Investigation of detection and retention parameters of organic solvents and organophosphorus toxics on mixed polyphenylmethylsiloxane/ H-ZSM-5 zeolite

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Abstract

During the last decade many and considerable advances are being realized in the field of detection and measurement using surface acoustic wave (SAW) and quartz crystal microbalances (QCM) based sensors. Thus, the current work attempts to investigate the contribution of polymers based polysiloxane mixed with zeolite in sensitive layers used in the above cited sensors types for detection of organic and organophosphorus toxics. The inverse gas chromatography technique (IGC) which is proven as versatile method for the polymer's surface exploration was used to understand phenomenon governing the adsorption occurred on the mixed polymer zeolite. The polyphenylmethylsiloxane/HZSM-5 was used as stationary phase to determine the specific retention volumes and the interaction parameters, on two ranges of temperature (200-230°C and 270-300°C).
The obtained results with the organophosphorus solutes reveal the existent of strong affinity of retention, which let us to suggest that the prepared blend can be used as sensitive layers for the detection of toxics.

Key words: HZSM-5 zeolite, polyphenylmethylsiloxane/HZSM-5, inverse gas chromatography (IGC), organic solvents**,** organophosphorus toxics.

I. Introduction

Due to the increased threat of chemical toxics, there is renewed interest in their environmental fate, because organophosphorus compounds are highly toxic and their use is restricted in non-surety laboratories, research on the environmental fate of organophosphorus is often conducted. The organophosphorus toxic were widely exploited as chemical agent for war and has created a trend for the development of detection analytical method and apparatus. The current sensing systems are ranging from sophisticated chromatographic methods to simple chemical sensors.

In the chemical sensors field, there is a great interest in the development of surface acoustic wave (SAW) and Quartz Crystal Microbalances (QCM) sensors. The use of a (SAW) sensor to detect chemical vapors was first reported in 1979 and has since been widely studied.

In SAW sensors, the detection is based on the partition of the analytes between the environment surrounding the sensor and the sensing layer. Since this partition can be monitored by inverse gas chromatography (IGC), there is thus a close relationship between IGC and the detection of volatile species by a SAW sensor. For this reason, many works were devoted to the characterization of the sensing material by IGC at infinite dilution with the sensing material acting as a stationary phase [1, 2]. Inverse gas chromatography (IGC) has emerged as a promising method for polymers and polymer blend characterization [3]. It is often called the molecular probe technique The term inverse refers to the polymer or the blend that can be studied in the solid-phase as the stationary phase, unlike conventional GC where the separation of solvents (solutes) is the prime interest. IGC is a method of choice for the characterization and examination of the partitioning coefficient for the material (polymers or blend) susceptible to use as thin layers in sensors, because all small organic molecules will have measurable solubilities these materials. Hence the range of interactions which can be explored by the IGC technique is unlimited. IGC has been shown to

be valuable for the identification of several types of interaction in molecular and macromolecular systems and for the characterization of the bulk and surface of finely divided materials. It was shown that the IGC method can be useful in obtaining thermodynamic data on polymeric systems even when the morphology is complex [4, 5].

II. Experimental

II.1. Material

The polyphenylmethylsiloxane polymer was supplied by chrompack chemicals and the H-ZMS-5 zeolite was synthesized in our laboratory through the following protocol; The ZSM-5 zeolite (Si/Al ratio=25) was synthesized by hydrothermal way from a mixture of reactants with following composition: $1SiO_2$; $0,012Al_2O_3$; $0,27Na_2O$; $0,1TPABr$; $0,2H_2SO_4$; $54H_2O$. The temperature of crystallization is fixed to 170°C during 72 hours. H-ZSM-5 was obtained, via NH_4^+-ZSM-5, by de-ammonization at 500°C. The acidity nature of the obtained zeolite was characterized by adsorption and thermal desorption of ammonia (TPD NH_3). Different families of solutes were used in this work. Vanishingly small amounts were injected into the chromatographic column. These solutes will probe the dispersive, dipole, and hydrogen bonding interactions, the basic and acidic behavior with the prepared stationary phase. A total of 23 solutes, chromatographic grade including an organophosphorus compound type Parathion, were purchased from Aldrich and Merck; they were used as received. They were injected to probe the bulk properties of the prepared stationary phase.

