

Analysis of Physical and Thermodynamic Properties of Poly(2-cyclopentyliden-1,3-dioxolan-4-yl-methylmethacrylate-co-styrene) (CPDMMA-ST) Polymer Using Inverse Gas Chromatography

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In this study, thermodynamic and physical properties of poly(2-cyclopentyliden-1,3-dioxolane-4-yl-methylmethacrylate-co-styrene) (%55CPDMMA-%45ST) were investigated using inverse gas chromatography. Two groups of alcohols and alkanes with different chemical natures and polarities were used to determine certain properties of (CPDMMA-ST)-solute systems. The specific retention volume (V_g^0), glass transition temperature (T_g), adsorption enthalpy (ΔH_a), the sorption enthalpy (ΔH_1^S), sorption free energy (ΔG_1^S), sorption entropy (ΔS_1^S), weight fraction activity coefficients of solute probes at infinite dilution (Ω_1^∞), partial molar enthalpy of solute probes at infinite dilution (ΔH_1^∞) and Flory-Huggins interaction parameters (χ_{12}^∞), between polymer and solvents were determined in the temperature range of 313-473 K. In addition, the solubility parameters of CPDMMA-ST at infinite dilution was determined by plotting the graph of $[\delta_1^2 - (\Delta G_1^\infty/V_1)]$ versus solubility parameters (δ_1), of probes.

Keywords: Polymer, Inverse gas chromatography, Poly(2-cyclopentyliden-1,3-dioxolan-4-yl-methylmethacrylate-co-styrene).

INTRODUCTION

Inverse gas chromatography (IGC) is a useful method for the studying certain thermodynamic and physical properties of (polymer-solute) systems. Thus, inverse gas chromatography has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials and to investigate polymer-polymer miscibility¹⁻⁵. Furthermore, inverse gas chromatography is a reliable method for the characterization of amorphous and semi crystalline polymers. The method is simple, fast and economical and provides valuable thermodynamic information for the characterizing of polymeric substances.

Inverse gas chromatography was developed by Smidsord and Guillet⁶ and has been applied to many polymeric systems. In addition, inverse gas chromatography has been used to provide information regarding polymer-solvent and polymer-polymer systems, including solubility parameters, interaction parameters, diffusion constants, enthalpies of mixing, surface energies and areas, adsorption isotherms, glass transition temperatures, melting point temperatures and degrees of crystallinity. Furthermore, inverse gas chromatography is capable of obtaining information on the physicochemical properties, structure and chemical interactions of macromolecules⁷⁻¹⁴.

Dipaola-Baranyi and Guillet¹⁵ have shown that inverse gas chromatography can serve as a simple method for estimating the solubility parameters of polymers when using a polymer as a the stationary phase.

In this study, we examined the polymer-solvent interaction parameters and the solubility parameters in terms of the thermodynamic and physical properties of poly(2-cyclopentyliden-1,3-dioxolane-4-yl-methyl methacrylate-co-styrene) (CPDMMA-ST) by using inverse gas chromatography in the temperatures from 60-200 °C.

Data reduction

Probe specific retention volumes (V_g^0) are calculated from the following standard chromatographic relation¹⁶:

$$V_g^0 = (F \times 273.2 \times t_r) / W \times T \times 3/2 \times \{[(P_i/P_0)^2 - 1] / [(P_i/P_0)^3 - 1]\} \quad (1)$$

where t_r is the retention times of probe, F is the flow rate of the carrier gas measured at room temperature, W is the mass of the polymeric stationary phase, T is the column temperature, P_i and P_0 are inlet and outlet pressures, respectively.

