Dielectric and Chromatographic Characterization of Polyethylene Glycols as Stationary Phases

A. Y. El-naggar[a]; G. Turky[b]

[a] Evaluation and Analysis Dept., Egyptian Petroleum Research Institute, Nasr City, Egypt [b] Microwave Physics Dept, National Research Center, Egypt

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A.Y. EL-NAGGAR[a] and G. TURKY [b],*

[a]*Evaluation and Analysis Dept., Egyptian Petroleum Research Institute Nasr City, Egypt;* [b]*Microwave Physics Dept. National Research Center, Egypt*

Three types of polyethylene glycols of different molecular weights namely, 600, 4000 and 20000, were evaluated as liquid stationary phases in gas liquid chromatography. Thus, the retention mechanism for the studied polymer stationary phases, 15% by weight on chromosorb PAW and their thermodynamic parameters have been investigated via inverse gas chromatography. The effect of polymer molecular weight on their efficiency as liquid stationary phases for the gas chromatographic separation of different types of hydrocarbons is also studied. The dielectric constant of dilute solutions for the studied polymers as dissolved in solvent chloroform was studied corresponding to their polarities. Two different modes of clusters were determined due to the solute – solute and solute – solvent interaction through hydrogen bonds.

All studied polymers have higher performance for separation of cyclic and aromatic compounds. Good chromatographic separation of *n*-alcohols is obtained toward polyethylene glycol (PEG20000) of relatively higher molecular weight. The saturated hydrocarbons can be separated very efficiently using low molecular weight polyethylene glycol (PEG600).

Keywords: Polyethylene glycol; Stationary phase; Thermodynamic parameters; Inverse gas chromatography and dielectric constant

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* Corresponding author.

INTRODUCTION

The polyethylene glycols (PEGs) are ethylene oxide polymers which are represented by the following general formula: $HO—(—CH_2—CH_2—O—)_n—H$, where (n) the number of repeating monomer units. The PEGs are quite soluble in aqueous systems. X-ray analysis has revealed that the crystalline PEG may have two types of secondary dimensional structure. The low- molecular weight materials are thought to be characterized by a zigzag structure. There are many applications for these materials, they are used in pharmaceutical [1, 2] industry and widely used in cosmetic preparation.

Several years ago it was shown that a common gas chromatographic (GC) liquid phase such as PEG 20000 could be chemically bonded to diatomaceous earth supports [3]. This material was shown to be chromatographically active for petroleum compounds such as aromatic, n-alkenes and alcohols. Many authors [4 – 7] described the use of PEGs in the field of gas chromatography. The advantage of these column packing are that they are reasonably selective and low bleed, which are most important for our purposes. The study of the dielectric properties of these polymers is a good source of information concerning the structure of molecules and their polarity that correlates with their efficiency of separation in gas chromatography. The retention data obtained using gas – liquid chromatography (GLC) permits us to calculate some thermodynamic functions of solution including the heat of solution (ΔH) and the molar entropy (ΔS). The first reflects the interaction between the solutes and the studied polymers, and the latter is transferred from a gas to a liquid phase. ΔS of solution indicates a change in the entropy when two or more liquids are mixed.

The selectivity of a stationary phase in GLC is quantitatively estimated by a relative retention. Its logarithm is related to the Gibbs free energy of the phase transfer which may be divided into enthalpic and entropic terms. Thus the total selectivity of a stationary phase can be represented as the summation of enthalpic and entropic selectivities [3]. The enthalpic selectivity may be calculated using the principal of additivity [4].

In the present study we attempted to study the dielectric constant, of the investigated polyethylene glycol samples having different molecular weights, which reflects the polarities on the GC separation of petroleum compounds (polar, moderate and non-polar).

EXPERIMENTAL

Coating with Polyethylene Glycols

The stationary phases used for this purpose were polyethylene glycols having different molecular weights 600, 4000 and 20000 (obtained from Merck and used without further purification). The solid support chromosorb, P AW, was coated with 15% loading of the studied polymer stationary phases by a conventional technique of rotary evaporation. The polyethylene glycols were dissolved in the proper amount of chloroform and added to chromosorb P AW (100–120 mesh). The mixture was heated in a rotary evaporation while stirring till complete evaporation of chloroform. The coated support was dried at 120°C for 24 h.

