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Inverse gas chromatographic characterization of poly(ethylene oxide)

Zeki Y. Al-Saigh*

Department of Chemistry and Geology, Columbus State University, 4225 University Avenue, Columbus, GA 31907-5645, USA

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Abstract

The inverse gas chromatography method was utilized to obtain the thermodynamic properties and the surface energy of a semicrystalline polymer, poly(ethylene oxide) (PEO). PEO was used as a stationary phase in the chromatographic column and 16 solutes with a different chemical nature were used as eluents such as alkanes, acetates and alcohols. Each family has provided information on the type and strength of the PEO–solute interactions. Alkanes showed endothermic interaction parameters χ_{12} and the molar heat of mixing in a temperature range of 70–130°C. Acetates and alcohols showed better interactions with the PEO layer and butanol was found to be the best solvent for PEO among all solutes used. The variation in molecular weight of PEO above 4000 g mol^{-1} showed no apparent effect on the interaction coefficients. The dispersive contribution of the surface energy of PEO was measured as a function of temperature, which ranged between 8.00 and 13.00 mJ m^{-2}, indicating a poor surface energy of PEO. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Inverse gas chromatography; Poly(ethylene oxide); Thermodynamic properties

1. Introduction

In recent years, literature has shown the inverse gas chromatography (IGC) method to be effective, accurate and versatile as a method for the characterization of polymer systems [1–3]. Its versatility comes from the fact that IGC can be applied successfully to the characterization of simple or complex systems such as amorphous, or crystalline polymers and polymer blends. It is selective because systems can be studied over a wide range of temperatures and compositions. For information on the features of IGC, the reader is referred to our earlier reviews [1–3].

Undoubtedly, poly(ethylene oxide) (PEO) as a water soluble polymer has properties with industrial and commercial interest. It is often used as a stationary phase for commercial GC columns. PEO possesses solid polymer–electrolyte properties upon mixing with an appropriate electrolyte salt [4,5]. Recently, this property has received much attention because it may lead to developing polymer–electrolyte batteries. Other applications range from adhesives, pharmaceuticals, cosmetics, packaging films, paper coatings, textile wraps and lubricant additives. Although there have been numerous applications of IGC on PEO during the 1970s and 1980s [6–15], and because of the conductivity properties of PEO, the goals of this paper are to revisit the application of the IGC method to high molecular weight PEO with the modifications cited in our earlier publication [16], and to extend this application to calculations of the surface energy of PEO and to affirm our earlier conclusion that IGC is capable of obtaining a wealth of information on a polymeric system.

2. Theory

2.1. Thermodynamics of IGC

The elution behavior on the chromatographic column was recently examined and a complete analysis of the thermodynamics of inverse gas chromatography was reported earlier [16]. By measuring the net retention time of solutes, flow rate of carrier gas, temperature of the column, mass of the polymer in the stationary phase, and the pressure of the carrier gas at the inlet and outlet of the column, the reduced specific retention volume, V_g^o, can be calculated from the chromatographic experiment. The term V_g^o describes the elution behavior of solutes on a chromatographic column, and it is defined as [1–3]:

$$V_g^o = \frac{\Delta TF 273.15}{T_r w} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \quad (1)$$

where $\Delta t = t_p - t_m$ is the difference between retention time

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* Tel.: +1-706-568-2075; Fax: +1-706-569-3133.

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of the solute t_p and of the marker t_m, F is the flow rate of the carrier gas measured at room temperature T_r, w is the mass of the stationary phase, and P_i and P_o are the column inlet and outlet pressures, respectively.

The term V_g^o, plays a major role in the calculation of the thermodynamic parameters and the surface energy. The surface interaction between the polymer and the solute is expressed in terms of the free energy of mixing ΔG_{mix} which is the key term in the miscibility of the polymer–solute system.

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2}$$

A negative value of ΔG_m indicates that the polymer–solute system is miscible. If ϕ_i is the volume fraction of the ith component, then the free energy of mixing as described by Flory–Huggins theory [17] is:

$$\Delta G_{mix} = RT\{n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi\} \tag{3}$$

where n_1 is the number of moles of the ith component, RT has its usual meaning and χ is a parameter which is inversely proportional to the absolute temperature. The parameter χ was introduced as an enthalpic contact parameter; the two logarithmic terms represent the (combinatory) entropy of mixing. The strength of the interaction between PEO, polymer (2) and the solute (1) is represented by the parameter χ_{12}, which was derived earlier and reported elsewhere [16].

$$\chi_{12} = \ln \frac{273.15R\nu_2}{V_g^o V_1 P_1^o} - 1 + \frac{V_1}{M_2\nu_2} - \frac{B_{11} - V_1}{RT}P_1^o \tag{4}$$

Eq. (4) has been routinely used for the calculation of χ_{12} obtained from the IGC experiments. V_1, P_1^o, M_2, ν_2, and B_{11} are the solute molar volume, the solute saturated vapor pressure, the polymer molecular weight, the polymer specific volume, and the second virial coefficient, respectively.

