

Effect of Polymer Loading on the Electrical and Thermodynamic Properties in Relation to Gas Chromatographic Applications

A. Y. EL-NAGGAR,¹ G. M. TURKY²

¹ Egyptian Petroleum Research Institute, Nasr City, 11727 Cairo, Egypt

² Microwave Physics Dept., National Research Center, Tahrir Str., Dokki, Cairo, 12622 Giza, Egypt

Received 20 June 2000; accepted 22 February 2001

ABSTRACT: Different layers, 5, 10, 15, and 25% (w/W), of the three studied polyethylene glycols (PEGs) having different molecular weights, 600, 4000, and 20,000, were used for coating on chromosorb pink acid washed (P AW). The polarity and selectivity of the prepared packing columns and their thermodynamic parameters were determined via inverse gas chromatography. The effect of polymer-layer thickness on the polarity was studied dielectrically. The dependence of specific retention volume, enthalpy, and entropy upon the loading of polymer on support were also studied. In all investigated polymers, the loads 5 and 10% deactivate the support surface, resulting in a decrease in its capacitances, which reflects the polarity. The loads 15% PEG20,000 and 25% PEG4000 can elute *n*-alcohols and exhibit high efficiency of separation; however, in the case of PEG600, loading has to exceed 25% to be sufficient for eluting *n*-alcohols. The lower thickness of the coated polymers was preferred for good separation of saturated hydrocarbons and also for cyclohexane and aromatic hydrocarbons. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1709–1717, 2001

Key words: stationary phase; chromosorb; P AW; polarity; dielectric; gas chromatography

INTRODUCTION

Several polymers were extensively employed as liquid stationary phases in gas chromatography (GC).¹ Typical examples are silicon oils, polypyrrole, polyethylene, polyethylene oxides, and polyesters. It was discovered² that polymers that thermally depolymerize or give reproducible thermal cracking products could be analyzed by pyrolysis GC. Reviews on the subject were published by Guillet³ and also by Alishoev and Berezkin.⁴

Many years ago, the synthesis of coated polyethylene glycols (PEGs), especially of molecular weight 20,000 on chromosorb, and its surprising chromatography was reported.⁵ This material has become a popular GC stationary phase.⁶ The dielectric properties are considered to be a good tool to define the polarity of the studied stationary phases, which is an important factor of GC separation. The complex dielectric function, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, is defined as a factor between an outer alternating electric field $E(\omega)$ and the resulting polarization P of the medium, where for small electric field strengths^{7,8} $P(\omega) = [\epsilon^*(\omega) - 1]\epsilon_0 E$, ϵ_0 denotes the permittivity in vacuum and $\omega = 2\pi\nu$. The complex dielectric function or permittivity is a material property depending

Correspondence to: G. M. Turkey (gturky@hotmail.com).

Journal of Applied Polymer Science, Vol. 82, 1709–1717 (2001)
© 2001 John Wiley & Sons, Inc.

Table I Column Parameters of the Different Studied Polymer Loads

Polymer	Coating Solvents	Loading % (w/w)	Polymer Mass (G/1g support)
PEG600	Chloroform	5, 10, 15, 25	0.064, 0.111, 0.158, 0.252
PEG4000	Chloroform	5, 10, 15, 25	0.064, 0.111, 0.158, 0.252
PEG20,000	Chloroform	5, 10, 15	0.064, 0.111, 0.158

on frequency, temperature, pressure, and structure.

Layer thickness is an important factor not only from a basic viewpoint, but also because it affects polarity in GC practice. Kapila et al.⁹ studied the layer thickness of polymer on the silica gel of different surface areas. In a previous article,¹⁰ the effect of PEG20,000 loading on two types of silica gels was also studied. The calculated layer thickness varied considerably throughout a range of surface areas; it appeared that lower surface areas correlated with thicker polymer layers. Others investigated the properties of thin films on the support.^{11–13} Habboush et al.¹⁴ dealt with the comparative GC behavior of polyester stationary phases at different column temperatures.

In the present study, some preliminary results obtained using different layer thicknesses of three different PEGs as stationary phases are reported. The effect of loading on the polarity determined via dielectric properties and thermodynamic interactions between each layer thickness and some solutes of different polarities were also determined. The preferred layer thickness will be discussed critically within the framework of GC separation of saturated hydrocarbons, aromatic hydrocarbons, and *n*-alcohols.