For the probe, the molar heat enthalpy (ΔH_1^S) and the molar free energy (ΔG_1^S) of sorption that are probe absorbed by the polymer are given by the following equation:

$$\Delta H_1^S = -R \partial V_g^0 / \partial (1/T) \quad (2)$$

$$\Delta G_1^S = -RT \ln (M_1 V_g^0/273.2R) \quad (3)$$

By incorporating eqns. 2 and 3, we calculated the entropy of sorption of solutes as follows:

$$\Delta G_1^S = \Delta H_1^S - T\Delta S_1^S \quad (4)$$

where V_g^0 is the specific retention volume of the probe, T is the column temperature (K), M_1 is the molecular weight of probe and R is the gas constant. The adsorption enthalpy of the probes that is adsorbed by the polymer, ΔH_a , was calculated using the following equation¹⁷:

$$\partial V_g^0/\partial(1/T) = -\Delta H_a/R \quad (5)$$

Partial molar free energy of mixing ΔG_1^∞ (cal/mol) and partial molar enthalpy ΔH_1^∞ (cal/mol) at infinite dilution are calculated according to the following equation¹⁰:

$$\Delta H_1^\infty = R(\delta \ln(a_1/w_1)^\infty / \delta(1/T)) \quad (6)$$

$$\Delta G_1^\infty = R \ln (a_1/w_1)^\infty \quad (7)$$

The weight fraction activity coefficient, Ω_1^∞ , of the solute probe at infinite dilution is calculated according to the following equation⁵:

$$\Omega_1^\infty = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11}-V_1)/RT] \quad (8)$$

(CPDMMMA-ST)-solute interaction parameters of the different solutes, χ_{12}^∞ , at infinite dilution were defined using the following equation:

$$\chi_{12}^\infty = \ln [(273.2 \times R \times V_2)/(V_g^0 \times V_1 \times P_1^0)] - 1 - P_1^0/RT(B_{11}-V_1) \quad (9)$$

where R is the gas constant, V_2 is the specific volume of the polymer, V_1 is the molar volume of the solute, P_1^0 is the vapor pressure and B_{11} is the second virial coefficient of the solute in the gaseous state. In addition, V_1 , P_1^0 and B_{11} were calculated at the column temperature.

Second virial coefficients, B_{11} , were computed using the following equation¹⁵:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (10)$$

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 solubility parameters of polymers (δ_2) were determined by using the following relation:

$$\delta_1^2 - \Delta G_1^\infty/V_1 = 2\delta_1\delta_2 - \delta_2^2 \quad (11)$$

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

If the left-hand side of this equation is plotted against δ_1 , then a straight line with a slope of $(2\delta_2/RT)$ and an intercept of $-\delta_2^2/RT$ is obtained. Solubility parameters of polymer, δ_2 , can be calculated from the slope and intercept of the straight line¹⁵.

EXPERIMENTAL

The chromatographic grade molecular probes used in this study, including ethyl alcohol (C_2), 1-propyl alcohol (C_3), 1-butyl alcohol (C_4), n -hexane (C_6), n -heptane (C_7), n -octane (C_8), and n -nonane (C_9) were obtained from Merck Chemical Co. Methane was used as a non-interacting marker to correct for the dead volume in the column. The CPDMMMA-ST were

supplied from the Chemistry Department of Firat University, Elazig, Turkey and the Chromosorb W (80-100 mesh) was obtained from Sigma Chemical Co.

The polymer accounted for 10 % of the charging material. The glass transition temperature (T_g), was approximately 373 K for (CPDMMMA-ST)

A Shimadzu GC-14A model gas chromatograph equipped with a dual flame ionization detector (FID) was used in this analysis. Dry nitrogen gas (research grade) was used as a carrier gas. The pressures (mm-Hg) read at the inlet and outlet of the column using a mercury manometer were used to compute corrected retention volumes using a standard procedure. The flow rate was measured at the end of the column using a soap bubble flow meter. A flow rate of approximately 115 mL min⁻¹ was used throughout our experiment. The column consisted of a 1 m copper pipe with 3.2 mm ID. The copper column was washed with distilled water, benzene and acetone and then was dried. A column packing material was prepared by coating 80-100 mesh size Chromosorb W with CPDMMMA-ST. The prepared material was packed into the copper column (3.2 mm ID \times 1 m). The column was conditioned at 200 °C with a fast carrier gas flow rate for 48 h prior to use. Probes were injected into the column using 1 μ L Hamilton syringes. Three consecutive injections were performed for each probe for each set of measurements. An injection volume of 0.3 μ L was selected and the retention times of the probes were measured using a chromatopac CR6A (Shimadzu).

