Thermodynamical characterization of poly (ethylene glycol) and tosylate functionalized poly(ethylene glycol) interaction with some nonpolar and polar solvents via inverse gas chromatography

FEYZA SESIGUR, DOLUNAY SAKAR DASDAN*, OZLEM YAZICI, FATIH CAKAR, OZLEM CANKURTARAN, FERDANE KARAMAN
Department of Chemistry, Yildiz Technical University, Istanbul 34210, Turkey

Tosylate functionalized poly(ethylene glycol) (PEG-Tos) which was synthesized via the tosylation of the corresponding poly(ethylene glycol) (PEG) with *p*-toluenesulfonyl chloride was thermodynamically characterized at temperatures in K between 303 and 373 by inverse gas chromatography technique (IGC)**.** The retention diagrams of n-hexane, n-heptane, n-octane, n-nonane, n-decane, dichloromethane, chloroform, acetone, tetrahydrofuran, ethyl acetate and ethanol on the PEG and PEG-Tos were plotted between these temperature ranges. Some polymer-solvent thermodynamic interaction parameters, such as weight fraction activity coefficient, Ω_1^∞, Flory-Huggins polymer-solvent interaction parameters, χ_{12}^∞ were determined for studied solvents at infinite dilution of PEG and PEG-Tos at temperatures above mentioned. Then, the partial molar heat of sorption, $\Delta\overline{H}_1^s$, the partial molar heat of mixing at infinite dilution, $\Delta\overline{H}_1^\infty$ and as well as the molar heat of vaporizations of solvents, $\Delta\overline{H}_v$ were determined. In addition, the solubility parameter of PEG and PEG-Tos δ_2 was determined at room temperature by extrapolation of the values of solubility parameters from studied temperatures to 298 K.

(Received July 23, 2014; accepted February 10, 2016)

Keywords: Poly (ethylene glycol), p-toluenesulfonyl poly(ethylene glycol), Inverse gas chromatography, Polymer-solvent interactions, Solubility parameter

1. Introduction

IGC technique has demonstrate to be useful in analyzing the thermodynamic interactions between substance and solvent. The interactions between one solvent and the polymer are usually characterized by the values of Flory–Huggins interaction parameter, while, in this direction, the pure compound solubility parameters are also quite useful [1]. The knowledge of solubility parameters is very important for a number of relevant applications, where the solubilization properties of systems involving polymers are of great importance, such as drug delivery [1], nanoparticle fabrication [2] and coating applications [3].

In this study, we aimed to understand the effect of tosylate on the thermodynamic properties of PEG. The retention diagrams of some solvents on the PEG and PEG-Tos were obtained by IGC, then, its thermodynamic interactions and solubility parameters with the studied solvents were determined.

2. Experimental

An Agilent Technologies 6890N Model gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents on prepared columns in this study. The synthesis procedure of PEG-Tos and IGC technique which includes packed column preparetion, carrier gas, solvent injection and other details were given in Ref 4.

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.

PEG, ($H(OCH_2CH_2)_nOH$) (M_n=400 g/mol, T_g= 4-8 ^{0}C) was purchased from Sigma-Aldrich. The studied solvents of analytic grade purity which is capillary GC grade, ≥ 99.9 % such as n-hexane (Hx), n-heptane (Hp), n-octane (O), n-nonane (N), n-decane (D), dichloromethane (DCM), chloroform (Ch), acetone (Ac), tetrahydrofuran (THF), ethyl acetate (EA) and ethanol (EtOH) were dried with molecular sieves and used without further purification.

3. Results and discussion

3.1. Thermodynamic Characterization of PEG and PEG-Tos by IGC

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [5-8].

$$V_g^0 = \frac{273Q(t_R - t_A)J}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate (set to 3.7 ml/min), T_r is column outlet temperature; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor, 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 equation [9]

$$\ln \Omega_1^\infty = \ln\left(\frac{273R}{V_g^0 p_1^0 M_1}\right) - \frac{p_1^0(B_{11} - V_1^0)}{RT} \quad (2)$$

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 parameter, χ_{12}^∞ given in the theories of Flory-Huggins polymer-solvent interaction parameters are defined in the following Eq.(3).

$$\chi_{12}^\infty = \ln\left(\frac{273Rv_2}{p_1^0 V_g^0 V_1^0}\right) - 1 - \frac{p_1^0(B_{11} - V_1^0)}{RT} \quad (3)$$

where v_2 is specific volume of the polymer.