EXPERIMENTAL

Materials

The polymer samples were subjected to inverse gas chromatographic (IGC) technique with the aim of investigating their performance as stationary phases. In this respect, the different eluants used for this purpose were reagent grade and used without further purification. The following solvents of very different characteristics were used: *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, benzene, toluene, ethylbenzene, cumene, methanol, ethanol, *n*-propanol, and butanol. The samples of polyethylene glycols 600,

4000, and 20,000 were obtained from Merck (Darmstadt, Germany).

Coating with Polymer and Column Preparation

The solid support chromosorb, pink acid washed (P AW) was coated with different layer thickness, 5, 10, 15 and 25% (w/W), of the studied polymer stationary phases by the conventional technique of rotary evaporation. The PEGs were first dissolved in a suitable solvent (chloroform) and deposited on the chromosorb by slow evaporation of the solvent with gentle stirring and heating in a rotary evaporation until complete evaporation of chloroform. The coated support was dried at 120°C for 24 h; the chromatographic support was packed with the aid of a mechanical vibrator into stainless steel columns 7 feet in length and 0.25 mm internal diameter. The packed column was activated at moderate temperature (120–170°C) in a stream of nitrogen according to the maximum recommended temperature of the used polymer. The weight and percentage of the stationary phases were determined by direct weighing. The column parameters are described in Table I.

Dielectric Measurements

In the course of dielectric measurements, voltage is applied across a sample between two conductive electrodes. The used measuring cell is a parallel plate that makes a sandwich containing the sample powder. It is simple to define the dielectric permittivity in relation to low-frequency measurements as the capacity of the condenser containing the material because the permittivity equals the ratio of the capacitance measured with sample in and sample out of the active electrode region. The sample-out capacitance is constant in using the same dimensions cell.

LCR meter bridge type AG-4311B from Ando Electric Co. Ltd., Japan, was used. This apparatus covers a measuring frequency range of 100 Hz to 100 kHz and a measuring signal level range of 1 MV to 5 V, and it can also make deviations and

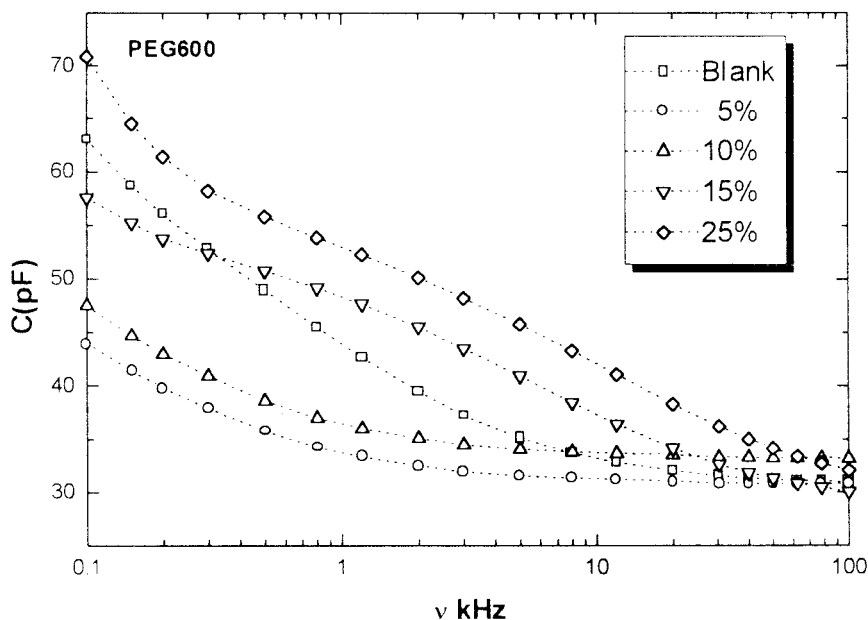


Figure 1 Capacity versus frequency in kHz for chromosorb P AW coated with different percentages of PEG600.

high-resolution measurements with relatively high accuracy. The internal measuring frequency can be selected from among a total of 31 values. The capacitance, C , and the dissipation factor, ($D = \tan \delta = \epsilon''/\epsilon'$), were displayed at the same time on the screen of the LCR meter. All measurements were carried out at room temperature.

Gas Chromatography

Measurements were carried out on a Perkin-Elmer 8700 GC equipped with flame ionization detector (FID). Nitrogen (oxygen-free) was used as a carrier gas at a flow rate of 12 mL min^{-1} . Flow rates were measured from the end of the column with a soap bubble flow rate. Methane as an unretained marker was used to correct the dead volume in the column. The retention time was directly measured by using the connected computer unit. At least four measurements were made for every molecular probe and for each temperature in each layer thickness of the columns. The injector and detector temperatures are 200 and 250°C , respectively. All mixed solvents were separated at an oven temperature of 60°C . The GC studies were carried out under the same conditions.