V_g^o can also be utilized for the calculation of the molar heat (enthalpy) of sorption of solutes absorbed by the amorphous layer of PEO (ΔH_1^s) as in the following equation:

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

The molar heat of mixing, ΔH_1^∞, of PEO–solutes can be calculated using the weight fraction activity coefficient of the solute at infinite dilution, Ω_1^∞, as follows:

$$\Omega_1^\infty = \frac{273.15R}{V_g^o P_1^o M_1}\exp\,[-P_1^o(B_{11} - V_1)]RT \tag{6}$$

2.2. Determination of surface energy of polymers

In general, the surface interaction of solutes with the polymer layer can be attributed to the interaction of dispersive forces or a combination of dispersive forces with H-bonding or with dipole–dipole forces. In the case of PEO, the polymer–solute interactions are due to dispersive forces when alkane solutes are used, dipole–dipole forces or a combination of dipole–dipole/dispersive forces when acetate solutes are used and H-bonding or a combination of H-bonding/dispersive forces when alcohol solutes are used.

From the chromatographic measurements, V_g^o of solutes (Eq. (1)) can be used to calculate the surface energy, γ_s. This method of characterization was first reported by Fowkes [18] who determined the surface energy of several components. Generally, the contribution of dispersive forces and all other types of forces can be added and expressed as the energy of adhesion as follows:

$$\gamma_a = \gamma^d + \gamma^{sp} \tag{7}$$

where γ^d is the contribution of dispersive forces and γ^{sp} is the contribution of specific interaction forces such as H-bonding, dipole–dipole, acid–base, etc.

The IGC method has been successfully applied in recent years to determine the surface properties of divided solids [19–28]. From the gas chromatographic measurements, V_g^o is determined by using Eq. (1) which can be related to the equilibrium constant K between the adsorbed solute and the polymer surface as follows:

$$V_g^o = KA \tag{8}$$

where K is the surface partition coefficient and A is the total surface area of the polymer stationary phase in the chromatographic column. Thermodynamically, the molar free energy of adsorption, ΔG_a can be related to V_g^o using the following relationship [29]:

$$\Delta G_a = -RT\ln V_g^o + C \tag{9}$$

where C is a constant depending on the weight and the specific surface area of the packing material and the reference adsorption state [30].

The energy of adhesion (Eq. (7)) is also related to the free energy of adsorption (Eq. (9)) as follows:

$$RT\ln V_g^o + c = 2Na\sqrt{\gamma_s^d\gamma_i^d} \tag{10}$$

where γ_s^d and γ_i^d are the dispersive components of the solid surface and the interactive solutes phase, respectively, N is Avogadro's number and a is the area of the adsorbed molecules (solutes).

In IGC experiments, a series of interactive solutes, like alkanes, can be injected into the chromatographic column in order to determine the dispersive surface energy, γ_s^d. A plot of ΔG_a or ($RT\ln V_g^o$) versus the number of carbons in the alkane series can be meaningful. Such a plot is linear and the slope of the straight lines will account for the incremental contribution by a CH_2 group to the free energy of adsorption (ΔG^{CH_2}).

Eq. (10) can be re-written to yield the dispersive surface energy as follows:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}}\left\{\frac{\Delta G^{CH_2}}{Na_{CH_2}}\right\}^2 \tag{11}$$

where γ_{CH_2} is the surface energy of a linear saturated hydrocarbon and a_{CH_2} is the area of one –CH2– group. Eq. (11) will be used to test the IGC method for obtaining the dispersive contribution to the surface energy of PEO.