II.2. Inverse gas chromatography

II.2.1. Stationary phase

In order to avoid any further interaction between the stationary phase and the support, one glass column of 1.5 m and 4 mm of inner diameter was loaded with 10% w/w in polymer, prepared by coating polyphenylmethylsiloxane on the zeolite according to the soaking method of Al-Saıgh and Munk [6]

II.2.2. Apparatus and measurements

A gas chromatograph UNICAM 4400 fitted with flame ionization detector and flow rate needle regulator was used. Methane was the noninter-acting marker and nitrogen purified through a molecular sieve was used as carrier gas. The column was conditioned at 100 °C under a stream of nitrogen for 8 hours prior to chromatographic measurements. After performing the Van Deempter curve, the flow rate was typically set at 25 ml/min as measured by a soap-bubble flow meter. The injector and detector temperatures were kept at 310°C. During the experiment, the column temperature was increased on two ranges of temperatures ranking from 200°C to 230°C and from 270°C to 300 °C by step of 5 °C. The room temperature was carefully monitored. The flow rate was monitored frequently by taking an average of three readings every time. These readings usually agreed within 0.5%. The inlet and outlet pressures were frequently monitored by a mercury manometer. The inlet pressure was generally in the range of 600 mmHg while the outlet pressure was always atmospheric. Probe vapors were injected manually at least in triplicate by a Hamilton gas-tight syringe. Retention time of solutes was measured on a completely automated data handling system, The chromatographic signal was analyzed as a function of time and the retention times were determined at the peak maxima; retention time error bars did not exceed 1–2%.

II.2.3. Data Analysis

Thermodynamic quantities can be easily obtained from the chromatographic quantities in IGC by measuring the specific retention volume V_g^0 which is commonly used to describe the elution behavior of solutes and it is defined as:

$$V_g^0 = \Delta t \cdot \frac{F}{w} \cdot \frac{273.15}{t_r} \cdot \frac{3}{2} \cdot \frac{\left(\frac{P_i}{P_0}\right)^2 - 1}{\left(\frac{P_i}{P_0}\right)^3 - 1} \tag{1}$$

$$V_g^0 = \Delta t \cdot \frac{F}{w} \cdot \frac{273.15}{t_r} \cdot \frac{3}{2} \cdot \frac{\left(\frac{P_i}{P_0}\right)^2 - 1}{\left(\frac{P_i}{P_0}\right)^3 - 1} \quad \text{Where } \Delta t = t_s$$

- t_m is the difference between the retention time of the solute t_s and the unretained solute t_m, F is the flow-rate of the carrier gas measured at room temperature T, w is the mass of the stationary phase, and P and P are the inlet and outlet pressures, respectively, and are used for the correction for the compressibility of the carrier gas. When a polymer is coated onto the solid support, the interaction parameters of the solute–polymer can then be calculated using V_g^0 measured according to Eq (1) as follows:

$$\chi_{12} = Ln\frac{273.15Rv_2}{V_g^0 v_1 P_1^0} - 1 + \frac{V_1}{M_2 v_2} - \frac{B_{11} - V_1}{RT} \cdot P_1^0$$

(2)

Where χ_{12} is the polymer–solute interaction parameter, 1 denotes the solute and 2 denotes the polymer, v_2 is the specific volume of the polymer at the column temperature T, M_1 is the molecular mass of the solute, V_1 is the molar volume of the solute, R is the gas constant, and B_{11} is the second virial coefficient of the solute in the gaseous state.

III. Results

In this work, we wished to investigate the retention properties and capacities of the mixed polymer/zeolite type (polyphenylmethylsiloxane/ H-ZSM-5) by IGC, IGC permits to evaluate the specific retention volumes V_g^0, the masse activity coefficient at infinite dilution Ω_i^∞ and the interaction parameters χ_{12}.

Through this work, twenty three probes including organophosphorus were injected, only the specific retention volumes were determined for the organophosphorus compound because it was rather difficult to find its properties data used in the Eq(2).

Through the obtained specific retention volumes values with the investigated stationary phase, it was clearly observed its high capacity to retain probes molecules; which is probably due to its strong acid character, its pores size distribution and the polarizabele character of the polyphenylmethylsiloxane polymer.

The studied stationary phase has developed significant interactions which underline the high aptitude to retain both the acid and basic probes such as such alcohols and cycloxanone. This character is probably attributed to the establishment of the dipoles-dipoles bonds issued from the presence of the oxygen atoms in the solutes and the polymers. Mixing the two materials (polymer and zeolithe) had conferred the prepared stationary phase a double acid/ fairly basic character issued from acidic nature of the zeolithe and fairly basic nature of the phenyl group present in the polymer.