RESULTS AND DISCUSSION

Dielectric Measurements

The measured capacity (C) values in pico Farad (pF) for four loads between 0 and 25% w/W of

PEG600 as an example are illustrated graphically in Figure 1, as a function of frequency.

Figure 1 shows that C decreases gradually by increasing frequency, which reflects the polarity of the investigated sample. This range of frequency seems to represent a piece of the dielectric dispersion step between very high and very low frequency. No relaxation peak can be expected in this range of frequency in the dielectric spectrum $\epsilon''(\nu)$. It is observed that the chromosorb P AW exhibits a considerable amount of polarity. PEG600, when used at 5 and 10% (w/W) on the chromosorb, deactivated its surface, resulting in decreasing its polarity.

Figure 2 shows that, at the same load (15%), there is an increase in polarity by increasing polymer molecular weight. This is attributed to the increase in the number of oxygen atoms contained within the chain and the increase of molecular weight of the polymer. One can expect that the higher molecular weight polymer, PEG20,000, gives high efficiency of GC separation for polar compounds such as alcohols.

The capacity, C , in pF, at a spot-frequency point of 5 kHz, represented in Figure 3, versus polymer loading in weight percentage for the three investigated PEGs. The 5% load of all studied polymers shows the same polarity, which is lower than that of the raw support material, in spite of their difference in molecular weight. This may be due to the fact that 5% polymer load

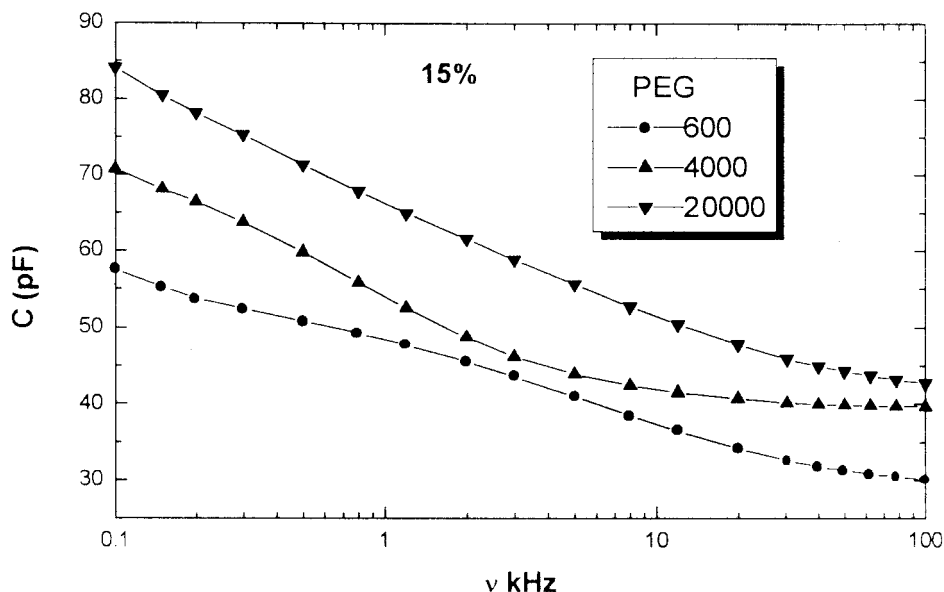


Figure 2 Capacity versus frequency for 15% of the three PEGs under consideration.

covers nearly the same considerable part of the support surface, which leads to the same decrease in surface area of support surface.

The raw material for the chromosorb is diatomite and is also known as diatomaceous earth or diatomaceous silica. Its skeleton consists primarily of hydrated microamorphous silica with some minor impurities, mainly metallic oxides,¹⁵ which were reduced during the process of acid washing. Martin¹⁶ showed that the surface area of the column packing prepared from the pink supports differed considerably because the concentration of liquid phase was varied from 0 to 25% by weight on the support. As liquid phase was added to the

chromosorb pink support, the surface area dropped from 3.9 m²/g with no liquid phase to 2.5 m²/g at 3% and then down to 0.9 m²/g at 25% liquid phase. The drop in surface area was initially very rapid as the smallest pores, which contribute the highest surface area, were filled first.