Gas Chromatography (GC)

The studied polymer samples were subjected to an inverse GC technique with the aim of investigating their performance as stationary phases. In this respect, different solutes were used for this purpose. These solutes included mixtures of n-paraffin (C_6—C_9), cyclic and aromatic compounds (cyclohexane, benzene, toluene, ethylbenzene and cumene) and normal alcohols (C_1OH—C_4OH). The GC used was Perkin Elmer 8700 equipped with flame ionization detector (FID). Nitrogen gas was used as a carrier at a flow rate of $12\,ml\,min^{-1}$. A stainless steel column (7 ft length, 1/8 id) was packed with the investigated samples by charging under vacuum. The packed column was activated at moderate temperature (120–170°C), in a stream of nitrogen, according to the mixture recommended temperature of the polymer used.

The gas chromatographic analysis were carried out at the same conditions such as, solid support, loading level, temperature, flow rate of carrier gas (N_2), column dimensions.

Static Permittivity

The static permittivity ε_s was measured at 2 MHz using a dipolmeter type DM01 from "Wissenschaftlich-Technische Werkstätten" (WTW), Germany, to an accuracy of $\pm 1\%$. This instrument operates by the

superposition (beat) method, in which the oscillations of two high frequency oscillations are brought to superposition in a mixing section. After subsequent amplification, the resulting beats are brought to the screen of a cathode ray tube as the indicator. By this method it is thus possible to observe even fraction of 1 Hz beat frequency. The sample holding cell, with the liquid dielectric to be measured, and the variable measuring condenser connected in parallel to it are parts of one of the oscillators. By changing the measuring condenser the sum of both the capacitance values mentioned above is set so that the same frequency results as by the other oscillator (zero beat). The instrument was calibrated first using liquids of known static permittivity. Measurements were performed throughout the temperature range 20–40°C. The temperature of the cell was controlled by an ultra-thermostat through a jacket surrounding the cell.

RESULTS AND DISCUSSION

Characterization of the Studied Polymers

Dielectric Constant

The static dielectric constants ε_s, of dilute solutions for polyethylene glycols dissolved in chloroform were measured and illustrated graphically in Figure 1 at 20, 30 and 40°C *versus* PEG weight percent concentration. The static dielectric constant increases linearly as a function of concentration due to the higher polarity of the investigated polymers. This polarity is attributed to the effect of regular molecular orientation due to intermolecular hydrogen bond. It is also noticed that ε_s decreases gradually by increasing temperature. This seems to be in good agreement with the linear relation between ε_s and $1/T$, where T is the absolute temperature, found by Ikada *et al.* [8] for lower molecular weight PEGs. On the other hand, there is no detectable effect of molecular weight on static permittivity shown in Figure 1. This feature seems to be unreasonable considering that the main contribution to the dielectric polarization of PEGs may be due to the orientation polarization of its hydroxyl groups. It is reasonable to expect that higher molecular weight PEGs, having a fewer hydroxyl groups per cc, show smaller dielectric constant. So, it could be
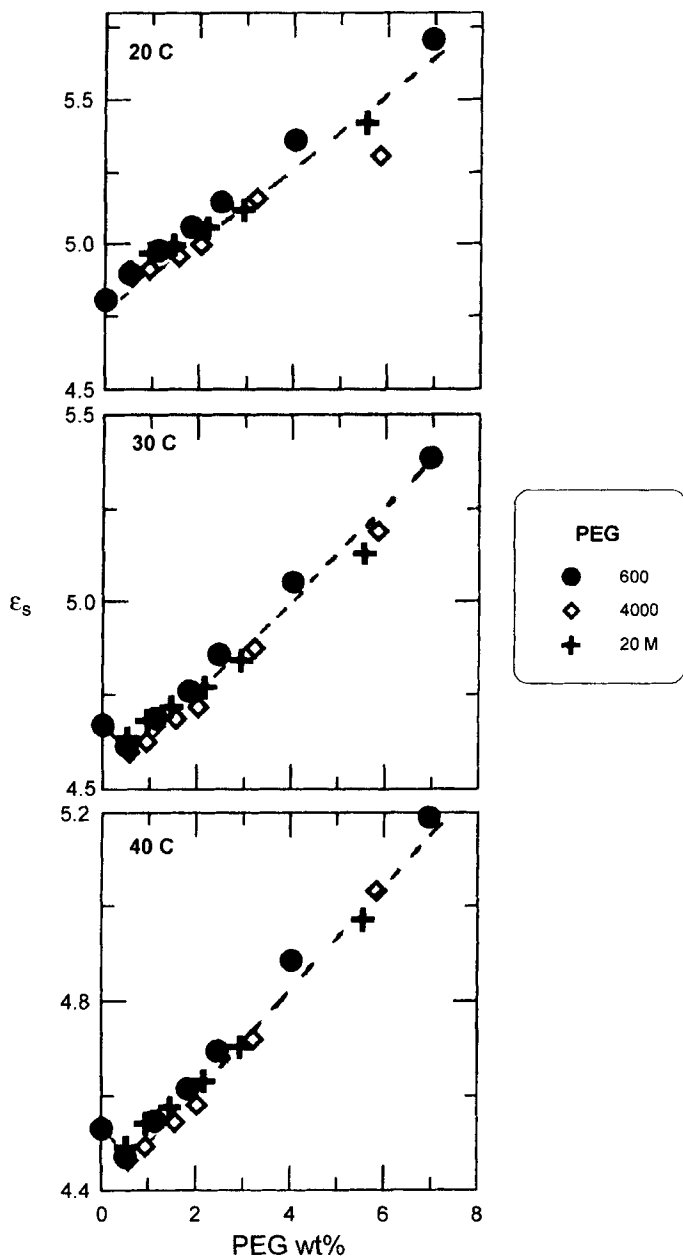
FIGURE 1 Static dielectric constant *versus* concentration X in wt.% at 20, 30 and 40°C for dilute solutions of studied PEGs dissolved in chloroform.