3. Experimental

3.1. Materials

Three chemically different families of solutes were selected in this work. Decreasingly small amounts of a series of alkanes, acetates and alcohols were injected into the chromatographic column. This enabled us to obtain information regarding the strength and the type of interaction forces between PEO and the gaseous mobile phase. Solutes were selected to represent three classes of interactions with the PEO backbone; non-polar, dipole–dipole, and polar. A total of 16 solutes were purchased from Aldrich as chromatographic grade. Their purity was checked by gas chromatography prior to use. High molecular weight poly(ethylene oxide) was supplied by Union Carbide (South Charleston, WV) in a powder form as Polyox. Molecular weight determination was carried out using GPC. PEO was dissolved in hexafluoro-isopropanol and the columns were calibrated with PMMA standards. PEO has an average weight molecular weight of 1 100 000. The melting temperature of PEO was determined using modulated differential scanning calorimetry (TA Instrument 2100) which revealed a T_m value of 73.00°C. This T_m value is in agreement with the earlier observed m.p. of 72.70°C [31]. Chromatographic support, Chromosorb W (AW-DMCS treated, 60/80 mesh) was obtained from Analabs. Chromatographic columns were made in the laboratory from 1/4 inch copper tubing which was purchased locally. All copper columns were washed with methanol and annealed for several hours before use. One column loading is used in this work, 0.5681 g of PEO (7% wt/wt) was coated onto 7.9597 g of Chromosorb W. PEO was dissolved in hot acetonitrile and then deposited onto the solid support using the method reported previously [16].

3.2. Instrumentations and procedure

Chromatographic measurements were made using a modified Hewlett Packard 5730A gas chromatograph equipped with a thermal conductivity detector. The chromatograph was modified to allow continuous monitoring of the carrier gas flow rate, the inlet and outlet pressure, and the column temperature. These modifications along with the complete chromatographic procedure were reported in our earlier publications [32]. The continuous monitoring is important because it reduces the experimental error significantly in the four measurable parameters mentioned. This procedure yielded better controlled measurable quantities. The monitored parameters are usually measured over a period of 7 h and then their values were averaged. Since the PEO used in this study is semicrystalline, every effort was made to avoid recrystallization of PEO by keeping the chromatograph operational at all times. During the course of the experiments, the oven temperature was uniformly increased until a complete set of data of the whole study was obtained. Control of the mass of PEO in the stationary phase has been modified and a new method for coating the polymer was developed and recently reported [16]. A flow rate of 8 ml min^{-1} was used throughout this work in order to eliminate the effect of flow rate (kinetic) on V_g^o values. From our previous experiments, the flow rate of the carrier gas (nitrogen in this case) between 0 and 10 ml min^{-1} has no significant effect on the retention volumes. Flow rates above 10 ml min^{-1} may cause a considerable error in the retention volumes, particularly if helium is used as a carrier gas [33].

The chromatographic modifications were extended to include a completely automated data handling system. An analog/digital data acquisition board (IEEE-488) in the form of a Keithly-type digital multimeter was interfaced with a personal computer containing a second IEEE-488 board. This allowed for precise measurements of the retention times of the solutes injected into the chromatographic column. The chromatographic signal was analyzed as a function of time, and the data was stored for further thermodynamic calculations which were also performed by the PC. The retention of solutes on zero loading column (support only) were stored in a separate file and interpolated over a wide range of temperatures. These retention volumes were then subtracted from those measured on loaded columns. This procedure was used to correct for the effect of the 'inert' solid support on the retention volumes. This automated system was fast and ideal for routine IGC measurements.

4. Results and discussion

4.1. Specific retention volumes

Specific retention volumes V_g^o of 16 solutes having a different chemical nature were obtained on 7% PEO. These V_g^o values were corrected for the effect of the solid support and flow rate. A series of alkanes was used ranging from pentane to dodecane, to provide insight into the effect of the dispersive forces on the interactions between solutes and PEO as the number of CH_2 groups increases. Two series of four acetates and alcohols were selected to provide information on the dipole–dipole and H-bonding interaction forces, or the dual effect of these forces and the dispersive forces with PEO backbone. Table 1 shows the specific retention volumes of the three families over a wide range of temperatures (67–130°C). Retention volumes decreased as temperature increased for all solutes indicating that the interactions of solutes and, therefore, solubility of PEO in these solutes increase as temperature increases. On the other hand, retention volumes increased as the number of carbons increased