RESULTS AND DISCUSSION

The V_g^0 of probes were obtained using one polymer loading at a series of temperatures. The V_g^0 values of these probes were calculated according to the eqn. 1. The retention volume was confirmed to be independent of solute sample size in all of the studied cases¹⁸. Specific retention volume data are essential in determining the physicochemical or thermodynamic properties of a polymer by inverse gas chromatography. To obtain these data, the amount of the polymer that has been coated onto the support, the gas flow rate, the column pressures and temperature must be known. The V_g^0 values are given in Table-1. The specific retention volumes of the probes on the (CPDMMMA-ST) varied with temperature for each of the probe and generally decreased with increasing temperature. The T_g , of (CPDMMMA-ST) is given in Fig. 1. As shown in Fig. 1, the T_g of (CPDMMMA-ST) was approximately 373 K¹⁹.

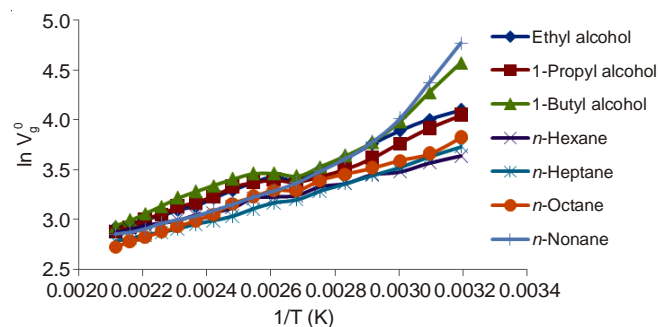


Fig. 1. Variation of logarithm of specific retention volumes, V_g^0 (mL/g) of alcohols and alkanes with reciprocal of absolute column temperature and the glass transition temperature (T_g) for CPDMMMA-ST

TABLE-1
VARIATION OF THE LOGARITHM OF SPECIFIC RETENTION VOLUMES ($\ln V_g^0$, mL/g), OF ALCOHOLS AND ALKANES WITH TEMPERATURE USING CPDMMMA-ST AS STATIONARY PHASE

Temperature (1/T) 10 ⁻³	Ethyl alcohol	1-Propyl alcohol	1-Butyl alcohol	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane
2.114	2.928	2.882	2.937	2.876	2.782	2.728	2.854
2.159	2.956	2.928	2.995	2.905	2.814	2.779	2.877
2.207	3.013	3.007	3.060	2.943	2.846	2.826	2.908
2.257	3.036	3.052	3.132	2.968	2.874	2.877	2.960
2.309	3.096	3.126	3.217	2.993	2.907	2.929	2.996
2.364	3.131	3.170	3.28	3.045	2.951	2.988	3.032
2.421	3.216	3.230	3.339	3.070	2.988	3.052	3.090
2.481	3.295	3.327	3.405	3.119	3.032	3.158	3.154
2.544	3.370	3.372	3.460	3.213	3.105	3.227	3.223
2.610	3.428	3.397	3.463	3.224	3.168	3.293	3.289
2.680	3.392	3.373	3.434	3.238	3.200	3.291	3.372
2.754	3.497	3.434	3.529	3.328	3.285	3.393	3.488
2.832	3.612	3.506	3.641	3.363	3.363	3.456	3.612
2.915	3.756	3.613	3.772	3.450	3.441	3.516	3.773
3.003	3.890	3.761	3.980	3.480	3.522	3.591	4.009
3.095	4.002	3.911	4.271	3.567	3.625	3.658	4.369
3.194	4.099	4.045	4.567	3.633	3.728	3.821	4.766

