Selectivity of Polymers as Liquid Stationary Phases in Gas Chromatography

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Abstract: The selectivity of three types of Polymers of different polarities namely, polyethylene glycol 20M, OV-101 and OV-275 were evaluated as liquid stationary phases in gas liquid chromatography. Thus, the retention behavior for the studied polymer stationary phases and their thermodynamic parameters have been investigated via inverse gas chromatography. The application of polymers on their separation efficiency of hydrocarbons, esters and alcohols is also studied corresponding to their polarities. All studied polymers have higher performance for separation of paraffinic hydrocarbons. Good chromatographic separation of alcohols, esters and aromatics is obtained toward the polar stationary phases OV-101 and OV-275. The latter is the best one exhibiting low duration time of analysis.

Keywords- Selectivity, stationary phases, Polymers, gas chromatography.

I. INTRODUCTION

Several polymers were extensively employed as liquid stationary phases in gas chromatography [1-3]. Typical examples are silicon oils, polypyrrole, polyethylene, polyethylene oxides, and polyesters. Reviews on the subject were published by Guillet [4] and also by Alishoev and Berezkin [5]. Many years ago, the synthesis of coated polyethylene glycols (PEGs), especially of molecular weight 20,000 on chromos orb, and its surprising chromatography was reported [5]. This material has become a popular GC stationary phase [6-9]. El-naggar and Turky [10] evaluated three types of polyethylene glycols of different molecular weights namely, 600, 4000 and 20000 as liquid stationary phases in gas liquid chromatography. They investigated the retention mechanism for the studied polymer stationary phases. Also, they [11] studied the effect of polymer-layer thickness on the polarity dielectrically. In the present study, some preliminary results obtained using different three polymers of different polarities used as liquid stationary phases are reported. The effect of polarity, retention behavior and thermodynamic propertied on the interactions between each polymer and some solutes of different polarities were also determined. The preferred polymer will be discussed critically within the framework of GC separation of paraffin's, aromatics and n-alcohols.

II. EXPERIMENTAL MATERIALS

The following solvents were reagent grade: n-pentane, n-hexane, n-heptane, n-octane cyclohexane, benzene, toluene, ethylbenzene, cumene, methanol, ethanol, n-propanol, and butanol. The studied polymers were given in Table 1.

Table 1. the chemical name of the studied polymers

No.	The polymer	Chemical name
1	OV-101	100% Dimethyl polysiloxane
2	Carbowax-20M	Polyethylene glycol
3	OV-275	65% Dimethyl, 35% divenyl polysiloxane

A. Coating with Polymer and Column Preparation

The solid support chromosorb P AW (pink acid washed) was coated with different **Polymers** with thickness layer 3% (w/w). The polymers were first dissolved in 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 chromatographic support was dried at 120°C at 24 h and packed into stainless steel columns 7 feet in length and 0.25 mm internal diameter.

B. Gas Chromatograph Apparatus

The gas chromatograph (GC) used is shimmadzu 2014 equipped with flame ionization detector and split/splitless injector. Helium was used as the mobile phase at optimum flow rate 30 ml min-1, the carriers hydrogen and air were used for FID at flow rate 45 and 450 ml min-1 respectively. GC analysis was achieved on three studied polymers as stationary phases inside stainless steel tubes of 4m in length and 1/8inch id. These columns are 3% from carbowax 20M, OV-275 and OV-101 on chromosorb PAW.

C. Polarity index (Rohrschnieder)

The Roschnieders components, nitro methane, benzene, pyridine, methyl ethyl ketone and ethanol in addition to the paraffinic series from pentane to decane were injected at oven temperature 120°C in order to obtain the retention index of each Roschnieders component. The helium flow rat was maintained at 30 ml min-1.The paraffinic hydrocarbons from pentane to decane, the alcohols from methanol to hexanol and the aromatics from benzene to xylens were separated at oven temperature programming starting from 50°C to 150 °C at a rate of 10 °C min-1. The helium flow rat was maintained at 20 ml min-1.

