



Physical and Thermodynamic Properties of Poly(2-*p*-bromophenyl-1,3-dioxolane-4-yl-methylacrylate) and Poly(2-*p*-chlorophenyl-1,3-dioxolane-4-yl-methylacrylate) Using Inverse Gas Chromatography

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In this study, the thermodynamic and physical properties of poly(2-*p*-bromophenyl-1,3-dioxolane-4-yl-methylacrylate) (PPBPDMA) and poly(2-*p*-chlorophenyl-1,3-dioxolane-4-yl-methylacrylate) (PPCPDMA) 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 [(PPBPDMA) and (PPCPDMA)]-solute systems. The specific retention volume (V_g^0), glass transition temperature (T_g), adsorption enthalpy (ΔH_a), sorption enthalpy (ΔH_1^S), sorption free energy (ΔG_1^S), sorption entropy (ΔS_1^S), weight fraction activity coefficients of the solute probes at infinite dilution (Ω_1^∞), partial molar enthalpy of the solute probes at infinite dilution (ΔH_1^∞) and Flory-Huggins interaction parameters (χ_{12}^∞), between the polymer and solvents were determined at 303-423 K. In addition, the solubility parameters of PPBPDMA and PPCPDMA at infinite dilution were determined by plotting the graph of [$\delta_1^2 - (\Delta G_1^\infty/V_1)$] versus the solubility parameters (δ_1) of the probes.

Keywords: Polymer, Inverse gas chromatography, Thermodynamic and Physical properties.

INTRODUCTION

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

Inverse gas chromatography was developed by Smidsrød 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 the stationary phase.

In this study, we examined polymer-solvent interaction parameters and solubility parameters in terms of the thermodynamic and physical properties of poly(2-bromophenyl-1,3-dioxolane-4-yl-methylacrylate) (PPBPDMA) and poly(2-chlorophenyl-1,3-dioxolane-4-yl-methylacrylate) (PPCPDMA) by using inverse gas chromatography at temperatures from 303-423 K.

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

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

where t_r is the retention time of the 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 and P_i and P_0 are the 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 adsorbed by the polymer are given by the following equation:

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

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

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

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

The 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 was calculated according to the following equation⁵:

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

The [(PPBPDMA) and (PPCPDMA)]-solute interaction parameters of the different solutes (χ_{12}^∞) at infinite dilution were defined using the following equation:

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

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 vapour 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 the polymers (δ_2) were determined 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. The solubility parameters of the 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) and *n*-octane (C_8), were obtained from Merck Chemical Co. Methane was

used as a non-interacting marker to correct for the dead volume in the column. The PPBPDMA and PPCPDMA were supplied from the Chemistry Department of Firat University, Elazig, Turkey and the Chromosorb W (80-100 mesh) was obtained from Sigma Chemical Co.

Instrumentation and procedure: The polymer accounted for 10 % of the charging material. The glass transition temperature, T_g , was approximately 333 K for PPBPDMA and 323 K for PPCPDMA.

A Shimadzu GC-14A model gas chromatographer 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 the 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 a 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 PPBPDMA and PPCPDMA. The prepared material was packed into the copper column (3.2 mm ID × 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 µL Hamilton syringes. Three consecutive injections were performed for each probe for each set of measurements. An injection volume of 0.3 µL was selected and the retention times of the probes were measured using a Chromatopac CR6A (Shimadzu).

RESULTS AND DISCUSSION

The V_g^0 of the probes were obtained using one polymer loading at a series of temperatures. The V_g^0 values of these probes were calculated according to eqn. 1. The retention volume was confirmed to be independent of the solute sample size in all of the studied cases¹⁸. Specific retention volume data are essential for determining the physico-chemical 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 the temperature must be known. The V_g^0 values are given in Tables 1 and 2. The specific retention volumes of the probes on the PPBPDMA and PPCPDMA varied with temperature for each of the probe and generally decreased with increasing temperature. The T_g of PPCPDMA and PPBPDMA are given in Fig. 1(a) and 1(b). As shown in Fig. 1(a), the T_g of PPCPDMA was approximately 323 K. As shown in Fig. 1(b), the T_g of PPBPDMA was approximately 333 K. In the study conducted with PPCPDMA, the T_g was 63 °C and the average molecule weight was approximately 21600¹⁹. In the study conducted with PPBPDMA, the T_g was 68 °C and the average molecule weight was approximately 850470²⁰. The difference in the T_g between the two similar polymers (based on their chemical properties) is due to the average molecule weight. The average molecular weight of PPBPDMA was substantially higher (850470) than that of PPBPDMA (21600), which resulted in the different T_g values between them.