A plot of the Ln (V_g^0) versus the 1/T (K) for the alcohols leads to a linear curve which indicated that the retention is proportional to the carbon atom number in the backbone of the solute
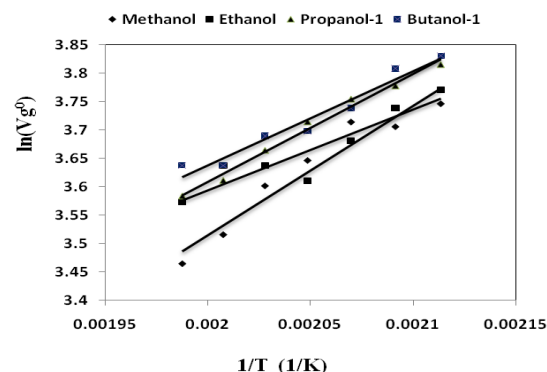

Figure I. Representation of $\ln V_{g,i}^0 = f\left(\frac{1}{T}\right)$ *of alcohols probes at seven temperatures; T_1=473,15 K, T_2=478,15 K, T_3=483,15 K, T_4=488,15 K, T_5=593,15 K, T_6= 598,15 K, T_7= 503,15 K*

The plot of Ln (V_g^0) versus the 1/T (K) for the aromatic probes shows that the stationary phase has presented a quite significant interactions resulting from the establishment of acid-base interaction induced by the strong acid character of the zeolite and the fairly basic character of the aromatic

These retentions are also favourite by the dispersive interaction settled down between the aromatic ring and those of the phenyl groups presents in the stationary phase. However the values obtained with the para-xylene show the influence of the steric effects.
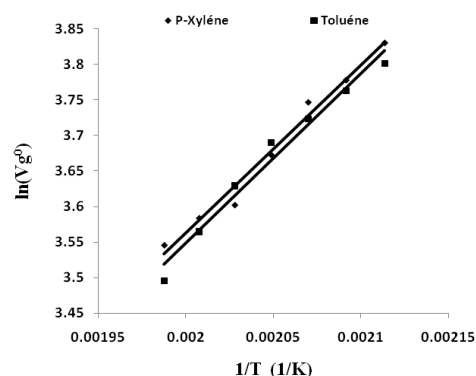

Figure I. Representation of $\ln V_{g,i}^0 = f\left(\frac{1}{T}\right)$ *of aromatic probes at seven temperatures; T_1=473,15 K, T_2=478,15 K, T_3=483,15 K, T_4=488,15 K, T_5=593,15 K, T_6= 598,15 K, T_7= 503,15 K.*

III.1. The organophosphorus solutes retention volumes.

The present data reflect a strong retention of the organophosphorus Parathion, which is mainly due to the presence of the aromatic ring and the nitrogen atom on organophosphorus compound, which has favourite the establishment of the acid-base interaction and dispersive interaction between Parathion's aromatic ring and the phenyl group of the stationary phase,
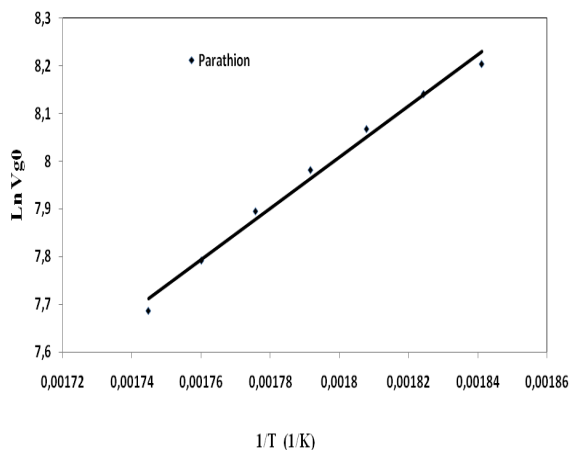

Figure 2. Representation of $\ln V_{g,i}^{0} = f\left(\frac{1}{T}\right)$ of organophosphorus (Parathion) at seven temperatures; $T_1=543,15$ K, $T_2=548,15$ K, $T_3=553,15$ K , $T_4=558,15$ K, $T_5=563,15$ K, $T_6=568,15$ K, $T_7=573,15$ K,

IV. Conclusion

The idea of coating polymer on the zeolithe was to get profit from the advantageous of the two materials; the high adsorption capacity of the zeolithe H-ZSM-5 and its uniform pore size distribution combined with the fairly basic nature of the polymer polyphenylmethylsiloxane gained from the presence of the phenyl group on the polymer backbone. It was noticed through the conducted study which investigates the retention aptitude of the prepared stationary phase the high capacity to retain both the acid and basic molecules and especially the organophosphorus solutes. This is probably due to the strong acid character of zeolite, the polarizable character of the polyphenyl-methylsiloxane polymer.

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