concluded that two types of hydrogen bonds exist here, one is between the hydrogen atom of the chloroform and oxygen atom contained in the PEGs chain represents solute – solvent interaction. The other is due to the hydroxyl groups of the PEGs chains represents solute – solute interaction. At very low concentrations of PEGs, ε_s first reduces and then increases linearly, at 30 and 40°C. This could be attributed to two different modes of association, circular and linear, which may reflect the influence of the solvent used. The transition from circular to linear mode of association is increasing with solute content and was found also for some other associated liquids [9 – 11].

Figure 2 illustrates the effect of PEGs concentration on the differential static permittivity $\Delta\varepsilon_s/x$, where Δ is the difference between solution and solvent and x is in wt fraction. It is clear from the figure that circular mode of association occurs at very dilute solution of PEG due to solute solvent interaction at higher temperatures 30 and 40°C which reduces the polarity. On increasing solute concentration, hydroxyl groups at the end of PEGs chains approach each other, thus reducing the solute – solvent interaction. In all studied polymer samples, the behavior at temperature 20°C shows an opposite trend in that manner corresponding to 30 and 40°C.

Thermodynamic Parameters

Thermodynamic parameters including heat of solution (ΔH), free energy (ΔG) and entropy (ΔS) may be useful in interpreting the mechanism of GC separation. In our work it is of interest because the separation process may take place by partition mechanism gas liquid chromatography. Heat of solution (ΔH) could be estimated by the following equation given by Greene and Pust [12]:

$$t_m = LAB/F \exp(-(\Delta H/RT)) \tag{1}$$

where t_m = retention time, L = linear velocity of zone, A = lintestial area of column, B = constant, F = gas velocity and ΔH = heat of solution.