Table 1
Specific retention volumes, V_g^o, in a temperature range of 67–130°C

Solutes	67	77	87	107	117	127
Pentane	7.16	6.48	4.88	3.67	3.45	2.64
Hexane	9.36	6.49	6.12	4.161	3.53	3.26
Heptane	16.47	13.21	9.511	6.55	7.68	7.41
Octane	33.81	24.15	17.89	12.98	12.10	10.51
Nonane			36.19	24.35	19.07	16.09
Decane			59.88	42.20	31.55	25.54
Undecane			36.19	72.35	53.28	41.08
Dodecane				126.26	89.11	65.97
Methyl acetate	45.67	29.13	21.96	16.61	12.28	7.84
Ethyl acetate	41.53	50.07	42.62	21.37	16.15	10.67
Propyl acetate	61.85	76.94	54.35	34.62	25.94	18.47
Butyl acetate		145.47	101.75	59.13	43.27	31.47
Methanol	67.90	51.31	35.80	23.93	17.54	12.05
Propanol	80.83	56.78	22.68	22.169	16.36	10.78
Butanol				55.95	40.25	28.86

in the alkane series as a result of increasing the dispersive forces as the number of CH_2 groups increases. Dodecane showed the highest interaction with PEO among the alkane family. Plots of ln V_g^o versus the inverse of temperature for the three families in the temperature range 67–130°C are shown in Figs. 1–4. These plots are known as retention diagrams which resulted in linear relationships for all solutes except for ethyl and propyl acetate due to possible condensation at the injection port. The linear relationship is an indication that an equilibrium between solutes and PEO has been established at the temperature range within the linear portion. In this case, V_g^o values are amenable for thermodynamic analysis.

The acetate series showed no systematic increase with carbon number, as in the alkanes, due to the absence of the dispersive forces as the number of carbon atoms in the acetate backbone increases. However, butyl acetate showed a higher interaction than the other acetates, indicating higher dipole–dipole or a combination of dipole–dipole and dispersive interaction forces with PEO. Similarly, alcohols showed a similar trend to acetates with butanol having the highest interaction among the three families. It is apparent that butanol is the best solvent for PEO among the 16 solutes used due to the combination of H-bonding/dispersive forces. To help understand the interaction between PEO and solutes, the slopes of the straight lines in Figs. 1–4 may be meaningful. The slopes of these lines are translated into the molar heats of sorption of solutes into the PEO

Table 2
Molar heat of sorption, ΔH_1^s, of PEO–solutes at 100°C

Solutes	ΔH_1^s (kcal mole^{-1})
Pentane	−4.35
Hexane	−4.38
Heptane	−3.83
Octane	−5.12
Nonane	−5.73
Decane	−5.98
Undecane	−8.34
Dodecane	−9.56
Methyl acetate	−6.97
Ethyl acetate	−6.70
Propyl acetate	−5.97
Butyl acetate	−8.14
Methanol	−8.08
Ethanol	−8.60
Propanol	−8.23
Butanol	−9.74

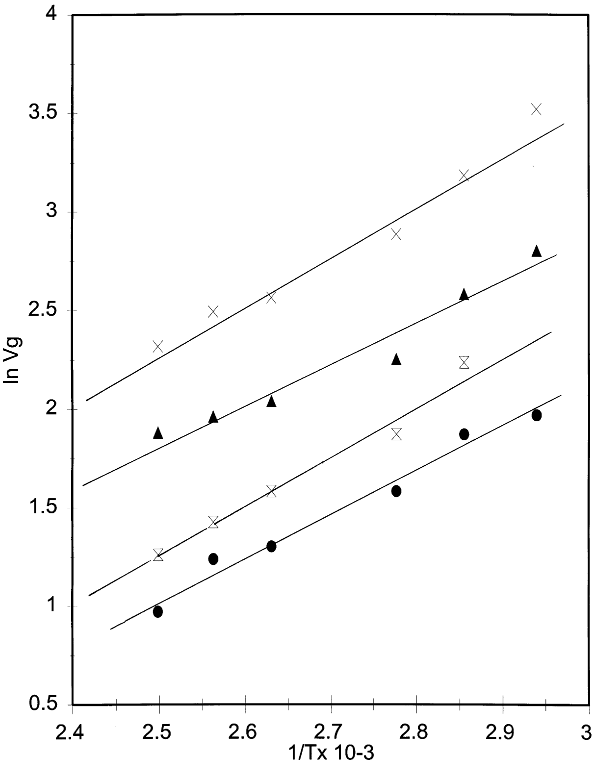

Fig. 1. Specific retention volumes, V_g^o, of pentane, hexane, heptane and octane in a temperature range of 70–130°C: (●) pentane, (⧖) hexane, (△) heptane, (×) octane.