D. Thermodynamic Parameters

The determination of thermodynamic parameters (ΔH, ΔG and ΔS) were achieved by injecting normal hexane, benzene and ethanol at different oven temperatures: 70°C, 80°C, 90°C, 100°C and 110°C. these solutes were selected as representative compounds of

their families, paraffin's, aromatics and alcohols respectively. The helium flow rat was maintained at 30 ml min^{-1}.

III. RESULTS AND DISCUSSIONS

Characterizations of Stationary Phases

(a) Rohrschneiders scheme [12]

Characterization and evaluation the behavior of the studied polymer stationary phases according to Rohrshneiders method was given in Table 2, belonging to different structural classes on the studied phases as well as on squalane as given in Table 3, chosen as the reference standard phase for this calculation. It has been found that the OV-101 has the lowest values of the Rohrschneider constants among the studied polymers. These low values suggest that the dimethyl polysiloxane stationary phase poorly retains the compounds that contain the corresponding organic functions. This leads to low selectivity for this type of compound. The overall polarity of the OV-101 stationary phase has the lowest value reflecting low interactive forces between it and Rohrschneider solutes as a function of compound class.

In case of OV-275 all its Rohrschneider constants have highest values than those of the rest studied polymers. Among the Rohrschneider standards, nitro methane and Pyridine exhibit the highest values compared with the other five standards, followed by methyl ethyl ketone and benzene. Reflecting the good ability of the OV-275 stationary phase to separate nitro compounds, the aromatics including nitrogen compounds, ketones and aromatic hydrocarbons. The high value of the overall polarity of OV-275 stationary phase indicating the high interactive forces between it and Rohrschneider solutes as a function of their families. Also, suggesting that the caynoprpyle stationary phase strongly retains the compounds that contain the corresponding organic functions. This leads to an improve selectivity for this type of compound. The Rohrschneider constants of the poly ethylene glycol 20,000 (Carbowax-20M) exhibit moderate values below OV-275 and above OV-101 indicating their moderate polarity. These values decrease in the following order: Pyridine, nitromethane, benzene, methyl ethyl ketone and Ethanol reflecting the order of its efficiency of gas chromatographic separation toward the corresponding families of theses constants.

Compounds	Symbol	Squalane	OV-101	Carbowax-20M	OV-275
Benzene	X	0	16	722	819
nitromethane	Y	0	55	917	1806
Pyridine	Z	0	52	1019	1709
MEK	U	0	39	624	1011
Ethanol	S	0	54	623	807
Summation	Sum ΔI	0	216	3905	6152

Table2. The difference in retention index of Rohr Schneider constants of the polymers

Table 3. The retention index for the five reference compounds on squalane

I	X	Y	Z	U	S
squalane	648	550	869	550	483

(b) Selectivity index [13]

Selectivity can be expressed in terms of uniformity criterion $\overline{\Delta}$ it is used for estimating the degree of separation of multi component mixture; the uniformity criterion was given according to the following equation:

$$\overline{\Delta} = \frac{n_k \tau K_{eff}}{t}$$

where, n_k is the number of peaks on the chromatogram, τ is the base width of the narrowest peak, K_{eff} is the separation factor for the worst separated pair of components, and t is the duration of analysis. Table 4 shows the calculated criterion for model systems comprising saturated, aromatic hydrocarbons and normal alcohols. It has been found generally that all studied polymer stationary phases differ in their efficiencies of separation according to the separated solutes. Saturated hydrocarbons can be separated by the three studied polymers but in different degree of efficiency, the dimethyl poly siloxane is the most efficient stationary phase as illustrated from its criterion may be due to their low polarity which is compatible with the polarity of saturated hydrocarbons. For separation of aromatic hydrocarbons, the most polar caynopropyl poly siloxane has the highest criterion number($\overline{\Delta}$ = 802). So it is the most efficient stationary phase for these purpose followed by the polyethylene glycol 20,000 ($\overline{\Delta}$ =702). For separation of normal alcohols, only caynopropyl poly siloxane stationary phase is success in separation of them giving peak sharp and prevent tailing and broadening may be due to its high polarity is compatible with that of normal alcohols. Therefore, the higher the polarity of the polymer, the higher the value of its selectivity index. This means that the most polar stationary phase exhibits high uniformity criterion number reflecting its high efficiency of separation of polar compounds.