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

$$\Delta\overline{H}_1^s = -R\left[\frac{\partial(\ln V_g^0)}{\partial(1/T)}\right] \quad (4)$$

where T is column temperature in K.

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

$$\Delta\overline{H}_1^\infty = R\left[\frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)}\right] \quad (5)$$

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

$$\Delta\overline{H}_v = \Delta\overline{H}_1^\infty - \Delta\overline{H}_1^s \quad (6)$$

The solubility parameter of the polymer, δ_2 is found by combining of the theories Flory-Huggins and Hildebrand-Scathard where is δ_1 solubility parameter of solvent [5,10]:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1^0}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT}\right) \quad (7)$$

3.2. Conclusions

The specific retention volumes, V_g^0 of the studied solvents were obtained experimentally from IGC measurements using Eq.(1). The retention volume diagrams of solvents on PEG and PEG-Tos were given in Fig. 1 (a) and Fig. 2 (a) for polar and Fig. 1 (b) and Fig. 2 (b) for nonpolar solvents between 303 K and 373 K, respectively.

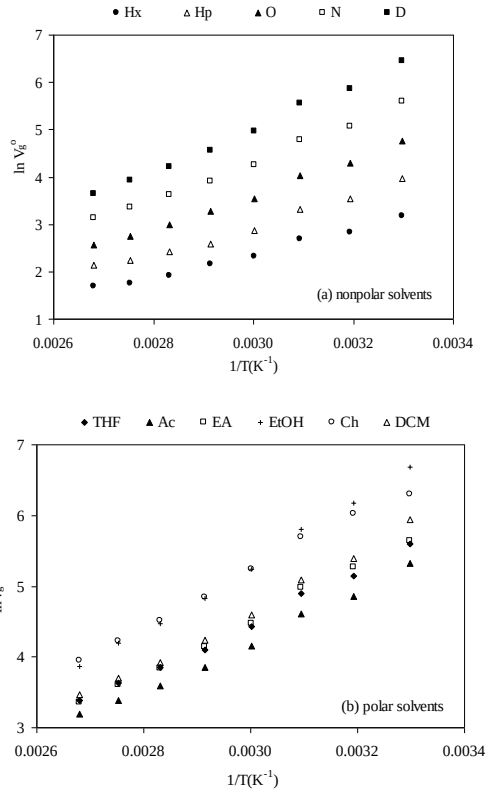

Fig. 1. The specific retention volume diagrams, V_g^0 of (a) nonpolar and (b) polar solvents on PEG between 303 K and 373 K

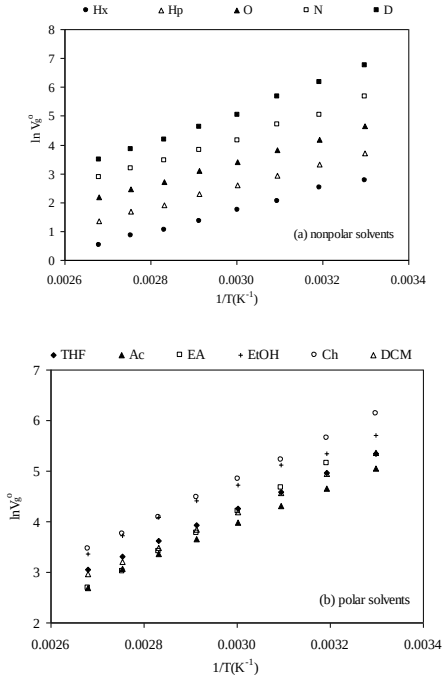

Fig. 2. The specific retention volume diagrams, V_g^0 of (a) nonpolar and (b) polar solvents on PEG-Tos between 303K and 373 K

These graphics are known as retention diagrams which resulted in linear relationships for all studied solvents. The linear relationship is an indication that equilibrium between solvents and adsorbents has been established at the temperature range within the linear portion. In this case, V_g^0 values play a major role in thermodynamic analysis due to describing the elution behavior of solutes on adsorbents.

The weight fraction activity coefficients of the studied solvents at infinite dilution, Ω_1^∞ were determined from Eq.(2) and results were given in Table 1 for PEG and Table 2 for PEG-Tos.