The free energy of solution can be expressed as follows [13]

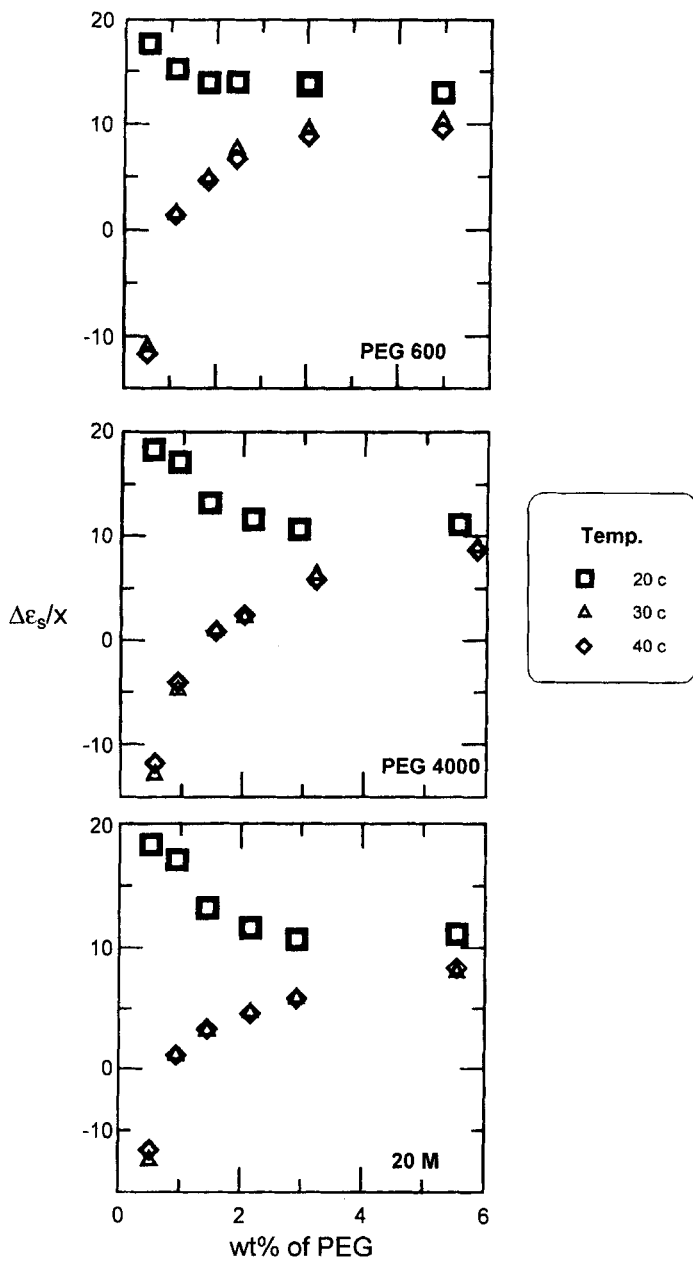$$(\Delta G) = RT\log V_g \tag{2}$$

FIGURE 2 $\Delta\varepsilon_s/x$ dependence on concentration X for all samples under investigation at different temperatures (x is in wt. fraction).

where T is the column temperature and V_g is the retention volume [14]. The entropy of solution can be calculated by knowing (ΔH) and (ΔG) due to

$$(\Delta S) = (\Delta H - \Delta G)/T \qquad (3)$$

Thermodynamic parameters (ΔH), (ΔG) and (ΔS) of the solutes normal octane, benzene and ethanol on the three studied stationary phases are listed in Table I. The advantage of the gas chromatographic technique compared to classical static equilibrium methods for obtaining thermodynamic data for mixing polymer and solutes lies mainly in the speed of obtaining data.

The effect of polymer molecular weight on the GC separation of *n*-paraffines, aromatics and *n*-alcohols could be illustrated by considering the thermodynamic parameters of these solutes on the used polymers. It is clear from Table I that, the thermodynamic parameters $(-\Delta H$ and $-\Delta S)$ for *n*-octane exhibit their maxima at the lower molecular weight PEG600. This behavior will be reflected by the high efficiency of GC separation of saturated hydrocarbons shown in Figure 3C.