Table 4 Uniformity criterion $\overline{\Delta}$ for different mixtures depending upon the studied polymers as stationary phases

Families	OV-101	Carbowax-20M	OV-275
Paraffines	0.959	0.693	0.574
Aromatics	0.475	0.702	0.802
Alcohols	0.409	0.518	0.890

Efficiency of polymers as stationary phases for gas chromatographic separation

The efficiency of gas chromatographic separation for the studied polymer samples can be evaluated in terms of resolution and separation factor. Resolution could be considered as an important chromatographic parameter, it is used as a quantitative measure of the degree of separation between two adjacent peaks**.**

$$R = (2\Delta t / W_1 + W_2)$$

R = degree of separation between two adjacent peaks, Δt = the time interval between peaks, W_1 = width of the first peak at the base and W_2 = width of the second peak at the base Separation factor is the ratio of the adjusted retention times of two components; it measures only the separation of the centers of mass of the two peaks:

$$\alpha = t_{r(2)} / t_{r(1)}$$

Results of these two parameters for the studied polymer stationary phases using the selective solutes are summarized in Tables (5- 7) and portrayed in Figures (1-3). It has been found that gas chromatographic separations using polymers as stationary phases have different separation efficiencies.

(a) Separation of normal paraffinic hydrocarbons

The separation of normal paraffinic mixture (C_6- C_{10}) is capable of testing specific interaction between solute and studied stationary phases. The resolution and separation factor of paraffinic mixture were given in Table (5), and shown in Fig. (1). By definition the separation factor is greater than unity because species 1 elutes faster than species 2. it has been found that **Δ** values of paraffin's on all studied polymers can separate paraffin's but with different degrees of separation efficiencies.

They depict the separation of n-Alkanes mixture on the selected columns. It has been found that; dimethyl polysiloxane stationary phase gives suitable surface for eluting paraffin's as the previous works. The resolution values of normal paraffin's on OV 101 is the highest followed by carbowax-20M and OV-275 stationary phases as given in Table (4). So, the mixture of n-alkanes can be separated with high efficiency by the order: OV-101, carbowax-20M and OV-275 columns which compatible with their uniformity criterion values (Δ = 0.959, 0.693 and 0.574) respectively. The dimethyl polysiloxane (OV-101) exhibits the most efficient separation of n-alkanes with sharp and symmetrical peaks. Unfortunately, OV-275 column has bad separation of paraffin; this may be related to its high polarity and its low uniformity criterion value toward paraffin's. With respect to polyethylene glycol (carbowax-20M), paraffin's can separated, but with slightly lower efficiency of separation (Δ = 0.693) as compared with the OV-101, this is due to its moderate polarity and selectivity values toward paraffinic hydrocarbons. It was postulated that, the elution was directly correlated not only to stationary phases polarity but also to polarity of

solutes. Accordingly, the polarity and selectivity are the main factors affecting the separation.

(b) Separation of aromatic hydrocarbons

The resolution and separation factor of aromatic hydrocarbons were given in Table (6), and the gas chromatographic separation was shown in Fig. (2). they depict the performance of the studied polymers on the separation of aromatic mixture. Cyanoprpyl polysiloxane is the best studied stationary phase for separating aromatic hydrocarbons obtaining good separation with high resolution value. This could be directly linked with its polarity and selectivity which elute specifically the molecules containing π-electrons.