The ΔH_a and ΔH_1^S values of CPDMMMA-ST-probe systems were calculated by plotting $\ln V_g^0$ against $1/T$ (K⁻¹) using eqns. 5 and 2, respectively. Table-2 shows experimentally obtained sorption enthalpy, ΔH_1^S , at temperatures 373-403 K. Table-3 shows the experimentally obtained adsorption enthalpy ΔH_a at temperatures of 313-373 K, respectively. ΔH_a and ΔH_1^S values of probes that were determined from the slopes of straight lines in Figs. 2 and 3 for CPDMMMA-ST were positive, except for *n*-nonane. At the temperatures below T_g , positive ΔH_a values indicate that the polymer do not interact with probes. However, negative ΔH_a value indicate that the CPDMMMA-ST interacts

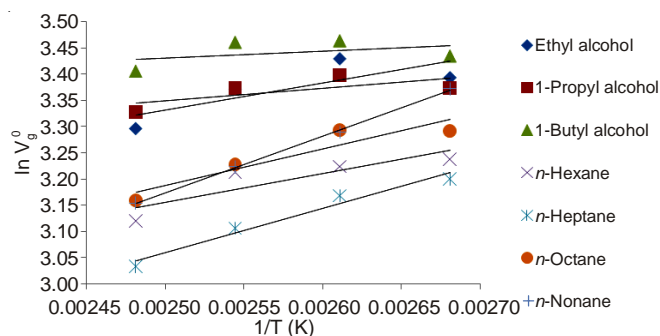


Fig. 2. Variation of logarithm of specific retention volumes (V_g^0 , mL/g) of alcohols and alkanes with reciprocal of absolute column temperature for CPDMMMA-ST for ΔH_1^S (cal/mol)

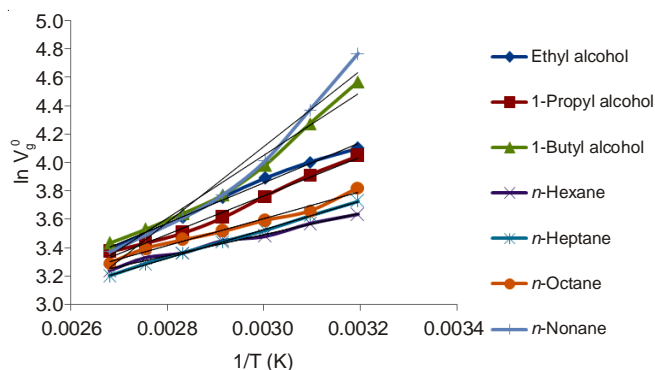


Fig. 3. Variation of logarithm of specific retention volumes (V_g^0 , mL/g) of alcohols and alkanes with reciprocal of absolute column temperature for CPDMMMA-ST, for ΔH_a (cal/mol)

with *n*-nonane. ΔG_1^S and ΔS_1^S values of (CPDMMMA-ST)-probe systems were calculated from eqns. 3 and 4, respectively and are given in Table-2. The ΔS_1^S and ΔH_1^S values were negative and the ΔG_1^S values were positive. These values are expected for polymer-non solvent systems^{8,20}. ΔH_1^∞ values of polymer-probe system were calculated by plotting $\ln a_1/w_1$ against $1/T$ (K⁻¹) (Fig. 4.) using eqn. 6. Table-4 shows experimentally obtained partial molar heats, ΔH_1^∞ . The ΔH_1^∞ values were positive and correspond with the expected values for polymer-non-solvent systems¹⁵.

