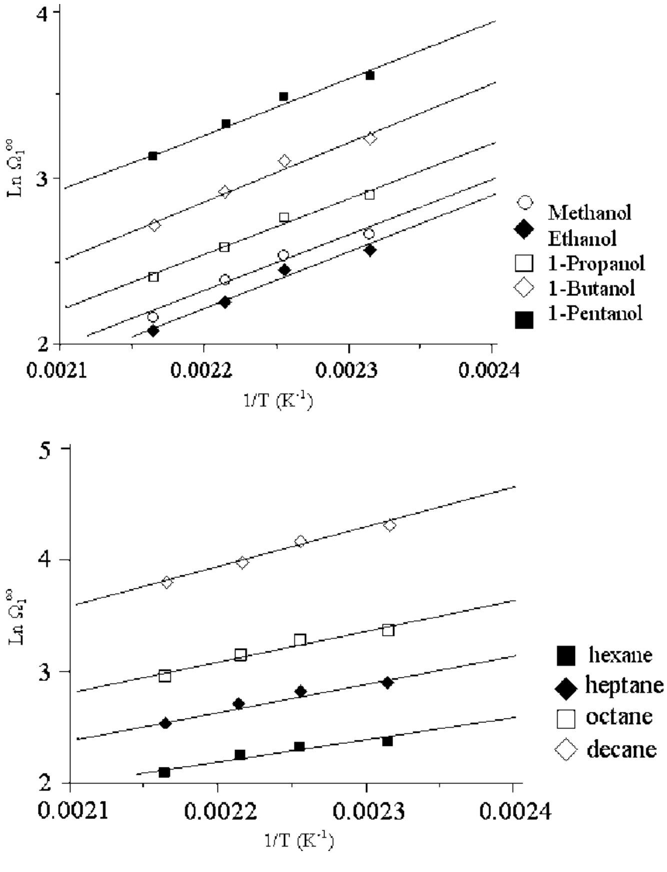


Fig. 3. Variation of logarithm of weight fraction activity coefficients, Ln Ω_1^∞, with reciprocal of absolute column temperature, $1/T$ (K^{-1}) for some selected alkanes and alcohols on PTMCBHEMA.

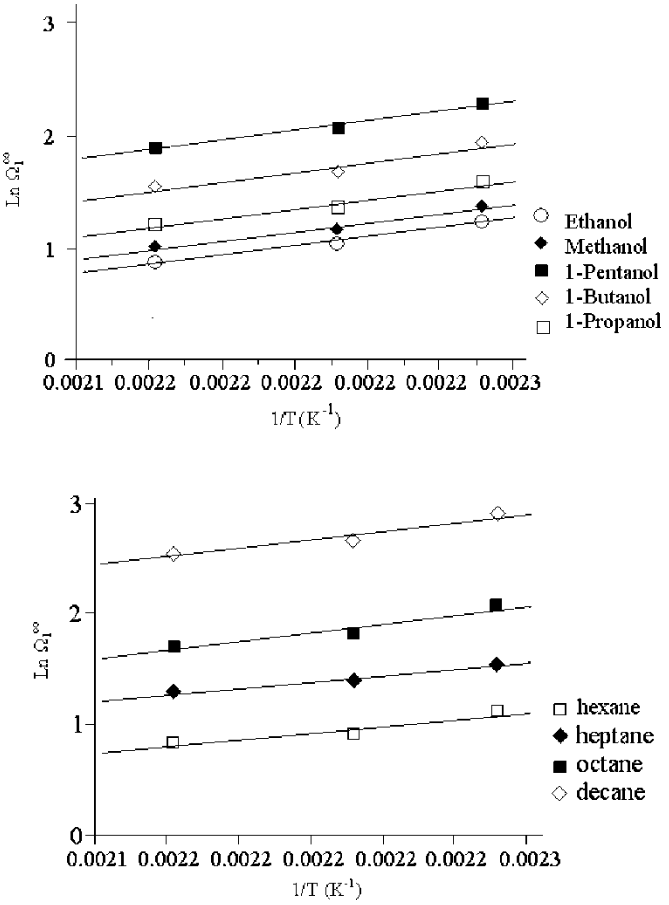


Fig. 4. Variation of logarithm of weight fraction activity coefficients, Ln Ω_1^∞, with reciprocal of absolute column temperature, 1/T (K^{-1}) for some selected alkanes and alcohols on PMCBOEMA.

parameters, χ_{12}^∞, the partial molar free energy of mixing, ΔG_1^∞, weight fraction activity coefficients, Ω_1^∞, and partial molar heats of mixing at infinite dilution of the solutes, $\Delta\bar{H}_1^\infty$ and of polymer-probes systems were observed. The χ_{12}^∞, Ω_1^∞ and ΔG_1^∞ values of polymers-solvents systems decreased with increasing in the column temperature for all probes. According to Ω_1^∞ and χ_{12}^∞, while methanol and ethanol are good solvents for poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] and poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-acrylonitrile] at 453 K, there are non-solvents for poly[2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethylmethacrylate-styrene]. Alkanes had been found to be non-solvents for each polymer and copolymer (27).