The surface of the siliceous materials is covered with the silanol group (Si—OH) and the siloxane group (Si—O—Si).^{17,18} The support alone exhibits some polarity due to the surface hydroxyl groups and the oxygen atoms of the siloxane groups. Coating the chromosorb *p* with 5 and 10% PEGs covers the surface of the chromosorb and reacts with maximum surface hydroxyl groups, resulting in deactivation of chromosorb P. The coating with 15 and 25% PEGs increases the polarity of the coated support due to the creation of the free hydroxyl groups and oxygen atoms of the PEGs itself, which form multilayers on the support surface.

Thermodynamic Parameters

The advantage of the GC technique compared to the classical static equilibrium methods for obtaining thermodynamic data of mixing polymer and solvents lies mainly in the speed of obtaining data.

Thermodynamic parameters, including enthalpy (ΔH), free energy (ΔG), and entropy (ΔS), may be useful in interpreting the mechanism of GC separation. In our work it is of interest to note that the separation process may take place by

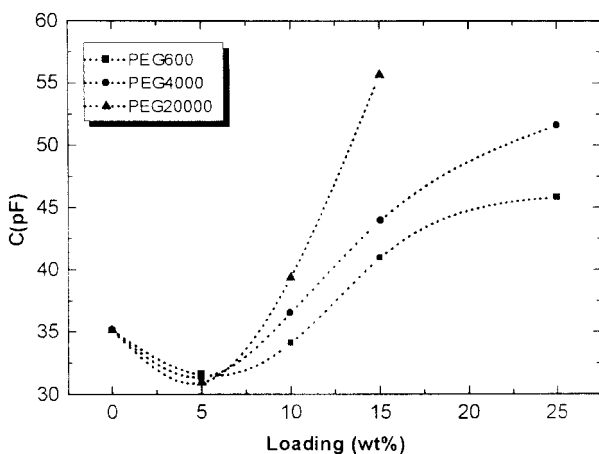


Figure 3 Effect of loading on the capacity *C* (pF) for the investigated PEGs at a spot frequency of 5 kHz.

Table II Thermodynamic^a Parameters at 80°C Using the Studied PEG Loads

Loading PEGs	5%			10%			15%			25%		
	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$
	a. n-Nonane											
20,000	1.63	1.21	8.04	1.66	1.18	8.05	1.72	1.32	8.62	—	—	—
4000	1.98	1.34	9.41	2.05	1.29	9.46	2.14	1.31	9.80	2.29	1.45	10.61
600	2.48	1.37	10.90	2.51	1.35	10.93	2.69	0.98	10.40	2.79	1.31	11.62
	b. Ethylbenzene											
20,000	0.67	1.09	4.98	0.73	1.11	5.19	0.95	1.25	6.20	—	—	—
4000	1.00	1.28	6.47	1.13	1.18	6.55	1.23	1.19	6.87	1.30	1.39	7.61
600	1.46	1.43	8.18	1.52	1.44	8.40	1.62	0.90	7.15	1.70	1.29	8.46
	c. n-Propanol											
20,000	3.62	1.30	13.94	4.05	1.33	15.26	4.68	1.41	17.25	—	—	—
4000	2.89	1.24	11.70	3.10	1.29	12.44	3.59	1.37	14.04	4.39	1.40	16.39
600	1.51	1.19	7.64	1.85	1.20	8.65	2.01	1.33	9.47	3.68	1.37	14.28

^a ΔH and ΔG in k cal mol⁻¹ and ΔS in cal mol⁻¹.

partition mechanism. Heat of solution (ΔH) could be estimated by the equation^{10,19,20}

$$t_m = LAB/F \exp(-\Delta H/RT) \quad (1)$$

where t_m is the retention time (min), L is the column length (cm), A is the internal area of column (cm²), B is the constant, F is the flow rate (in ml/min), R is the universal gas constant, and T is the absolute temperature of column (K).

The free energy of solution can be expressed as²¹⁻²³

$$\Delta G = RT \log V_g \quad (2)$$

where V_g is the retention volume.²¹ The entropy of solution can be calculated by knowing ΔH and ΔG from the relation

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

Thermodynamic parameters ΔH , ΔG , and ΔS of the different solvents, *n*-nonane, ethylbenzene, and propanol, on the studied stationary phases of different loadings are listed in Table II.

The effect of layer thickness of polymer on the GC separation of *n*-paraffins, aromatics, and *n*-alcohols could be deduced by considering the thermodynamic parameters of these solutes on each layer thickness of the used polymer.