It is considered as an ideal chromatogram as compared with A and B in the same figure. The enthalpy values of *n*-octane on PEGs20000

TABLE I   Thermodynamic parameters of the different solutes using the investigated PEGs

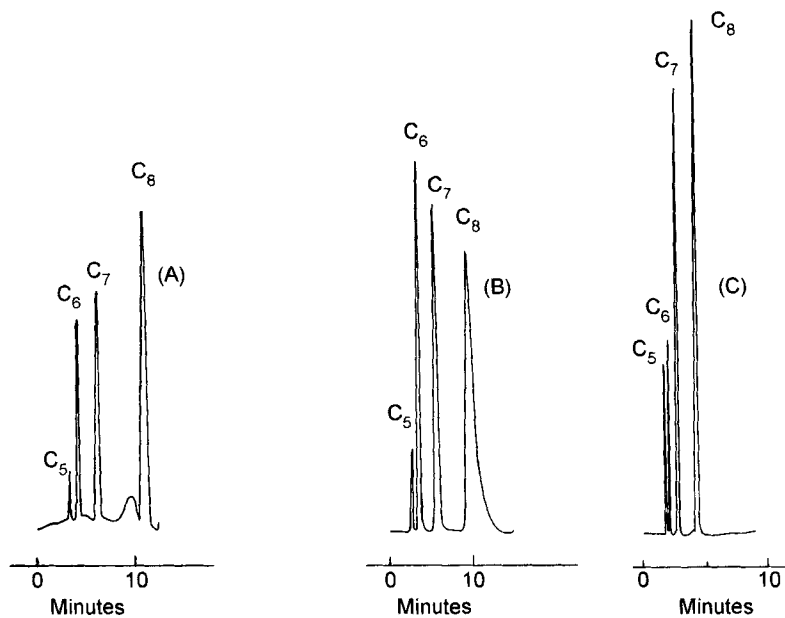| Parameter PEGs	$-\Delta H$ Kcal mol^{-1}	ΔG cal mol^{-1}	$-\Delta S$ cal mol^{-1}K^{-1}
n-Octane			
PEG 20000	0.254	1321	4.008
PEG 4000	0.314	1290	4.082
PEG 600	0.561	989	4.156
Benzene			
PEG 20000	0.077	1298	3.500
PEG 4000	0.096	1266	3.467
PEG 600	3.548	959	3.548
Ethanol			
PEG 20000	3.146	1289	11.890
PEG 4000	1.951	1317	8.762
PEG 600	0.849	1053	5.100

FIGURE 3 Separation of saturated hydrocarbons $(nC_5—nC_8)$ at 60°C on (A) PEG20000, (B) PEG4000 and (C) PEG600.

and 4000 indicate the lower interaction between n-paraffines and these two polymers compared with PEG 600. So, PEGs 20000 and 4000 can also separate n-paraffines but with peak tailing and long duration of analysis.

The negative enthalpy value $(-\Delta H)$ of benzene shows maxima at PEG600 which reflects the high interaction between them. The entropy values of benzene on the three polymer stationary phases are nearly comparable, but PEG600 shows relatively higher of its negative value. This will be reflected in the GC separation of cyclohexane and aromatic hydrocarbons as shown in Figure 4.