The $\Delta\bar{H}_1^\infty$ values of PTMCBHEMA and PMCBOEMA-probe systems were found from the slopes of Ln Ω_1^∞ vs. 1/T (K^{-1}) (Figures 3 and 4). According to the literature, for PTMCBHEMA and PMCBOEMA-probe systems, the partial molar free energy of mixing, ΔG_1^∞, and the partial molar heats of mixing at infinite dilution of the solutes, $\Delta\bar{H}_1^\infty$, were calculated and collected in Tables 7 and 8, respectively. The $\Delta\bar{H}_1^\infty$ values of PTMCBHEMA and PMCBOEMA-probe systems changed from 4.39 to 7.29 kcal/mol and from 5.97 to 9.00 kcal/mol, respectively, as seen from Tables 7 and 8. According to the literature (13), the molar evaporation enthalpy, ΔH_v, were calculated and collected in Tables 7 and 8. The ΔH_v values of PTMCBHEMA and PMCBOEMA-probe systems changed from 6.46 to10.00 kcal/mol and from 7.15 to 10.74 kcal/mol, respectively, as seen from Tables 7 and 8.

The solubility parameter of a polymer, δ_2, can be determined by using Equation 18 (28). The solubility parameter δ_2 is determined from either slope or intercept of a straight line obtained by plotting the left-hand-side of Equation 18 vs. δ_1. The solubility parameter of PTMCBHEMA and PMCBOEMA were evaluated from either the slope or intercept of Figures 5 and 6 as 5.79 (cal/cm^3)$^{0.5}$, 6.28 (cal/cm^3)$^{0.5}$ and 6.80 (cal/cm^3)$^{0.5}$, 6.68 (cal/cm^3)$^{0.5}$ at 443 K, respectively. The values of solubility parameters of PTMCBHEMA and PMCBOEMA, δ_2, decreased with increasing temperature (see Table 9). Also, according to the swelling coefficient (Q) method, the solubility parameter, δ_2, of PTMCBHEMA and PMCBOEMA have been calculated as 10.25 (cal cm^{-3})$^{0.5}$ 10.75 (cal cm^{-3})$^{0.5}$ at 25°C (29).

Table 7. The partial molar free energies of mixing, ΔG_1^∞ (cal/mol) and the partial molar enthalpy of mixing, $\Delta\bar{H}_1^\infty$ (cal/mol), molar evaporation enthalpy, ΔH_v (cal/mol) of PTMCBHEMA with selected some alcohols and alkanes systems

	ΔG_1^∞				$\Delta\bar{H}_1^\infty$		
Probe/T(K)	433	443	453	463	433–463	ΔH_v (Eq.17)	ΔH_v (Eq.3)
Methanol	2273	2217	2116	1955	6870	10005	8565
Ethanol	2199	2130	2002	1883	6875	9872	9326
1-Propanol	2477	2409	2307	2185	6751	9292	9588
1-Butanol	2772	2704	2601	2471	7166	9595	10339
1-Pentanol	3100	3041	2964	2845	6793	9110	10638
Hexane	2032	1995	1951	1868	4386	6461	6863
Heptane	2476	2430	2376	2285	5220	7484	7723
Octane	2883	2841	2792	2692	5619	7698	8616
Decane	3701	3634	3564	3452	7290	9871	10422

Table 8. The partial molar free energies of mixing, ΔG_1^{∞} (cal/mol) and the partial molar enthalpy of mixing, $\Delta \bar{H}_1^{\infty}$ (cal/mol), molar evaporation enthalpy, ΔH_v (cal/mol) of PMCBOEMA with selected some alcohols and alkanes systems

	ΔG_1^{∞}			$\Delta \bar{H}_1^{\infty}$	ΔH_v (Eq.17)	ΔH_v (Eq.3)
Probe/T(K)	443	453	463	443–463		
Methanol	1173	1000	876	8291	9645	8535
Ethanol	1073	905	762	8524	9940	9255
1-Propanol	1359	1197	1053	8721	9945	9482
1-Butanol	1649	1496	1346	8996	10740	10228
1-Pentanol	1987	1843	1702	8916	10502	10519
Hexane	921	799	710	5973	7145	6798
Heptane	1343	1230	1125	6619	7707	7661
Octane	1762	1629	1510	7863	9039	8551
Decane	2516	2381	2275	8422	9676	10330

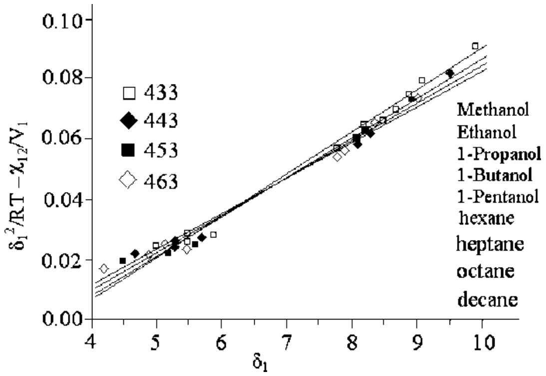


Fig. 5. Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at different temperatures for PTMCBHEMA.