The negative value of enthalpy ($-\Delta H$) of *n*-nonane (Table IIa) and ethylbenzene (Table IIb) increases as a function of increasing layer thick-

ness for each studied PEG. This indicates that the interactions increase in the case of the thicker polymer film. It is clear that, at the same layer thickness, the interaction between *n*-C₉ and PEGs increases with a decrease in the molecular weight of polymer; this was demonstrated from their enthalpy as shown in Table IIa.

The negative enthalpy values of propanol, given in Table IIc, increase with the increase of polymer loading. The enthalpy ($-\Delta H$) of 15% PEG20,000 exhibits the highest value, corresponding to its high dielectric polarity, shown in Figure 3, reflecting its high interaction with *n*-alcohols; the 25% of PEG4000 has a comparable enthalpy value as shown in 15% PEG20,000. The thin film (25%) of PEG600 exhibits a negative enthalpy value not sufficient to obtain the same degree of interactions obtained before.

It is observed that the low-molecular-weight PEG600 needs thicker thin film (higher than 25%) to obtain a sufficient interaction with alcohols, whereas for the higher molecular weight polymer PEG20,000, the 15% load was enough to obtain suitable interactions with alcohols.

The entropy values of *n*-nonane and ethylbenzene on the different thin films of the studied three PEGs (Table IIa,b) ranged from 8.042 to 11.618 for *n*-C₉ and from 4.980 to 8.464 for ethylbenzene. For the same thin film, $-\Delta S$ of *n*-C₉ and ethylbenzene slightly increase with decreasing polymer molecular weight. On the other hand, the ($-\Delta S$) value of propanol is higher and ranges from 7.637 to 17.246 and increases as a function

of polymer loading, reflecting its higher interaction. For the same thin film, the negative entropy decreases with a decrease in polymer molecular weight.

GC Applications

In the case of separation of saturated hydrocarbons, all studied thin films, 5, 10, 15, and 25%, of the three different PEGs can separate the saturated hydrocarbons (n -C₅— n -C₈) as shown for PEG4000 as a representative example, in Figure 4. This can be explained in their comparable enthalpy and entropy values given in Table IIa.

The low thin film 5% (w/W) of each studied polymer leads to good chromatographic resolution of n -paraffins with lower duration of analysis due to the lower polarity shown dielectrically in Figure 3. So, it can be concluded that there is no need for the thicker thin films of PEGs to separate n -paraffins.

All studied thin films, of the three PEGs, can separate cyclohexane and aromatic hydrocarbons. Thus 10% (w/W) load of each PEG exhibits good GC separation of cyclohexane and aromatic hydrocarbons (benzene, toluene, ethyl benzene, and cumene), resulting in high resolution and sharp and symmetric peaks, as shown in Figure 5. The cyclohexane and benzene, toluene, and xylene (BTX) mixture show some polarity, considering the presence of cyclic ring and also the three double bonds inside the ring; their elution on PEG600 takes the shortest time because it exhibits the lower polarity in comparison with the other two polymers.

The order of elution of alcohols from the investigated PEGs will differ with changes in the amount of polymer phase. This may be due to adsorption of solute on the surface of the stationary phase as well as on the surfaces of the support. There are two types of hydrogen bonding sites in chromosorb: the silanol, where the group is the proton donor in the hydrogen bond, and the siloxane, where the group acts as a proton acceptor. The GC separation of alcohols depends on the extent of adsorption of alcohols on the coated support, which also depends on the strength of the hydrogen bond that the alcohol forms with the surface hydroxyl groups. The 5, 10% of PEG20,000, 5, 10, 15% of PEG4000 [shown as an example in Fig. 6(a,b)], and 5, 10, 15, 25% of PEG600 loads to a considerable tailing for alcohols. This is because of the hydrogen bond formation during the elution of alcohols, resulting in