TABLE-2
PARTIAL MOLAR ENTHALPY (ΔH_1^S , cal/mol), PARTIAL MOLAR FREE ENERGY OF MIXING (ΔG_1^S , cal/mol) AND PARTIAL MOLAR ENTROPY (ΔS_1^S , cal/mol) OF CPDMMMA-ST WITH ALCOHOLS AND ALKANES

Probe	ΔH_1^S (cal/mol)	ΔG_1^S (cal/mol)				ΔS_1^S (cal/mol)			
	373-403 K	403 K	393 K	383 K	373 K	403 K	393 K	383 K	373 K
Ethyl alcohol	-1024.82	2314.815	2199.204	2098.612	2070.822	-8.287	-8.204	-8.155	-8.299
1-Propyl alcohol	-476.005	2076.877	1989.548	1920.176	1888.148	-6.335	-6.274	-6.256	-6.338
1-Butyl alcohol	-255.806	1845.842	1757.612	1710.334	1686.879	-5.215	-5.123	-5.134	-5.208
<i>n</i> -Hexane	-1086.51	1954.681	1832.938	1777.708	1720.661	-7.546	-7.429	-7.478	-7.526
<i>n</i> -Heptane	-1686.53	1903.760	1798.984	1705.232	1636.896	-8.909	-8.869	-8.856	-8.910
<i>n</i> -Octane	-1377.31	1697.495	1601.604	1510.808	1472.877	-7.630	-7.580	-7.541	-7.641
<i>n</i> -Nonane	-2151.92	1608.094	1514.359	1425.726	1327.087	-9.330	-9.329	-9.341	-9.327

TABLE-3
ADSORPTION ENTHALPY (ΔH_a , cal/mol) OF
CPDMMMA-ST WITH ALCOHOLS AND ALKANES

Probe	ΔH_a (cal/mol)
	313-373 K
Ethyl alcohol	2766.198
1-Propyl alcohol	3785.926
1-Butyl alcohol	230.054
<i>n</i> -Hexane	3500.836
<i>n</i> -Heptane	2944.172
<i>n</i> -Octane	3905.072
<i>n</i> -Nonane	-3418.715

TABLE-4
PARTIAL MOLAR ENTHALPY OF SOLUTE PROBES
AT INFINITE DILUTION (ΔH_1^∞ , cal/mol) OF CPDMMMA-ST
WITH ALCOHOLS AND ALKANES SYSTEMS

Probe	ΔH_1^∞ (cal/mol)
	473-403 K
Ethyl Alcohol	7297.257
1-Propyl Alcohol	7113.062
1-Butyl Alcohol	7578.616
<i>n</i> -Hexane	5506.97
<i>n</i> -Heptane	6300.777
<i>n</i> -Octane	6281.503
<i>n</i> -Nonane	7734.596

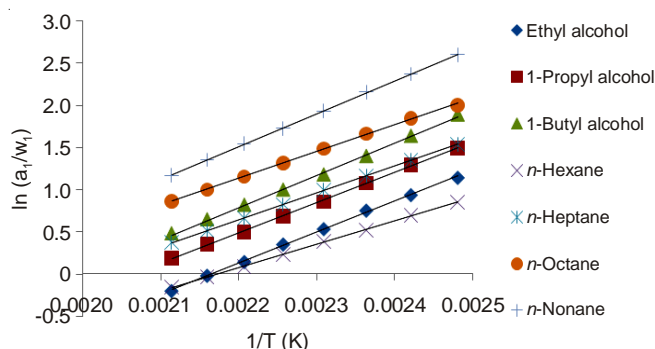


Fig 4. Weight fraction activity coefficient of solute probes at infinite dilution Ω_1^∞ with reciprocal of absolute column temperature for CPDMMMA-ST with alcohols and alkanes

The values of Ω_1^∞ and χ_{12}^∞ were obtained using eqns. 8 and 9 respectively and are presented in Tables 5 and 6.