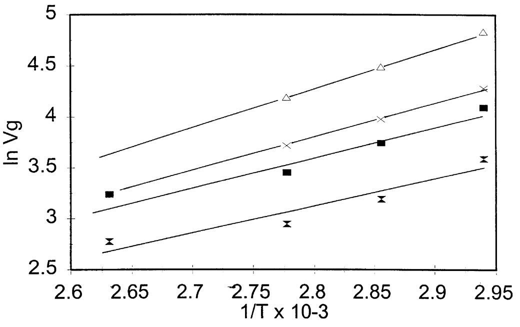

Fig. 2. Specific retention volumes, V_g^o, of nonane, decane, undecane, and dodecane in a temperature range of 70–130°C: (☒) nonane, (■) decane, (×) undecane, (△) dodecane.

layer according to Eq. (5). Accordingly, Table 2 shows the values (slopes) for ΔH_1^s at an average temperature of 100°C for the three families. In case of alkanes, as the number of CH_2 group increases, the molar heat of sorption becomes more exothermic. Acetates and alcohols showed more exothermic values than alkanes.

4.2. Interaction parameters and surface characterization

PEO–Solute interaction parameters, such as Flory–Huggins interaction parameters χ_{12} at infinite dilution of solute, were calculated using Eq. (4), in the temperature range 67–130°C. These calculations were limited to the availability of Antoine equation constants, these constants for the acetate and alcohol families were not available at the temperature range used in this work. Accordingly, χ_{12} was only calculated for the alkane family. The specific volume of PEO was calculated using the equation [34], [35]

$$\nu_2 = 0.9217 + 6.90 \times 10^{-4}(t - 70) \quad (12)$$

Table 3
PEO–solute interaction parameters, χ_{12}, in a temperature range of 67–130°C

Solute	67	77	87	107	117	127
Pentane	1.10	0.91	0.91	0.66	0.47	0.49
Hexane	1.76	1.80	1.55	1.36	1.26	1.07
Heptane	2.08	1.94	1.93	1.67	1.21	1.17
Octane	2.23	2.16	2.08	1.71	1.46	1.34
Nonane			2.15	1.79	1.67	1.53
Decane			2.41	1.93	1.84	1.70
Undecane				2.07	1.97	1.85
Dodecane				2.20	2.10	2.00

Table 3 shows the relationship of χ_{12} of alkanes with the number of carbons in the family and the temperature. Table 3 indicates values of χ_{12} ranging between + 0.40 to + 2.40 for all alkanes and the temperature range used. These values indicate the poor interaction between alkanes and PEO. Values of χ_{12} followed the same trend as V_g^o, decreased as temperature increased and increased as number of carbons increased. Endothermic excess heat of mixing, ΔH_1^∞, was also observed. Table 4 shows the values of the molar heats of mixing of alkanes which ranged from 2.92 to 5.00 kcal mol^{-1} which complimented χ_{12} values. Table 5 shows a comparison of χ_{12} values from several alkane–PEO systems measured by different groups. Our data appeared to agree well with others in spite of the difference in MW of PEO. Leung [8] observed similar results when the IGC method was applied to low molecular weight (1000–2000)

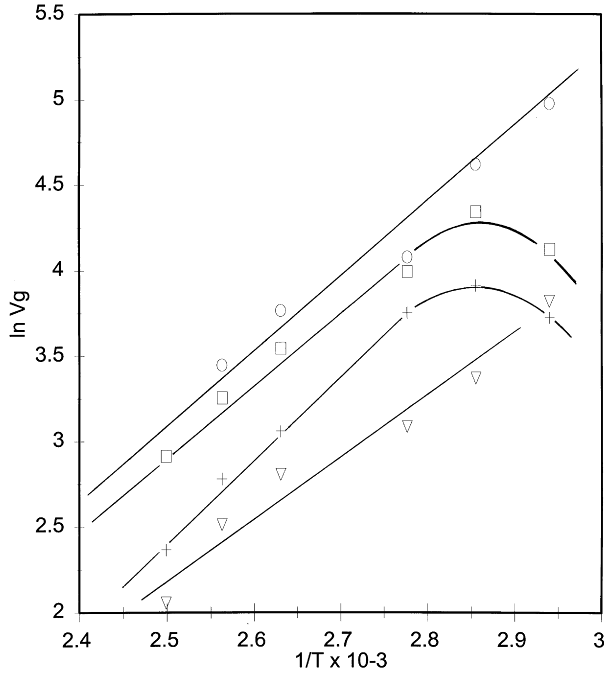

Fig. 3. Specific retention volumes, V_g^o, of acetates in a temperature range of 70–130°C: (▽) *n*-methyl acetate, (×) *n*-ethyl acetate, (□) *n*-propyl acetate, (○) *n*-butyl acetate.