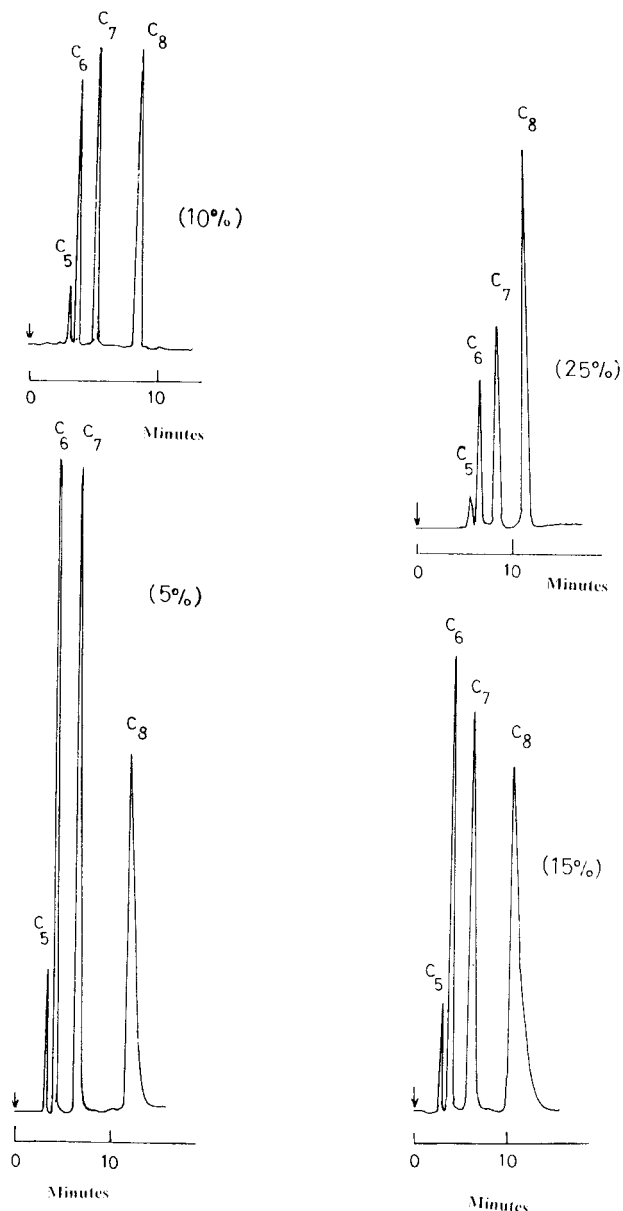


Figure 4 Gas chromatographic separation of n -paraffins at 60°C on PEG4000 of different loadings.

this peak tailing and the noticed peak asymmetry shown in the figure. The observed tailing of these lower loads may be due to their lower polarities and lower interactions, as previously explained. On the other hand, 15% PEG20,000 and 25% PEG4000 [Fig. 6(a,b)] are the most selective loadings for the separation of n -alcohols and exhibit high efficiency of GC separation.

It can be concluded that the thin film 15% PEG20,000 is quite enough to separate polar substances (n -alcohols). This agrees very well with the relatively higher polarity of the 15%