Figure (2) illustrates the chromatographic separation of aromatic hydrocarbons mixture on OV-101, Carbowax-20M and OV-275. The low polarity and low selectivity of the polymer OV-101 as liquid stationary phase make its surface unsuitable for separating aromatics, this bad separation was evidenced with its lower uniformity criterion value (Δ = 0.475). Consequently, the separation of aromatic hydrocarbons were improved on the polymer OV-275 which exhibit high resolution values along each two consecutive aromatic components in the mixture. This result was evidenced with its high selectivity value towards aromatics (Δ = 0.890). Moreover, the separation of aromatics on the carbowax-20M was achieved giving good separation but accompanied by long. Duration time of analysis. this was evidenced with the moderate uniformity criterion values (**Δ**= 0.702). Also, good separation of aromatics was achieved on cyanoprpyle polysiloxane having high separation factor, high resolution and high uniformity criterion toward aromatics. this suggested that the polarity, selectivity, resolution and uniformity criterion are the main factors affecting the efficiency of separation. On the other hand, reasonable separation of aromatic hydrocarbons was achieved using polyethylene glycol- 20M which has moderate polarity, moderate resolution values and moderate uniformity criterion value. This was reflected on the chromatogram shown in fig 2. having long duration time of analysis.
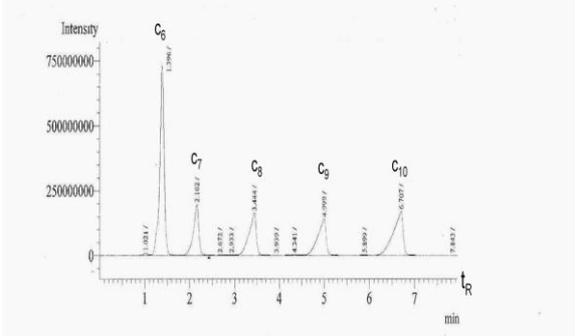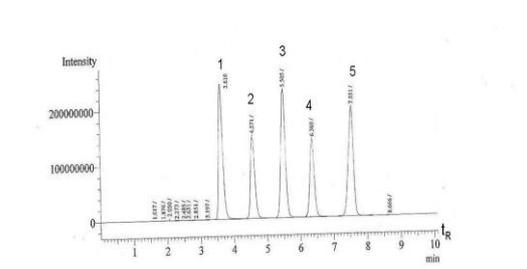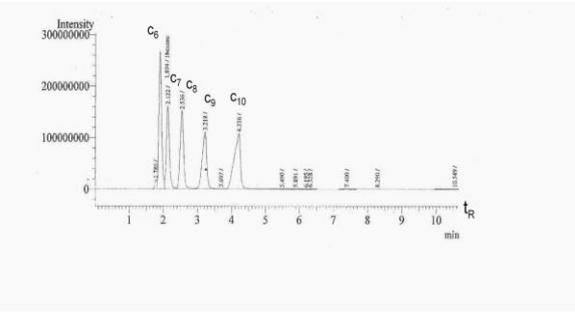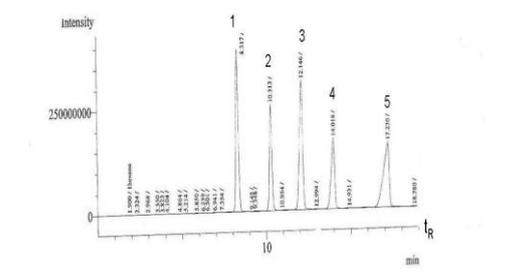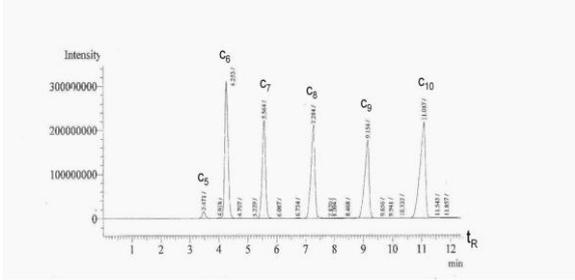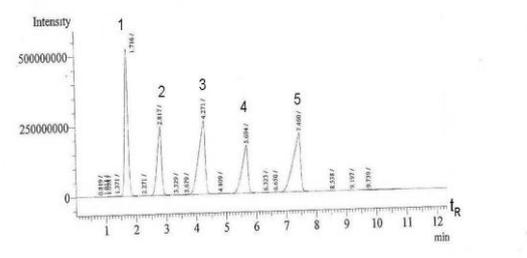
(c) Separation of alcohols