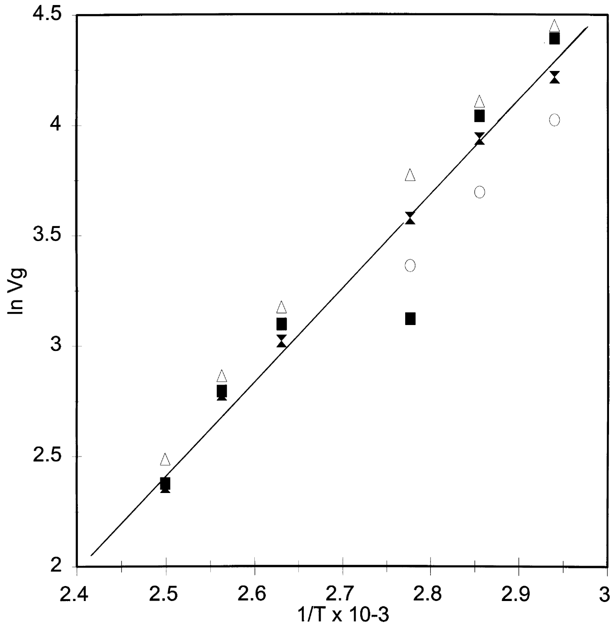

Fig. 4. Specific retention volumes, V_g^o, of alcohols in a temperature range of 70–130°C: (○) *n*-methanol, (△) *n*-ethanol, (■) *n*-propanol, (☒) *n*-butanol.

Table 4
Molar heat of mixing, ΔH_1^∞, of PEO–solute

Solutes	ΔH_1^s (kcal mole^{-1})
Pentane	2.92 at 97°C
Hexane	2.95 at 97°C
Heptane	4.70 at 97°C
Octane	4.17 at 97°C
Nonane	4.30 at 107°C
Decane	4.97 at 107°C
Undecane	3.36 at 117°C
Dodecane	3.11 at 117°C

methoxy-poly(ethylene oxide). Positive interaction coefficients were obtained ranging from 1.9 to 3.3 for alkanes n-C_5 to n-C_{12}.

There has been speculation as to whether or not the molecular weight of polymers has any effect on χ_{12} when the polymer is used in a chromatographic column [6,13]. Martire [13] has shown that IGC is a sensitive method for calculation of polymer molecular weights in the range of 10^4 by determining the constants of empirical equations derived from theoretical considerations. Since there is no direct relationship between V_g^o and the polymer molecular weight, varying the molecular weight of the polymer in the stationary phase may reveal information on the dependence of χ_{12} on the molecular weight of polymers in IGC experiments. To answer this question, a comparative data on PEO in Table 5 was compiled. We limited our comparison to alkanes only and avoided solutes with mixed interaction forces. Table 5 clearly demonstrates that the molecular weight of PEO in the stationary phase has no apparent effect on χ_{12} values. Molecular weight of PEO varied from 1000 to 1 100 000, while χ_{12} values ranged from 1.93 to 3.2, a difference of only approximately 1.00 for a wide range of molecular weights. This is in good agreement with the fact that the interaction of the mobile phase is occurring only within the surface layer and not penetrating into the bulk of PEO. Since PEO is a thin film of a few microns coated on a solid support, these data suggest that this information was obtained on the surface rather than the bulk properties of PEO. Cheng and Bonner [9] came to the same conclusion when they applied the IGC method to PEO of 4×10^6 in the temperature range 50–150°C. Klein and Jeberien [7] plotted the interaction parameters of PEO–solutes of different molecular weight ranging from small to 20 000. They obtained a sharp decrease in χ_{12} in the low molecular weight region (0–1000), then χ_{12} values tend to become independent of the molecular weight of the stationary phase. Our conclusion is affirmed by Marcille et al. [14] with their observation made by applying IGC to the polyisobutylene–alkane system. However, a recent publication by Wolf et al. [36] suggested otherwise. Using gas chromatography and a head space accessory on a poly(dimethyl siloxane)–toluene system, the χ parameter depended on the polymer molecular weight. It is not clear from this paper if infinite dilution or finite dilution gas chromatography experiments have been performed.