Table 1. The weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^∞ with PEG

T(K)	Hx	Hp	O	N	D	DCM	Ch	Ac	THF	EA	EtOH
303	30.4	55.4	61.7	84.5	103.7	1.0	1.5	5.2	5.0	5.7	6.0
313	29.0	54.1	59.2	80.0	97.2	1.2	1.0	5.6	5.2	5.4	5.9
323	23.1	44.6	47.3	61.5	71.9	1.2	1.0	5.0	4.6	4.8	5.2
333	23.9	46.7	49.1	63.8	75.0	1.4	1.1	5.6	5.1	5.4	5.7
343	20.5	43.8	13.4	56.5	67.2	1.5	1.2	5.6	5.1	5.4	5.6
353	19.7	37.0	38.7	50.0	58.6	1.6	1.2	5.4	4.9	5.2	5.4
363	17.5	32.1	34.9	43.5	50.7	1.6	1.3	5.1	4.6	4.9	6.6
373	14.6	26.9	30.3	37.9	44.4	1.6	1.3	4.7	4.5	4.8	4.9

Table 2. The weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^∞ with PEG-Tos

T(K)	Hx	Hp	O	N	D	DCM	Ch	Ac	THF	EA	EtOH
303	68.0	73.7	78.9	77.8	76.5	1.8	1.3	6.8	6.4	5.5	15.9
313	59.5	67.5	73.9	83.4	72.5	1.9	1.4	6.7	6.2	6.0	13.3
323	65.8	64.5	65.1	68.1	64.0	2.0	1.6	6.6	6.2	6.4	10.2
333	63.5	62.0	64.4	71.1	67.5	2.1	1.5	6.6	6.0	7.1	9.5
343	68.3	57.7	57.0	61.4	61.9	2.2	1.7	6.6	6.0	7.6	8.6
353	69.3	61.9	57.9	58.5	61.4	2.1	1.9	6.7	6.1	7.9	7.9
363	63.9	56.3	51.9	51.8	54.3	2.5	2.0	6.8	6.3	8.9	7.9
373	70.3	58.4	50.1	48.4	52.4	2.6	2.1	7.7	6.3	9.2	8.0

According to Guillet [10], the solvent is good if Ω_1^∞ <5 but it is poor if Ω_1^∞ >10. The values between 5 and 10 indicate moderately good solubility. The parameter Ω_1^∞ derived from fundamental relations of physical chemistry does not include any uncertainty coming from theoretical assumptions. The values of Ω_1^∞ found in this study suggest that studied n-alkanes are poor solvents for PEG and PEG-Tos. DCM and Ch are good solvents while EtOH, EA, Ac and THF are moderately good solvents for PEG. DCM and Ch are good, EtOH is poor while Ac, THF and EA are moderately good solvents for PEG-Tos. It was stated that p-toluenesulfonyl moiety on PEG affected the solution behaviour of PEG for some solvents while the temperature was increasing.

The PEG and PEG-Tos -solvent interaction parameters, such as Flory Huggins interaction parameters χ_{12}^∞ at infinite dilution were determined from Eq.(3) in the temperature range 303-373 K and were given in Table 3 for PEG and Table 4 for PEG-Tos.

Table 3. Flory-Huggins polymer-solvent interaction parameters, χ_{12}^∞ of PEG with the solvents

T(K)	Hx	Hp	O	N	D	DCM	Ch	Ac	THF	EA	EtOH
303.2	2.6	2.9	3.2	3.5	3.8	-0.6	-0.4	0.5	0.7	0.8	0.7
313.2	2.6	2.9	3.2	3.4	3.7	-0.5	-0.5	0.6	0.7	0.7	0.6
323.2	2.4	2.7	3.0	3.2	3.4	-0.5	-0.5	0.4	0.6	0.6	0.5
333.2	2.4	2.7	3.0	3.2	3.4	-0.3	-0.4	0.5	0.7	0.7	0.6
343.2	2.2	2.7	2.8	3.1	3.3	-0.3	-0.4	0.5	0.7	0.7	0.6
353.2	2.2	2.5	2.7	2.9	3.2	-0.2	-0.3	0.5	0.6	0.7	0.5
363.2	2.1	2.3	2.6	2.8	3.0	-0.3	-0.3	0.4	0.5	0.6	0.4
373.2	1.9	2.2	2.5	2.7	2.9	-0.3	-0.3	0.3	0.5	0.6	0.4

Table 4. Flory-Huggins polymer-solvent interaction parameters, χ_{12}^∞ of PEG-Tos with the solvents