TABLE-1
VARIATIONS OF THE LOGARITHM OF THE SPECIFIC RETENTION VOLUMES ($\ln V_g^0$, mL/g), OF ALCOHOLS AND ALKANES WITH TEMPERATURE USING PPCPDMA AS THE 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
3.300	4.412	4.692	5.348	3.930	4.100	4.345
3.194	4.144	4.398	5.005	3.870	4.033	4.195
3.095	4.071	4.234	4.652	3.800	3.948	4.076
3.003	4.141	4.311	4.756	3.855	3.955	4.096
2.915	4.368	4.452	4.931	4.023	4.023	4.176
2.832	4.278	4.424	4.884	3.997	3.985	4.142
2.754	4.184	4.375	4.758	3.961	3.985	4.134
2.680	4.161	4.237	4.632	3.946	3.977	4.121
2.610	4.128	4.183	4.501	3.930	3.957	4.097
2.544	4.045	4.132	4.263	3.930	3.941	4.136
2.481	4.039	4.105	4.260	3.918	3.938	4.081
2.421	3.991	4.081	4.203	3.899	3.940	4.084
2.364	3.933	4.026	4.133	3.868	3.910	3.966

TABLE-2
VARIATIONS OF THE LOGARITHM OF THE SPECIFIC RETENTION VOLUMES ($\ln V_g^0$, mL/g) OF ALCOHOLS AND ALKANES WITH TEMPERATURE USING PPBPDMA AS THE 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
3.300	4.133	4.438	5.396	4.092	4.247	4.655
3.194	4.043	4.220	4.846	3.981	4.109	4.449
3.095	3.999	4.132	4.516	3.934	4.047	4.299
3.003	3.810	4.012	4.311	3.906	3.923	4.146
2.915	4.049	4.120	4.446	3.976	3.992	4.162
2.832	4.161	4.236	4.458	4.116	4.080	4.195
2.754	4.107	4.212	4.433	4.093	4.057	4.165
2.680	4.089	4.168	4.384	4.081	4.041	4.103
2.610	4.060	4.128	4.311	4.069	4.023	4.085
2.544	4.053	4.115	4.251	4.064	4.010	4.075
2.481	4.048	4.089	4.239	4.057	4.011	4.070
2.421	4.038	4.079	4.213	4.060	4.009	4.066
2.364	4.004	4.038	4.168	4.013	3.957	4.015

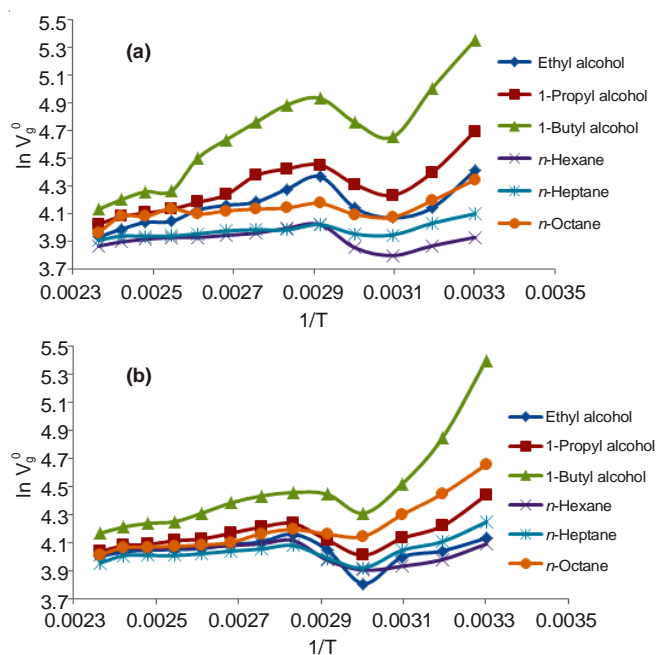


Fig. 1. Variations of the logarithm of the specific retention volumes (V_g^0 , mL/g) of alcohols and alkanes with the reciprocal of the absolute column temperature and the glass transition temperature (T_g) for (a) PPCPDMA and (b) PPBPDMA