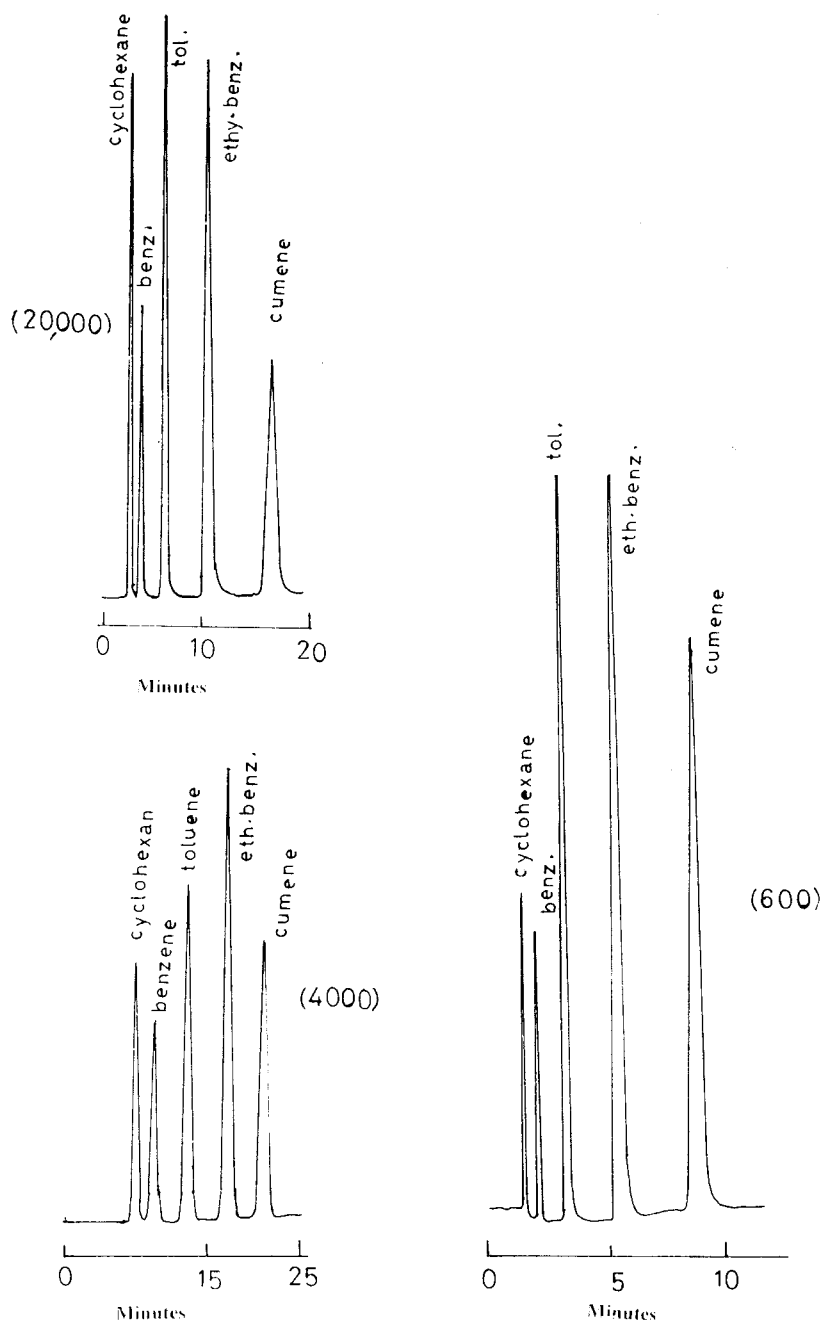


Figure 5 Gas chromatographic separation of cyclohexane and aromatic hydrocarbons at 60°C on 10% of PEG (a) 20,000, (b) 4000, and (c) 600.

PEG20,000 shown in Figure 3, leading to higher interaction with *n*-alcohols. This produces good GC separation. On the other hand, the load 25% PEG4000 gives a good GC separation of *n*-alcohols but the lower molecular weight polymer PEG600 needs thin film higher than 25% to be sufficient to separate *n*-alcohols with good enough resolution.

CONCLUSION

The polarity of 5, 10% (w/W) of all studied PEGs is lower than that of the chromosorb P. The 5% load of all investigated PEGs shows the same polarity independent of their molecular weights. This is attributed to the same support surface coverage. The lower loading, 5%, of each