T(K)	Hx	Hp	O	N	D	DCM	Ch	Ac	THF	EA	EtOH
303.2	3.0	3.2	3.3	3.4	3.5	-0.8	-0.2	0.8	0.9	0.8	1.6
313.2	2.9	3.1	3.3	3.5	3.4	-0.3	-0.2	0.7	0.9	0.9	1.5
323.2	3.0	3.1	3.2	3.2	3.3	0.1	-0.7	0.7	0.9	0.9	1.2
333.2	3.0	3.0	3.1	3.3	3.3	0.5	-0.4	0.7	0.8	1.0	1.1
343.2	3.0	2.9	3.0	3.2	3.6	0.1	0.0	0.7	0.8	1.1	1.0
353.2	3.0	3.0	3.1	3.1	3.2	0.5	0.1	0.7	0.8	1.1	0.9
363.2	2.9	2.9	2.9	3.0	3.1	0.2	0.2	0.7	0.9	1.2	0.9
373.2	3.0	2.9	2.9	2.9	3.1	0.2	0.2	0.8	0.8	1.2	0.9

The values of χ_{12}^{∞} confirm the evaluations on the values of Ω_1^{∞} since χ_{12}^{∞}<0.5 indicates good and χ_{12}^{∞}>0.5 indicates poor solubility. In the literature, χ_{12}^{∞} values of PEO-110000 ranges between +0.40 to +2.40 for studied alkanes such as pentane, Hx, Hp, O, N, D, undecane, dodecane at the temperature ranges between 340 and 400 K. These values indicate the poor interaction between alkanes and PEO. Values of χ_{12}^{∞} followed the same trend as V_g^0, slightly decreased as temperature increased except EA-PEG-Tos system and increased as number of carbons increased [11].

The partial molar heat, $\Delta\overline{H}_1^s$ of sorption of the solvents on the PEG and PEG-Tos were found from the slopes of the straight lines of $\ln V_g^0$ versus 1/*T* using Eq.(4) at the temperature range of 303-373 K and given in Table 5 for PEG and PEG-Tos. As well as the partial molar heats, $\Delta\overline{H}_1^{\infty}$ of mixing at infinite dilution were calculated from the slopes of the plots of $\ln\Omega_1^{\infty}$ versus 1/*T* in the temperature range 303-373 K using Eq.(5). The values of $\Delta\overline{H}_v$ calculated from Eq.(6) were also compared to the values of $\Delta\overline{H}_v$ for PEG and PEG-Tos.

Results for all of the studied solvents were given in Table 5.

Table 5. The partial molar heat of sorption, $\Delta\overline{H}_1^s$ (kJ/mol), the partial molar heat of mixing, $\Delta\overline{H}_1^{\infty}$ (kJ/mol) and molar heat of vaporization, $\Delta\overline{H}_v$ (kJ/mol) of PEG and PEG-Tos/solvents and the literature values of molar heat of vaporization, $\Delta\overline{H}_{VL}$ (kJ/mol) [12]

	PEG			PEG-Tos				
Solvents	$-\Delta\overline{H}_1^s$	$\Delta\overline{H}_1^{\infty}$	$\Delta\overline{H}_v$	$-\Delta\overline{H}_1^s$	$\Delta\overline{H}_1^{\infty}$	$\Delta\overline{H}_v$	$\Delta\overline{H}_{VL}$	T_b(K)
Hx	20.5	9.2	29.7	30.5	-0.4	30.1	28.8	341.9
Hp	25.1	9.2	34.3	31.4	2.9	34.3	31.8	371.6
O	29.7	10.9	40.6	33.0	6.3	39.3	34.3	398.8
N	33.4	10.4	43.8	37.2	7.1	44.3	36.8	424.0
D	38.0	10.9	48.9	42.2	6.7	48.9	39.3	447.3
DCM	33.4	-5.8	27.6	32.2	-4.6	27.6	28.0	313.0
Ch	33.0	-3.3	29.7	35.9	-6.3	29.6	29.7	334.3
Ac	28.8	0.8	29.6	30.9	-0.8	30.1	29.3	329.4
THF	29.7	1.2	30.9	30.9	0.4	31.3	29.7	339.1
EA	31.4	1.7	33.1	40.1	-7.1	33.0	32.2	350.3
EtOH	38.0	0.8	38.8	30.5	9.6	40.1	38.9	351.5

In case of nonpolar solvents on PEG-Tos, as the number of -CH_2- group increases, the partial molar heat of sorption becomes more exothermic than PEG. The molar heats of vaporization, $\Delta\overline{H}_v$ for all the studied polar and nonpolar solvents on PEG-Tos were higher than PEG. The molar heats of vaporization, $\Delta\overline{H}_v$ for all the studied polar and nonpolar solvents are comparable with literature values, indicating that the experimental values of the partial molar heat of sorption and the partial molar heat of mixing were appropriately responsible for thermodynamic analysis. Obtained values of enthalpies of vaporization are in acceptable consistency with the data available in literature. The agreement between $\Delta\overline{H}_v$ and $\Delta\overline{H}_{VL}$ is good for the solvents that boiling temperature is close to the average of the studied column temperatures. IGC is more reliable and basic method to obtaine molar heat of vaporization than other methods such as calorimetric techniques or application of the Clapeyron equation to the variation of vapour pressure with temperature.