The ΔH_a and ΔH_1^S values of the [(PPCPDMA) and (PPBPDMA)]-probe systems were calculated by plotting $\ln V_g^0$ against $1/T$ (K^{-1}) using eqns. 5 and 2, respectively. Tables 3 and 4 show the experimentally obtained sorption enthalpy, ΔH_1^S , at 343-383 K and 353-393 K. Tables 5 and 6 show the experimentally obtained adsorption enthalpy ΔH_a at 303-323 K and 303-333 K, respectively. The ΔH_a values of the probes that were determined from the slopes of the straight lines in Fig. 3 for PPCPDMA were positive, except for 1-butyl alcohol and 1-propyl alcohol. The ΔH_a values for PPBPDMA were positive, except for 1-butyl alcohol. At the temperatures below T_g , positive ΔH_a values indicate that the polymers do not interact with the probes. However, negative ΔH_a values indicate that the PPCPDMA interacts with 1-butyl alcohol and 1-propyl alcohol and that the PPBPDMA interacts with 1-butyl alcohol. The ΔG_1^S and ΔS_1^S values of the [(PPCPDMA) and (PPBPDMA)]-probe systems were calculated from eqns. 3 and 4, respectively and are given in Tables 3 and 4. The ΔS_1^S values of the probes were found from the slopes of the straight lines in Fig. 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^{21,22}.

TABLE-3
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 THE PPCPDMA WITH ALCOHOLS AND ALKANES

Probes/T (K)	ΔH_1^s (cal/mol)	ΔG_1^s (cal/mol)					ΔS_1^s (cal/mol)				
	343-383	343	353	363	373	383	343	353	363	373	383
Ethyl alcohol	-1572.13	1239.160	1338.047	1444.105	1500.691	1566.474	-8.196	-8.244	-8.309	-8.238	-8.195
1-Propyl alcohol	-1879.52	1000.833	1049.210	1114.874	1247.658	1321.841	-8.398	-8.297	-8.249	-8.384	-8.359
1-Butyl alcohol	-2888.50	531.021	579.948	687.228	798.969	920.472	-9.969	-9.826	-9.850	-9.886	-9.945
<i>n</i> -Hexane	-619.169	1047.345	1096.311	1153.329	1196.267	1239.920	-4.859	-4.860	-4.883	-4.867	-4.854
<i>n</i> -Heptane	-368.151	944.566	999.042	1026.753	1061.402	1105.159	-3.827	-3.873	-3.843	-3.833	-3.847
<i>n</i> -Octane	-463.984	751.368	796.583	824.897	857.291	898.518	-3.543	-3.571	-3.551	-3.542	-3.557

TABLE-4
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 THE PPBPDMA WITH ALCOHOLS AND ALKANES

Probes/T (K)	ΔH_1^s (cal/mol)	ΔG_1^s (cal/mol)					ΔS_1^s (cal/mol)				
	353-393	353	363	373	383	393	353	363	373	383	393
Ethyl alcohol	-732.666	1420.072	1499.724	1554.109	1617.672	1665.828	-6.098	-6.150	-6.131	-6.137	-6.103
1-Propyl alcohol	-902.455	1181.003	1231.810	1298.567	1364.020	1409.450	-5.902	-5.880	-5.901	-5.918	-5.883
1-Butyl alcohol	-1474.334	878.360	921.314	938.352	1065.328	1139.990	-6.665	-6.600	-6.468	-6.631	-6.652
<i>n</i> -Hexane	-356.428	1012.652	1057.866	1096.067	1134.713	1168.007	-3.878	-3.896	-3.894	-3.893	-3.879
<i>n</i> -Heptane	-480.635	931.925	975.398	1013.525	1054.448	1092.472	-4.002	-4.011	-4.006	-4.008	-4.003
<i>n</i> -Octane	-884.552	759.836	802.854	870.994	907.704	939.339	-4.658	-4.649	-4.707	-4.680	-4.641