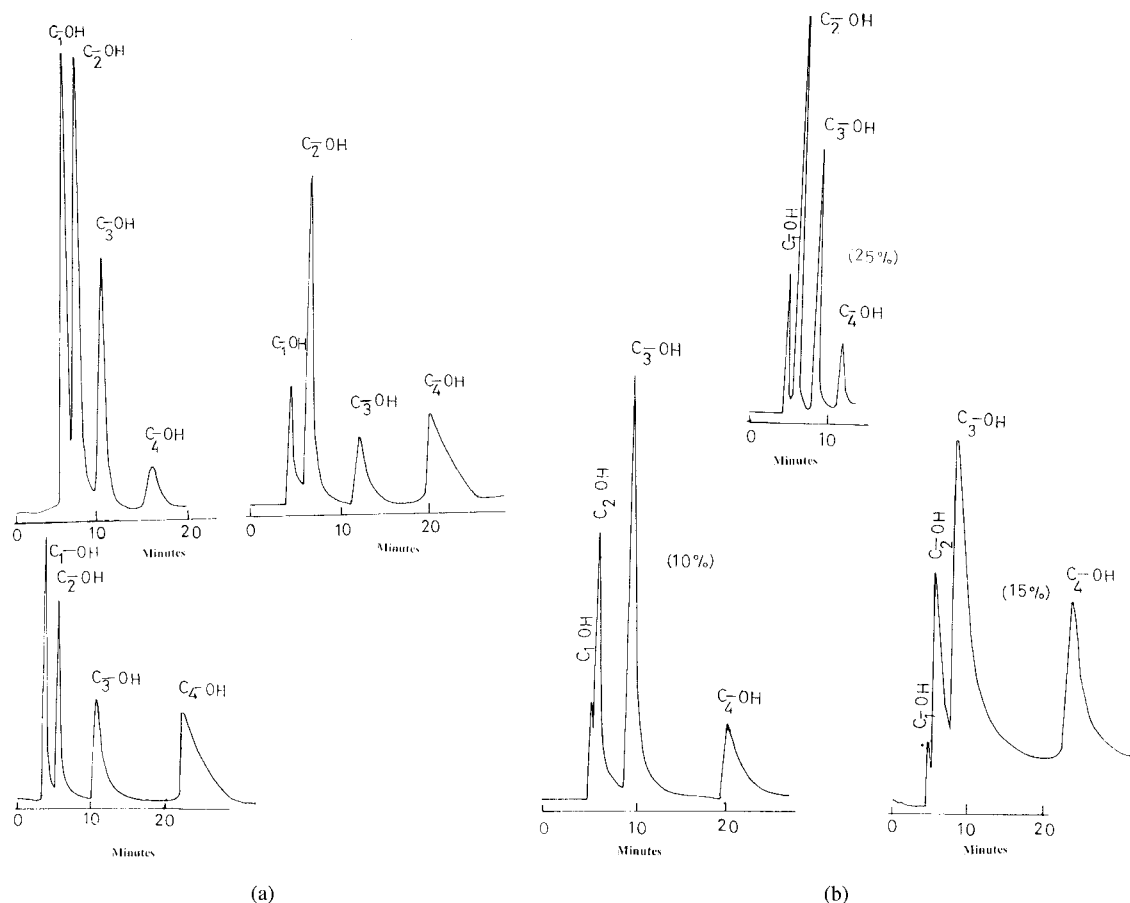


Figure 6 (a) Gas chromatographic separation of *n*-alcohols on 5, 10, and 15% PEG20000. (b) Gas chromatographic separation of *n*-alcohols on 10, 15, and 25% PEG4000.

polymer under investigation was shown to be enough for good GC separation of saturated and aromatic hydrocarbons. The loads 15% of PEG20,000 and 25% of PEG4000 are quite enough to exhibit a high efficiency of alcohol separation. PEG600 needs higher than 25% to be enough for eluting alcohols.

REFERENCES

- Hailan, G.; Wallace, G. *Anal Chem* 1989, 16(3), 198.
- Guillet, J.; Wooten, W.; Comb, R. *J Appl Polym Sci* 1960, 3, 61.
- Guillet, J. E.; *Soab Chem Specialties* 1965, 41, 145.
- Alishoev, V. R.; Berezkin, V. G. *Russ Chem Rev* 1967, 36, 545.
- Aue, W. A.; Hastings, C. R.; Kapila, S. *J Chromatogr* 1973, 77, 299.
- Karasek, F. W.; Hill, H. H. *Res Dev* 1975, 26, 30.
- Boettcher, F. *Theory of Dielectric Polarization*; Elsevier: Amsterdam; Vol. II, 1978.
- Schoenhals, A. *Dielectric Spectroscopy on the Dynamics of Amorphous Polymeric Systems*; Application note no. 1; *Dielectric Newsletter*, November 1999.
- Kapila, S.; Aue, W. A.; Augl, J. M. *J Chromatogr* 1973, 87, 35.
- Al-Fadly, A. M.; Faramawy, S.; El-Naggar, A. Y.; Youssef, A. M. *Sep Sci Technol* 1997, 32, 2993.
- Vetrova, Z. P.; Karabonov, N. T.; Yashin, Ya. T. *Chromatographia* 1977, 10, 341.
- Vetrova, Z. P.; Vyakhirev, D. A.; Karabonov, N. T.; Maidatsenko, G. G.; Yashin, Ya. I. *Chromatographia* 1975, 8, 643.

13. Rayss, J.; Wikkiewicz, Z.; Waksmundzki, A.; Dabrowski, R. *J Chromatogr* 1980, 188, 107.
14. Habboush, A. L.; Farroha, S. M.; Kreisha, A. Y. *High Res Chromatogr* 1991, 14, 242.
15. Ottenstein, D. M. *J Gas Chromatogr* 1963, 1(4), 11.
16. Martin, R. L. *Anal Chem* 1961, 33, 347.
17. Klein, P. D. *Anal Chem* 1962, 34, 733.
18. Lowen, W. K.; Broge, E. C. *J Phys Chem* 1961, 65, 16.
19. Green, S. A.; Pust, H. *J Phys Chem* 1958, 62, 55.
20. Munk, P.; Hattan, P.; Du, Q.; Abdel-Azim, A.-A. A. *J Appl Polym. Sci, Appl Symp* 1990, 45, 289.
21. Kessaissa, Z.; Papirer, E.; Donnet, J. B. *J Chromatogr* 1980, 196, 481.
22. Munk, P. *Polym Prep* 1991, 32, 515.
23. Faramawy, S.; El-Fadly, A. M.; El-Naggar, A. Y.; Youssef, A. M. *Surf Coat Technol* 1997, 90, 53.