The solubility parameters of PEG and PEG-Tos, δ_2 were determined from the slope and intercept of the straight lines plotted according to Eq. (7).

The magnitude of δ_2 was found as averaging of the values obtained from slope and intercept at studied temperatures.

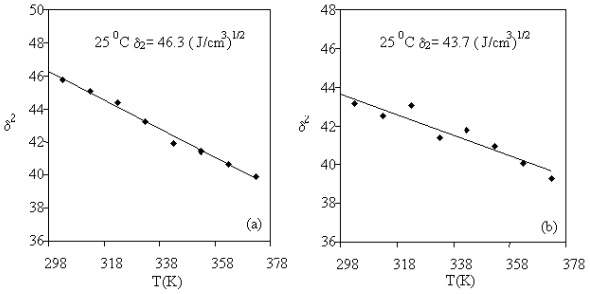

Fig. 3. δ_2 parameter for PEG (a) and PEG-Tos (b) at room temperature by extrapolating the average values of the δ_2 obtained at studied temperatures to 25 ^{0}C.

In Fig. 3 (a), δ_2 at room temperature was estimated approximately as 46.3 $(J/cm^3)^{1/2}$ by extrapolating the average values of the δ_2 obtained at studied temperatures to 298 K for PEG and 46.1 $(J/cm^3)^{1/2}$ calculated by group contribution method [13]. The solubility parameter obtained in this study is in agreement very well with calculated by group contribution method .The solubility parameter values of PEG with different molecular weights between 36.8 and 47.2 $(J/cm^3)^{1/2}$ given in literature [14,15].

In Fig. 3(b), δ_2 at room temperature was estimated approximately as 43.7 $(J/cm^3)^{1/2}$ for PEG-Tos by extrapolating the average values of the δ_2 obtained at studied temperatures to 298 K. No data have been found in the literature the solubility parameters of PEG-Tos.

4. Conclusions

The thermodynamic parameters of PEG and PEG-Tos were determined via IGC. It was seen that all studied nonpolar solvents do not interacted with PEG and PEG-Tos while DCM and Ch interacted good. The solubility parameter of PEG and PEG-Tos δ_2 was determined as 46.3 and 43.7 $(J/cm^3)^{1/2}$, at room temperature, respectively.

References

[1] U. Bertram, R. Bodmeier, Eur J Pharm Biopharm **63**, 310 (2006).
[2] C. Duclairoir, E. Nakache, H. Marchais, A. M. Orecchioni, Colloid Poly Sci **276**, 321(1998).
[3] C. M. Hansen, Prog Org Coat, **51**, 77 (2004).
[4] F. Sesigür, D. Sakar, O. Yazıcı, F. Cakar, O. Cankurtaran, F. Karaman, Journal of Chemistry, Article ID: 402325, (2014).
[5] G. S. Dritsas, K. Karatasos, C. Panayiotou, J Chromatogr A **1216**, 8979 (2009).
[6] O. Smidsrod, J. E. Guillet, Macromolecules, **2**(3), 272 (1969).
[7] S. Dincer, D. C. Bonner, Macromolecules **11**, 107 (1978).
[8] O. Yazici, D. Sakar, O. Cankurtaran, F. Karaman, J Appl Polym Sci, **122**(3), 1815(2011).
[9] R. C. Reid, J. M. Praustnitz, Properties of Gases and Liquids, McGraw Hill (1977).
[10] J. E. Guillet, New Developments in Gas Chromatography, Purnell, J.H. Ed.; Wiley-Interscience: New York (1973).
[11] Z. Y. Al-Saigh, Polymer **40**, 3479 (1999).
[12] B. A. Littlewood, Gas Chromatography, Academic Press/McGraw-Hill, New York (1970).
[13] D. W. V. Van Krevelen, Properties of Polymers, Elsevier Science BV (1997).
[14] C. D. Vaughan, J Soc Cosmet Chem **36**, 319 (1985).
[15] N. Takamiya, J. Kojima, Y. Tomari, Kog Kagaku Zasshi **62**, 1371 (1959).

*Corresponding author: dolunaykar@yahoo.com