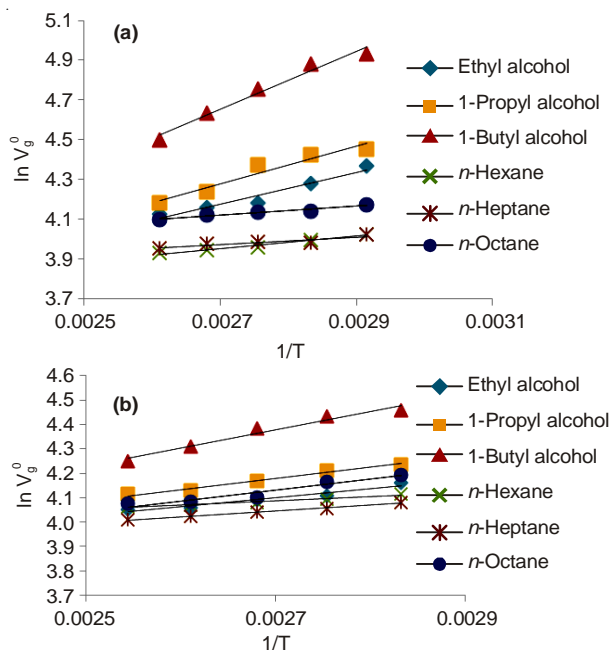


Fig. 2. Variation of the logarithm of the specific retention volumes (V_g^0 , mL/g) of alcohols and alkanes with the reciprocal of the absolute column temperature for (a) PPCPDMA and (b) PPBPDMA for ΔH_1^s (cal/mol)

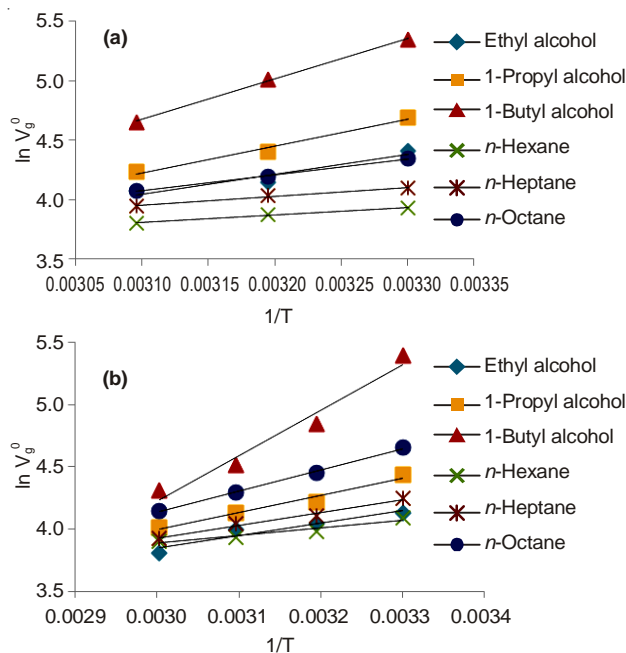


Fig. 3. Variations of the logarithm of the specific retention volumes (V_g^0 , mL/g) of alcohols and alkanes with the reciprocal of the absolute column temperature for (a) PPCPDMA and (b) PPBPDMA for ΔH_a (cal/mol)

TABLE-5
ADSORPTION ENTHALPY (ΔH_a , cal/mol) OF THE PPCPDMA WITH ALCOHOLS AND ALKANES AT 303-323 K

Probe	ΔH_a (cal/mol)
Ethyl alcohol	1578.624
1-Propyl alcohol	-305.612
1-Butyl alcohol	-5275.996
<i>n</i> -Hexane	3978.806
<i>n</i> -Heptane	4185.047
<i>n</i> -Octane	2214.343

TABLE-6
ADSORPTION ENTHALPY (ΔH_a , cal/mol) OF THE PPBPDMA WITH ALCOHOLS AND ALKANES AT 303-323 K

Probe	ΔH_a (cal/mol)
Ethyl alcohol	4067.976
1-Propyl alcohol	3648.104
1-Butyl alcohol	-6350.455
<i>n</i> -Hexane	4093.025
<i>n</i> -Heptane	2793.101
<i>n</i> -Octane	469.949

The partial molar heats of mixing at infinite solute dilution, ΔH_1^∞ , of the polymers-probe system were calculated by plotting $\ln(a_1/w_1)$ against $1/T(K^{-1})$ (Fig. 4) using eqn. 6. Tables 7 and 8 shows the experimentally obtained partial molar heats, ΔH_1^∞ . The ΔH_1^∞ values were positive and correspond with the expected values for polymer-non-solvent systems¹⁵.