The resolution and separation factor of alcohols (methanol, ethanol, propanol, butanol, pentanol and hexanol) on the studied polymer stationary phases were given in Table (7). The gas chromatographic separation of alcohols was shown in Fig. (3). The resolution of dimethyl polysiloxane exhibits the lowest value compared with other studied polymers. So, OV-101 can elute alcohols with unsymmetrical peaks and much skewed peaks with a long tail (Fig. 3), due to its low polarity as discussed above. This data was matched with its low criterion value and its low negativity of enthalpy toward alcohols. The resolution of OV-275 using alcohols as props exhibits the highest value than the other polymers. Also, it has the highest selectivity and highest negativity of enthalpy than the other studied polymer stationary

phases. These data reflecting on their separation of alcohols as shown in Fig 3. Generally, the high polar cyanopropyl polysiloxane stationary phase successes for eluting alcohols because of the similarity of their high polarities coming from their hydroxyl groups.

Thus, the better separation of light alcohols till hexaneol was achieved on cyanopropyl polysiloxane with sharp, symmetrical peaks and through an acceptable duration time of analysis. The Resolution of alcohols on

carbowax-20M column has values lower than OV-275 and higher than OV-101 (Table 6). This reflected on the Thus, the better separation of light alcohols till hexaneol was achieved on cyanopropyl polysiloxane with sharp, symmetrical peaks and through an acceptable duration time of analysis.

| Fig.1. GC of normal paraffins from n-pentane to n- decane on the studied polymer stationary phases at 50 ^{O}C to 150 ^{O}C at rate 10 ^{o}C min^{-1} and flow rate 30 ml min^{1}. | Fig.2 GC of aromatic hydrocarbons (benzene, 2-toluene, 3-ethylbenzene, 4-propylbenzene and 5-butylbenzene) on the studied polymer stationary phases at optimum conditions (50 ^{o}C; 10 ^{o}C/min to 150 ^{o}C). |

The Resolution of alcohols on carbowax-20M column has values lower than OV-275 and higher than OV-101 (Table 6). This reflected on the separation of alcohols giving peaks having some unsymmetrical and some tailing. This result was matched with polarity, selectivity

and negativity of enthalpy of carbowax-20M stationary phase using alcohols as probes.
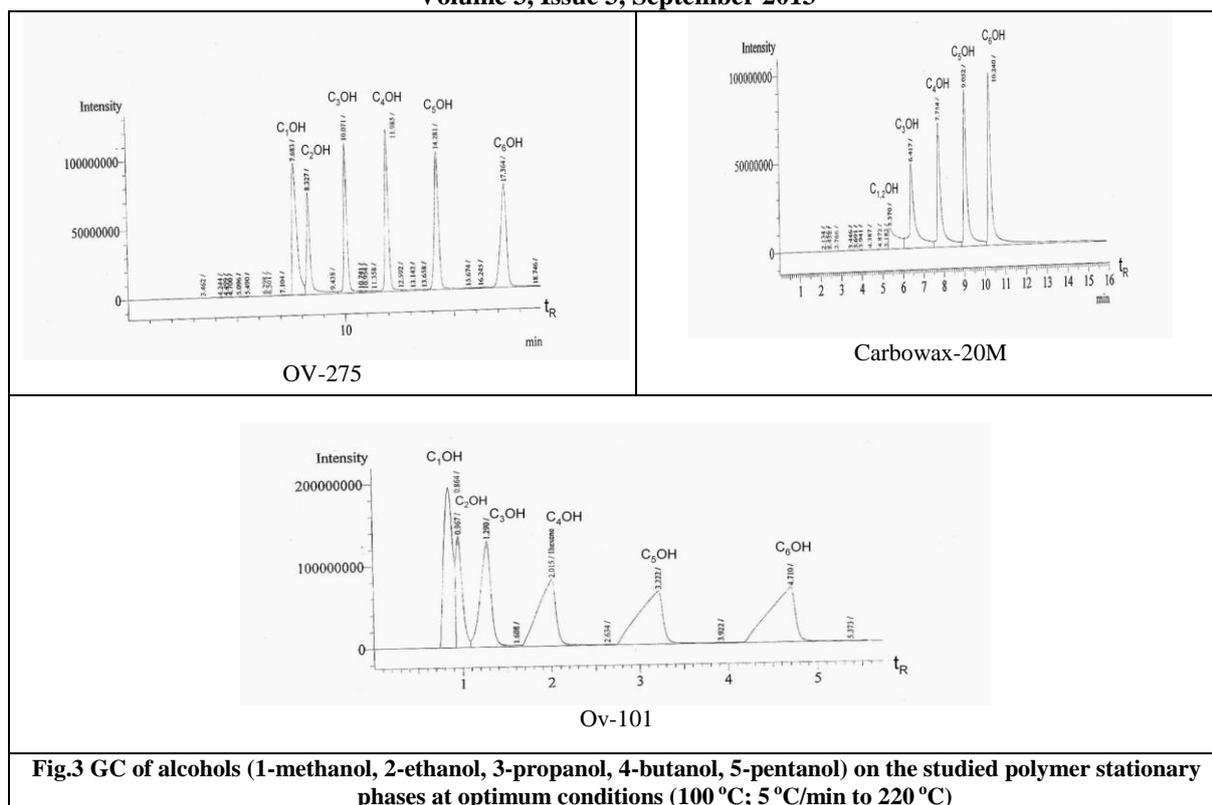
Fig.3 GC of alcohols (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-pentanol) on the studied polymer stationary phases at optimum conditions (100 ^{o}C; 5 ^{o}C/min to 220 ^{o}C)