Furthermore, Ω_1^∞ values greater than 5 have been considered to indicate poor polymer-solute systems, while lower values have been considered to indicate good solubility for such systems. The following rules were formulated by Guillet²⁰ and Purnell²¹:

$\Omega_1^\infty < 5$: good solvents
$5 < \Omega_1^\infty < 10$: moderate solvents
$\Omega_1^\infty > 10$: bad solvents

Here, χ_{12}^∞ values greater than 0.5 represent unfavorable polymer-solvent interactions, while values lower than 0.5 indicate favorable interactions in dilute polymer solutions^{21,22}. Based on these values (Tables 5 and 6) and according to the Ω_1^∞ and χ_{12}^∞ , all of the probes under the T_g are poor solvents for polymer. When the probes are above the T_g according to the Ω_1^∞ and χ_{12}^∞ values, ethyl alcohol, 1-propyl alcohol, *n*-hexane, *n*-heptane are good solvents. However, 1-butyl alcohol and *n*-octane are moderate solvent, *n*-nonane is poor solvent for CPDMMMA-ST. It can be concluded from Ω_1^∞ and χ_{12}^∞ values that as the heat increases, the probes can solve the polymers. In Tables 5 and 6, values increased as the number of carbons in the alcohols and alkanes increased. That is, at these temperatures the solubility of (CPDMMMA-ST) was decreased in the alcohols. The interaction parameters, χ_{12}^∞ and the weight coefficients, Ω_1^∞ did show with change in the number of carbons in the series. However, the Ω_1^∞ and χ_{12}^∞ values decreased in all of the series as the column temperature increased²³.

The solubility parameter of a polymer δ_2 , can be determined from either the slope or the intercept of a straight line obtained by plotting the left side of eqn. 11⁹⁻¹⁵ against δ_1 . These values are shown in Table-7. The solubility parameter of

TABLE-5
WEIGHT FRACTION ACTIVITY COEFFICIENT (Ω_1^∞) OF CPDMMMA-ST WITH ALCOHOLS AND ALKANES SYSTEMS

Probe	Ω_1^∞							
	473 K	463 K	453 K	443 K	433 K	423 K	413 K	403 K
Ethyl alcohol	0.818	0.98	1.153	1.419	1.704	2.121	2.549	4.099
1-Propyl alcohol	1.205	1.421	1.64	1.983	2.356	2.929	3.643	4.441
1-Butyl alcohol	1.612	1.904	2.263	2.707	3.244	1.636	5.134	6.612
<i>n</i> -Hexane	0.852	0.965	1.091	1.261	1.469	1.683	1.999	2.346
<i>n</i> -Heptane	1.457	1.676	1.944	2.286	2.704	3.193	3.849	4.664
<i>n</i> -Octane	2.37	2.726	3.177	3.732	4.428	5.28	6.347	7.426
<i>n</i> -Nonane	3.218	3.876	4.687	5.607	6.91	8.636	10.718	13.436

TABLE-6
INTERACTION PARAMETERS (χ_{12}^∞) OF CPDMMMA-ST WITH ALCOHOLS AND ALKANES SYSTEMS

Probe	χ_{12}^∞							
	473 K	463 K	453 K	443 K	433 K	423 K	413 K	403 K
Ethyl alcohol	-1.59	-1.42	-1.26	-1.06	-0.88	-0.66	-0.469	-0.26
1-propyl alcohol	-1.21	-1.05	-0.91	-0.72	-0.55	-0.33	-0.103	0.101
1-butyl alcohol	-0.91	-0.75	-0.48	-0.4	-0.21	0.01	0.256	0.515
<i>n</i> -Hexane	-1.65	-1.53	-1.41	-1.27	-1.12	-0.98	-0.809	-0.649
<i>n</i> -Heptane	-1.11	-0.97	-0.83	-0.67	-0.5	-0.33	-0.143	0.051
<i>n</i> -Octane	-0.63	-0.49	-0.34	-0.17	-0.002	0.177	0.364	0.525
<i>n</i> -Nonane	-0.35	-0.16	0.032	0.214	0.427	0.653	0.874	1.106

TABLE-7
SOLUBILITY PARAMETER [δ_2 (cal/cm³)^{0.5}]
OF CPDMMA-ST AT 423 AND 413 K

T (K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
423	13.479	49.92	6.739	7.065	0.99
413	13.746	52.745	6.873	7.262	0.99

CPDMMA-ST was evaluated from either the slope or intercepts of Fig. 5(a) and 5(b) 6.739 (cal/cm³)^{0.5} or 7.065 (cal/cm³)^{0.5} at 423 K, respectively. In comparing the solubility values of CPDMMA-ST at different temperatures, it can be seen that solubility parameters decrease with increasing temperature²⁴.