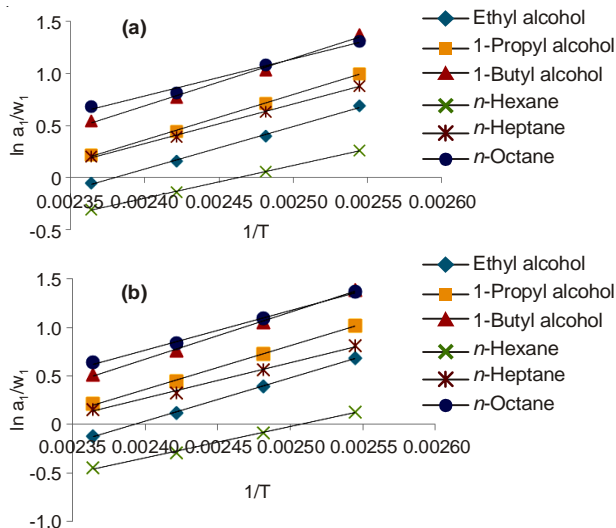


Fig 4. Weight fraction activity coefficient of the solute probes at infinite dilution (Ω_1^∞) with the reciprocal of the absolute column temperature for (a) PPCPDMA and (b) PPBPDMA with alcohols and alkanes

Probe	ΔH_1^∞ (cal/mol)
Ethyl alcohol	8127.227
1-Propyl alcohol	8624.772
1-Butyl alcohol	9105.03
<i>n</i> -Hexane	6244.346
<i>n</i> -Heptane	7506.687
<i>n</i> -Octane	7049.876

Probe/T (K)	ΔH_1^∞ (cal/mol)
Ethyl alcohol	8919.798
1-Propyl alcohol	8954.614
1-Butyl alcohol	9665.162
<i>n</i> -Hexane	6426.951
<i>n</i> -Heptane	7276.394
<i>n</i> -Octane	8109.94

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

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 Guillet and Purnel²³:

$$\begin{aligned} \Omega_1^\infty < 5 & : \text{good solvents} \\ 5 < \Omega_1^\infty < 10 & : \text{moderate solvents} \\ \Omega_1^\infty > 10 & : \text{poor solvents} \end{aligned}$$

Here, χ_{12}^∞ values greater than 0.5 represent unfavourable polymer-solvent interactions, while values lower than 0.5 indicate favourable interactions in dilute polymer solutions²⁴. Based on these values (Tables 9-12) and according to the Ω_1^∞ and χ_{12}^∞ , all of the probes under the T_g are poor solvents for both polymers. When the probes are above the T_g according to their Ω_1^∞ and χ_{12}^∞ values, they can dissolve the polymers. In Tables 9-12, the values increased as the number of carbons in the alcohols and alkanes increased. As shown in Tables 9-12, the interactions of both probes with the Ω_1^∞ and χ_{12}^∞ values are the same. In addition, the χ_{12}^∞ and Ω_1^∞ values did not depend on 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 increased²⁵.

Probes/T (K)	Ω_1^∞							
	393	383	373	363	353	343	333	323
Ethyl alcohol	1,996	2,523	3,415	4,772	6,351	8,711	16,853	28,767
1-Propyl alcohol	2,715	3,605	4,883	6,236	8,942	13,529	25,081	45,360
1-Butyl alcohol	3,946	4,475	5,796	7,777	10,772	16,732	33,835	66,738
<i>n</i> -Hexane	1,302	1,645	2,078	2,668	3,413	4,493	7,339	10,961
<i>n</i> -Heptane	2,412	3,094	4,019	5,380	7,417	10,056	15,549	23,233
<i>n</i> -Octane	3,696	5,166	6,917	9,563	13,600	19,352	31,715	50,560