IV. CONCLUSION

Rohr Schneider scheme of polarity helps to identified and arranged polymer stationary phases according to their polarities. Paraffinic hydrocarbons show higher selectivity values on the dimethyl polysiloxane stationary phase than the cyanopropyl polysiloxane and polyethylene glycol. The opposite occurs using alcohols and aromatic hydrocarbons, OV 275 followed by carbowax- 20M exhibit higher selectivity than OV-101, these data compatible with their polarities and reflecting on their gas chromatographic separations.

Chromatographic evaluation of the studied polymers as stationary phases in gas chromatography was done mainly through their use in the analysis of selected mixtures of different polarities including n-alkanes, aromatics and alcohols. The efficiency of separation for the studied samples was evaluated in terms of resolution, separation factor and uniformity criterion

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APPENDIX

Table 5. Resolution and Separation factor of paraffin's on the studied polymers as stationary phases

No.	Carbon Number	OV-101		Carbowax-20M		OV-275	
		α	R	α	R	α	R
1	C_6-C_7	1.3086	1.450	1.1204	1.05	1.549	0.284
2	C_7-C_8	1.3091	1.521	1.1951	1.12	1.593	0.329
3	C_8-C_9	1.2567	1.568	1.2689	1.06	1.452	0.293
4	C_9-C_{10}	1.2112	1.506	1.3101	1.16	1.342	0.267

Table 6. Resolution and Separation factor of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and propylbenzene and butyl benzene) on the studied polymers as stationary phases.

No.	Carbon No.	OV-101		Carbowax-20M		OV-275	
		Δ	R	Δ	R	Δ	R
1	C_6-C_7	1.642	0.440	1.240	0.950	1.266	1.221
2	C_7-C_8	1.516	0.415	1.178	0.733	1.204	1.236
3	C_8-C_9	1.333	0.339	1.154	0.623	1.157	1.352
4	C_9-C_{10}	1.308	0.374	1.229	0.804	1.186	1.245

Table 7: Resolution and Separation factor of alcohols (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-pentanol) on the studied polymers as stationary phases.

No.	Carbon Number	OV-101		Carbowax-20M		OV-275	
		α	R	α	R	α	R
1	C_1-C_2	1.108	0.019	0.000	0.000	1.084	1.320
2	C_2-C_3	1.348	0.056	1.195	0.511	1.209	1.520
3	C_3-C_4	1.562	0.101	1.208	0.622	1.190	1.621
4	C_4-C_5	1.599	0.124	1.167	0.649	1.192	1.652
5	C_5-C_6	1.464	0.125	1.131	0.566	1.216	1.596