On the other hand, the thermodynamic parameters of ethanol, as an example of n-alcohols, exhibit maximal values of negative enthalpy and entropy on PEG20000 reflecting the high interaction and the high change in entropy between them. This behavior agrees well with the GC separation of n-alcohols as shown in Figure 5.
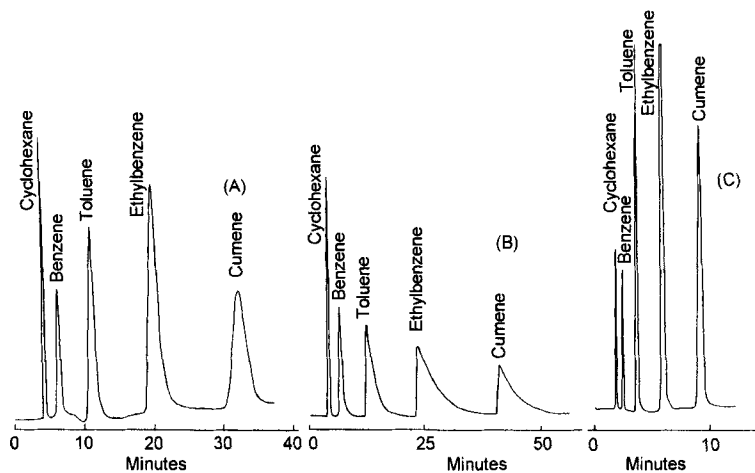
FIGURE 4   Separation of aromatic hydrocarbons (Cyclohexane, Benzene, Toluene, Ethyl benzene and Cumene) at 60°C on (A) PEG20000, (B) PEG4000 and (C) PEG600.
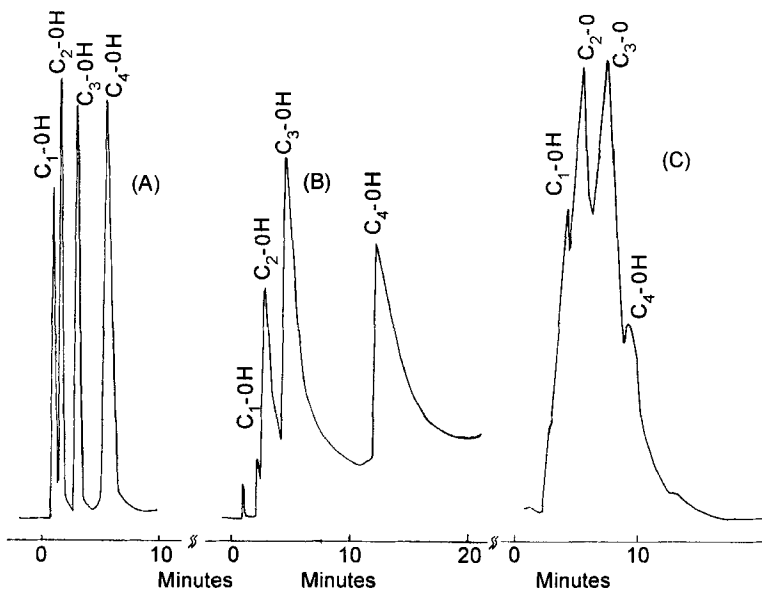
FIGURE 5   Separation of n-alcohols (nC_1—OH to nC_4—OH) at 100°C on (A) PEG20000, (B) PEG4000 and (C) PEG600.

Applications

Separation of Saturated Hydrocarbons

All studied polymer stationary phases can separate the saturated hydrocarbons (n-C$_5$—n-PC$_8$) but in different degrees of efficiency. The lowest molecular weight of PEG600 is the most efficient stationary phase for these separations as illustrated from its higher interaction with paraffins arrising from its enthalpy given in Table I. Also, Figure 3C shows that PEG600 separates normal paraffines (n-C$_5$—n-C$_8$) as an example of saturated hydrocarbons giving good resolution, peak sharpness, peak symmetry and lower duration of analysis. PEGs 20000 and 4000 can separate the saturated hydrocarbons but the separation is accompanied by peak tailing and long duration of analysis as shown in Figures 3A and B.

Separation of Cyclic and Aromatic Hydrocarbons

The three studied PEGs samples obtained gas chromatographic separation of cyclohexane and aromatic hydrocarbons (benzene, toluene, ethylbenzene and cumene) at column temperature 60°C. PEG600 shows the high efficiency of separation giving good separation, high resolution, peak sharpness and peak symmetry. The two PEGs20000 and 4000 give bad separation of aromatic hydrocarbons as shown in Figures 4A and B.

It is concluded that good separation of aromatic hydrocarbons is obtained towards the direction of the lower polymer molecular weight PEG600.

Separation of n-alcohols

Generally, PEGs can elute polar compounds such as normal alcohols, but the highest molecular weight PEG20000 succeeds in separation of n-alcohols, gives sharp peaks and peak symmetry and prevenstailing and broadening which occur in PEG4000 and PEG600 as shown in Figure 5. This is in agreement with their enthalpic values given in Table I indicating the higher interaction between PEG20000 and alcohols.

CONCLUSIONS

1. The static dielectric constant of the dilute solutions of the studied PEGs dissolved in chloroform indicates a comparable polarity without any detectable effect of molecular weight.
2. The low molecular weight polyethylene glycol, PEG600, was preferred in dealing with the separation of saturated hydrocarbons.
3. At higher column temperature (100°C) each sample of PEGs gives good resolution of cyclic and aromatic hydrocarbons. But at lower temperature (60°C), only the lowest molecular weight, PEG600 separates these compounds with high efficiency.
4. The good separation of polar compounds shifts toward the high molecular weight polyethylene glycol, PEG20000.

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