Probes/T (K)	Ω_1^∞							
	393	383	373	363	353	343	333	323
Ethyl alcohol	1,980	2,698	3,670	5,155	7,139	11,980	23,467	33,812
1-Propyl alcohol	2,762	3,810	5,230	7,333	10,790	18,856	33,812	52,832
1-Butyl alcohol	3,993	5,413	7,433	10,759	16,484	27,197	52,832	6,971
<i>n</i> -Hexane	1,139	1,433	1,815	2,337	3,029	4,707	6,971	16,050
<i>n</i> -Heptane	2,251	2,895	3,768	5,010	6,740	10,372	16,050	30,169
<i>n</i> -Octane	3,927	5,229	7,046	9,275	12,906	19,606	30,169	

TABLE-11
 INTERACTION PARAMETERS (χ_{12}^{∞}) OF PPCPDMA WITH ALCOHOL AND ALKANE SYSTEMS.

Probes/T (K)	χ_{12}^{∞}							
	393	383	373	363	353	343	333	323
Ethyl alcohol	-0.703	-0.460	-0.148	0.197	0.495	0.823	1.495	2.043
1-Propyl alcohol	-0.384	-0.092	0.222	0.477	0.848	1.274	1.904	2.509
1-Butyl alcohol	0.006	0.140	0.409	0.713	1.050	1.502	2.218	2.909
<i>n</i> -Hexane	-1.238	-1.003	-0.767	-0.515	-0.265	0.015	0.511	0.918
<i>n</i> -Heptane	-0.606	-0.354	-0.088	0.208	0.535	0.846	1.289	1.699
<i>n</i> -Octane	-0.169	0.171	0.469	0.799	1.159	1.520	2.022	2.498

 TABLE-12
 INTERACTION PARAMETERS (χ_{12}^{∞}) OF PPBPDMA WITH ALCOHOL AND ALKANE SYSTEMS.

Probes/T (K)	χ_{12}^{∞}						
	393	383	373	363	353	343	333
Ethyl alcohol	-0.711	-0.393	-0.076	0.274	0.611	1.141	1.826
1-Propyl alcohol	-0.366	-0.036	0.29	0.639	1.036	1.606	2.203
1-Butyl alcohol	0.018	0.331	0.657	1.038	1.475	1.987	2.663
<i>n</i> -Hexane	-1.372	-1.141	-0.902	-0.647	-0.384	0.061	0.459
<i>n</i> -Heptane	-0.675	-0.421	-0.153	0.137	0.44	0.877	1.321
<i>n</i> -Octane	-0.109	0.183	0.487	0.769	1.106	1.533	1.972

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-hand side of eqn. 11⁹⁻¹⁵ against δ_1 . These values are shown in Tables 13 and 14. The solubility parameter of PPCPDMA was evaluated from either the slope or intercept shown in Fig. 5(a) and 5(b) (7.132 (cal/cm³)^{0.5} or 6.999 (cal/cm³)^{0.5} at 423 K, respectively). The solubility parameter of PPBPDMA was evaluated using either the slope

or intercepts shown in Fig. 5(c) and 5(d) (7.136 (cal/cm³)^{0.5} or 6.974 (cal/cm³)^{0.5} at 423 K, respectively). As shown in Tables 13 and 14, at 413 and 423 K, the solubility parameters of the two polymers are similar. These results occurred due to the similarity of the chemical properties of the polymers. When comparing the solubility values of PPCPDMA and PPBPDMA at different temperatures, the solubility parameters decreased with increasing temperature²⁶.