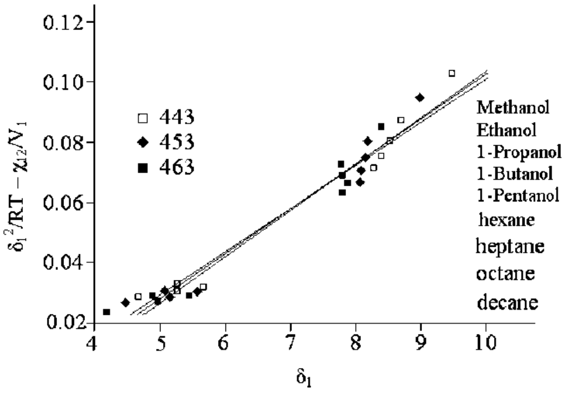


Fig. 6. Variation of the term $[(\delta_1^2/RT) - \chi_{12}^{\infty}/V_1]$ with solubility parameters of the solutes, δ_1 $(cal/cm^3)^{0.5}$ at different temperatures for PMCBOEMA.

Table 9. The solubility parameters, δ_2 $(cal/cm^3)^{0.5}$ of PTMCBHEMA and PMCBOEMA between 433–463 K and 443–463 K, respectively

	PTMCBHEMA				
T(K)	slope	intercept	cal. from slope, δ_2	cal. from intercept, δ_2	r
433	0.0141	−0.0509	6.04	6.61	0.99
443	0.0132	−0.0449	5.79	6.28	0.99
453	0.0127	−0.0424	5.70	6.17	0.99
463	0.0121	−0.0387	5.55	5.96	0.99
			PMCBOEMA		
443	0.0155	−0.0509	6.80	6.68	0.99
453	0.0151	−0.0484	6.77	6.59	0.98
463	0.0144	−0.0437	6.60	6.33	0.98

4 Conclusions

The inverse gas chromatography technique is simple, fast, and economical and provides valuable thermodynamic and physical chemistry information for characterization of polymeric materials. This technique was successfully applied to determine polymer-solvent and polymer-non-solvent interactions. The IGC technique was successfully applied to determine some thermodynamic properties of PTMCBHEMA and PMCBOEMA such as the adsorption enthalpy, molar evaporation enthalpy, sorption enthalpy, sorption free energy, sorption entropy, Flory-Huggins interaction parameters, partial molar free energy of mixing, weight fraction activity coefficients, solubility parameter of polymer, and the partial molar heats of mixing, at infinite dilution. Alcohols showed a stronger interaction with PTMCBHEMA and PMCBOEMA than did alkanes. The effects the ΔH_1^s, ΔS_1^s and ΔG_1^s sorption parameters of contributions of alcohols (–OH) and alkanes (–CH$_2$) functional groups were calculated as −0.21, −0.19 kcal mol^{-1}; −1.10, −0.50 cal mol^{-1} and −0.21, −0.17 kcal mol^{-1} for the PTMCBHEMA-probe system, respectively. The effects the ΔH_1^s, ΔS_1^s and ΔG_1^s sorption parameters of (–OH) and (–CH$_2$) functional groups were calculated as −0.38, −0.008 kcal mol^{-1}; −0.81, −0.39 cal mol^{-1} and −0.25, −0.19 kcal mol^{-1}, for PMCBOEMA-probe system, respectively. The hydroxyl group showed more interaction with the methyl group at the structures of PTMCBHEMA and PMCBOEMA. According to Flory-Huggins interaction parameters and the weight fraction activity coefficients as selected alcohols and alkanes non-solvent for PTMCBHEMA and PMCBOEMA were determined. Also, from the IGC results, the solubility parameter of a copolymer, δ_2, can be determined from either slope or intercept of a straight line obtained by plotting the left-hand-side of Equation 18 vs. δ_1. The solubility parameters, δ_2, of PTMCBHEMA and PMCBOEMA found to be 5.55 $(cal\ cm^{-3})^{0.5}$ and 5.96 $(cal\ cm^{-3})^{0.5}$ and 6.60 $(cal\ cm^{-3})^{0.5}$ and 6.33 $(cal\ cm^{-3})^{0.5}$ from slope and intercept of $[(\delta_1^2/\mathrm{RT}) - \chi_{12}^{\infty}/\mathrm{V}_1] = (2\delta_2/\mathrm{RT})\ \ \delta_1 - \delta_2^2/\mathrm{RT}$ equation, at 413 K, respectively.

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