Table 5
Comparative data on the effect of molecular weight (MW) of PEO on χ_{12} of PEO–solutes

Solute	χ_{12}	MW	Temperature (°C)	Reference
Heptane	1.93	10 700	70	[25]
Decane	2.42	10 700	70	[25]
Decane	3.2	10 700	100	[25]
Heptane	2.08	1 100 000	68	This Work
Heptane	1.80	1 100 000	100	This Work
Decane	2.17	1 100 000	100	This Work
Hexane	1.83	10 800	70	[26]
Decane	2.18	10 800	70	[26]
Heptane	2.18	2000	67	[27]
Decane	2.59	2000	67	[27]
Heptane	2.98	1000	57	[27]

To calculate the dispersive component of the surface energy, plots of ($RT \ln V_g^o$) versus the number of carbons in the alkane series were generated for each temperature using Eq. (9). A linear relationship was obtained in all these plots and the slopes of the straight lines were computed as the free energy of desorption of a CH_2 group, $\Delta G_a^{CH_2}$. Utilizing Eq. (11), the dispersive component of the surface energy of PEO was calculated as a function of temperature. The cross-sectional area of an adsorbed CH_2 group, a_{CH_2}, is considered to be 6 Å [12,37,40]. The surface-free energy of a solid containing only CH_2 groups, γ_{CH_2}, is computed as a function of temperature as follows:

$$\gamma_{CH_2} = 36.80 - 0.058\, T \tag{13}$$

where T is the temperature (°C). Table 6 shows the relationship of the dispersive surface energy of PEO with temperature. It ranged from 8.57 to 13.70 mJ m^{-2} and showed a sharp decrease at a temperature above 100°C. This is in agreement with earlier results reported by Papirer et al. [37] who observed a decrease of the surface energy of treated $CaCO_3$ with increasing temperature. This observation was attributed to a different kind of adsorption of solutes on the surfaces; alkane vapors may be penetrating the surface of PEO at temperatures higher than the melting temperature of PEO. At these temperatures, the surface of PEO expands, thus the surface energy decreases and allows the vapor to penetrate the surface. Similar observations were

Table 6
Dispersive surface energies of PEO and γ_{CH_2} (mJ m^{-2})

Temperature (°C)	CH_2 surface energy	Surface energy, γ_s^d
67.00	33.45	8.57
77.00	32.95	11.04
87.00	32.45	15.22
107.00	31.45	17.49
117.00	30.95	14.61
127.00	30.45	13.69

Table 7
Comparative data on γ_s^d (mJ m^{-2}) of several polymers and mercury

Polymer	γ_s^d (mJ m^{-2})	Temperature (°C)	Reference
PEO	11.04	77	This Work
PVMK	26.47	77	[3]
Hg	200.00	20	[41]
PVC	41.50	20	[42]
PMMA	40.00	20	[42]
Polypropylene	28.90		[43]
Polyurethane	20.30		[43]
Polyethylene	33.10		[42]
Cl-doped Ppy	42.00		[39]
NO_3^--doped Ppy	61.20		[29]
$[Fe(CN)_6]^{4-}$-doped Ppy	106.00		[29]
PTEF	19.00	20	[42]

Ppy, polypyrrole.

reported on a silica carrying alkyl grafts [38]. We are able to compare values for surface energy of PEO with other polymers measured by methods such as NMR and FTIR. Table 7 shows comparative data on the surface energies of several polymers relative to mercury.

It is clear that PEO has a low value of surface energy at 77°C as compared to polymers containing carbonyl groups or vinyl groups. However, PTEF surface energy seems to be the closest value to PEO. It is clear from this table that surface energy values correspond well with the types of interaction sites available in the polymer backbone. Comparing these data with the surface energy of conducting polymers [29,39], the surface energy of PEO is very low. The dispersive component to the surface energy of several polypyrroles is in the range 30–60 mJ m^{-2}, while conducting polypyrroles have a much higher surface energy, 106 mJ m^{-2} [29,39].

5. Conclusion

The surface interaction of several solutes with PEO and the surface energy of PEO were characterized using the IGC method. Sixteen solutes of different chemical nature were used in this study and their retention volumes revealed information regarding the strength of their interaction with PEO. Alkanes interacted more weakly with PEO than acetates and alcohols. The latter showed better solubility with butanol being a better solvent for PEO. The molar heat of sorption and mixing of these solutes were calculated which complimented the interaction parameters data. Varying the molecular weight of PEO has no apparent effect on the interaction forces. The IGC method was able to compute the dispersive component of the surface energy of PEO which revealed a low value as compared to other polymers.