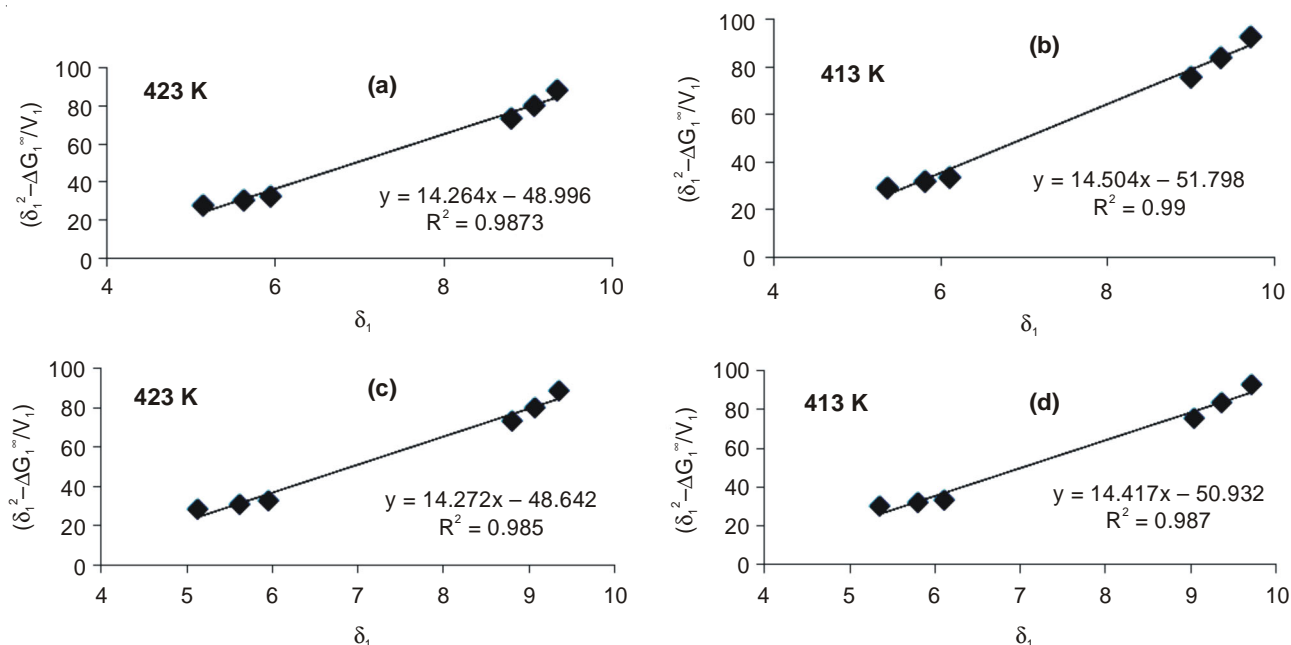

 Fig. 5. Variations of $(\delta_1^2 - \Delta G_1^{\infty}/V_1)$ with the solubility parameters of the solutes [δ_1 (cal/cm³)^{0.5}] at (a) 423 K and (b) 413 K for PPCPDMA and (c) 423 K and (d) 413 K for PPBPDMA

 TABLE-13
 SOLUBILITY PARAMETER [δ_2 , (cal/cm³)^{0.5}] OF PPCPDMA AT 423 AND 413 K

T (K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
423	14.264	48.996	7.132	6.999	0.987
413	14.504	51.798	7.252	7.197	0.990

TABLE-14
SOLUBILITY PARAMETER [δ_2 (cal/cm³)^{0.5}] OF PPBPDMA AT 423 AND 413 K

T (K)	Slope	Intercept	From slope δ_2	From intercept δ_2	r
423	14.272	48.642	7.136	6.974	0.985
413	14.417	50.932	7.208	7.136	0.987

Conclusion

Inverse gas chromatography (IGC) 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 PPCPDMA and PPBPDMA, such as the 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 the Flory-Huggins interaction parameters (χ_{12}^∞) at infinite dilution. The T_g was approximately 323 K for PPCPDMA and 333 K for PPBPDMA. According to the χ_{12}^∞ and Ω_1^∞ values, the probes solvated both polymers at T_g . In addition, the solubility parameter values of PPCPDMA, δ_2 , were determined to be 7.132 (cal/cm³)^{0.5} and 6.999 (cal/cm³)^{0.5} at 423 K and the solubility parameter values of PPBPDMA were determined to equal 7.136 (cal/cm³)^{0.5} and 6.974 (cal/cm³)^{0.5}, respectively, at 423 K from the slope and intercept, respectively, of the straight line obtained by plotting the left-hand side of eqn. 11 versus the δ_1 values of the probes.

Overall, the inverse gas chromatography technique can be successfully used because of the similar chemical properties of the two polymers and the thermodynamic data obtained by the inverse gas chromatography technique.

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