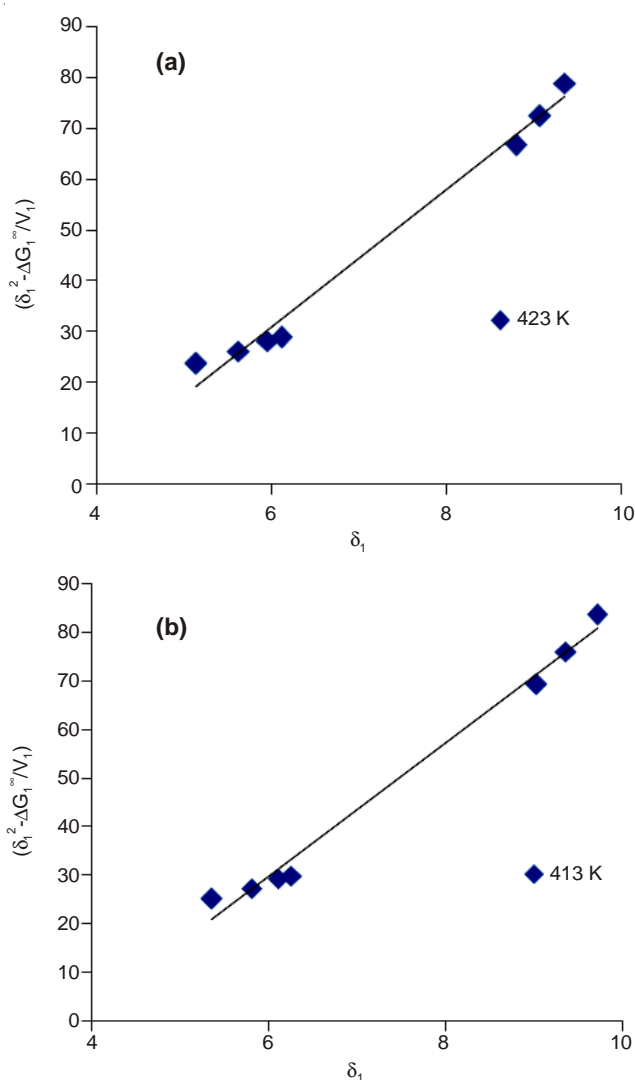


Fig 5. Variation of term $(\delta_1^2 - \Delta G_1^\infty/V_1)$ with solubility parameters of the solutes (δ_1 , cal/cm³)^{0.5} at temperatures (a) 423 K and (b) 413 K for CPDMMA-ST

Conclusion

Inverse gas chromatography is a simple, fast and economical technique that provides valuable thermodynamic and physical information for characterizing polymeric materials. In this study, inverse gas chromatography was successfully applied to determine certain thermodynamic and physical properties of CPDMMA-ST, such as glass transition temperature, T_g sorption enthalpy (ΔH_1^S), sorption free energy (ΔG_1^S), sorption entropy (ΔS_1^S), weight fraction activity coefficients (Ω_1^∞), partial molar free energy of mixing (ΔG_1^∞), partial molar heat of mixing (ΔH_1^∞) and Flory-Huggins interaction parameters, χ_{12}^∞ , at infinite dilution. The T_g was approximately 373 K for CPDMMA-ST. According to Flory-Huggins interaction parameters, χ_{12}^∞ and the weight fraction activity coefficients, Ω_1^∞ values, the probes solvated polymer at the temperature above T_g . Also, the solubility parameter values of (CPDMMA-ST), δ_2 , were determined as 6.739 (cal/cm³)^{0.5}, 7.065 (cal/cm³)^{0.5} respectively at 423 K from both slope and intercept of the straight line obtained by plotting the left-hand side of eqn. 11 versus δ_1 values of probes.

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