References

[1] Al-Saigh ZY. Trends in Polymer Science 1997;5:97.
[2] Al-Saigh ZY. Polymer News 1994;19:269.
[3] Al-Saigh ZY. Polymer International 1996;4:25.
[4] Visco SJ, Lin M, Armand MB, DeJongle LC. Mol Cryst Liq 1990;190:185.
[5] Gauthier M, Armand MB, Muller D. In: Skotheim TA, editor. Electroresponsive molecular and polymeric systems. New York: Marcel Dekker, 1988.
[6] Galin M. Polymer 1983;24:865.
[7] Klein J, Jeberien HE. Mackromol Chem 1980;181:1237.
[8] Leung Y. Polymer 1976;17:374.
[9] Cheng YL, Bonner DC. Macromolecules 1974;7:687.
[10] Fernandez-Berridi MJ, Guzman GM, Iruin JJ, Elorza JM. Polymer 1983;24:417.
[11] Chang YH, Bonner DC. J Appl Polym Sci 1975;19:2439.
[12] Dorris MG, Gray DG. J Colloid Interface Sci 1980;77:353.
[13] Martire DE. Anal Chem 1974;46:626.
[14] Marcille P, Audebert R, Quivoron C. J Chim Phys, Phys–Chim Biol 1975;72:78.
[15] Courval G, Gray DG. Macromolecules 1975;8:326.
[16] Al-Saigh ZY, Munk P. Macromolecules 1984;17:803.
[17] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[18] Fowkes FM. Ind Eng Chem Prod Res Dev 1967;56:40.
[19] Balard H, Papirer E. Progress in Organic Coating 1993;22:1.
[20] Papirer E, Schultz J, Turchi C. Eur Polymer J 1984;20:1155.
[21] Papirer E, Schultz J, Jagiello J, Baeza R, Clauss F. In: Mottola HA, Steinmetz JR, editors. Chemically modified surfaces. Amsterdam: Elsevier, 1992:334.
[22] Kuczinski J, Papirer E. Eur Polym J 1991;27:653.
[23] Papirer E, Roland P, Nardin M, Balard H. J Colloid Interface Sci 1986;113:6.
[24] Papirer E, Balard H, Vidal A. Eur Polym J 1988;24:783.
[25] Ligner G, Vidal A, Balard H, Papirer J. Colloid Interface Sci 1989;133:200.
[26] Filbert C. Diplome d’etudes approfondies. Mulhouse, France: Universite de Haute Alsace, 1989.
[27] Papirer E, Ligner G, Vidal A, Balard H, Mauss F. In: Leyden E, Collins WT, editors. Chemically modified oxide surfaces. New York: Gordon and Breach, 1990:361.
[28] Papirer E, Eckhardt A, Muller F, Yvon J, Mater J. Science 1990;25:5109.
[29] Chehimi MM, Abel M-L, Pigois-Landureau E, Delamar M. Synthetic Metals 1993;60:183.
[30] Meyer EF. J Chem Ed 1980;57:120.
[31] Painter PC, Shenoy SL, Bhagwagar DE, Fishburn J, Coleman MM. Macromolecules 1991;24:5623.
[32] Chen CT, Al-Saigh ZY. Macromolecules 1989;22:2974.
[33] Card TW, Al-Saigh ZY, Munk PJ. Chromatography 1984;301:261.
[34] Galin M. Macromolecules 1977;10:1239.
[35] Galin M. Macromolecules 1981;14:677.
[36] Petri HM, Schuld N, Wolf BA. Macromolecules 1995;28:4975.
[37] Schmitt P, Koerper E, Schultz J, Papirer E. Chromatographia 1988;25:786.
[38] Saint Flour C, Papirer E. J Colloid Interface Sci 1983;91:69.
[39] Chehimi MM, Pigois-Landureau E, Delamar MM. J Chim Phys 1992;89:1173.
[40] Papirer E, Balard H, Vidal A. Eur Polym 1988;24:783.
[41] Fowkes FM. Ind Eng Chem 1964;561:40.
[42] Wu S. Polymer interface and adhesion. New York: Marcel Dekker, 1982.
[43] Visco SJ, Lin M, Armand MB, DeJongle LC. Mol Cryst Liq 1990;190:185.