



Zeolitic imidazolate framework-methacrylate composite monolith characterization by inverse gas chromatography



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ABSTRACT

Thermodynamic characterization of butyl methacrylate-co-ethylene dimethacrylate neat monolith and zeolitic imidazolate framework-8 incorporated with butyl methacrylate-co-ethylene dimethacrylate composite monolith were studied using inverse gas chromatography at infinite dilution under 1 MPa column pressure and various column temperatures. The free energy of adsorption (ΔG_A), enthalpy of adsorption (ΔH_A) and entropy of adsorption (ΔS_A) were determined using a series of *n*-alkanes. The dispersive component of surface energy (γ_D^d) was estimated by Dorris-Gray and Schultz et al. methods. The composite monolith showed a more energetic surface than the neat monolith. The acidic, K_A , and basic, K_D , parameters for both materials were estimated using a group of polar probes. A basic character was concluded with more basic behavior for the neat monolith. Flory-Huggins parameter, χ , was taken as a measure of miscibility between the probes with the low molecular weight and the high molecular weight monolith. Inverse gas chromatography provides a better understanding of the role of incorporated zeolitic imidazolate framework (ZIF-8) into the polymer matrix in its monolithic form.

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1. Introduction

Materials characterization using inverse gas chromatography [IGC] is a well-known technique to investigate the thermodynamic properties of various solid materials [1–6]. In contrast to conventional chromatographic techniques, IGC is turned to stationary phase characterization by observing the behavior of standard solutes injected over a temperature range; as a result, the term “inverse” is typically used. The method is simple, inexpensive, accurate and rapid. The physicochemical characterization of polymers is the most widely used application of IGC; however, the majority of IGC studies examined linear polymers rather than crosslinked [7–12].

Monolithic stationary phases were first introduced approximately five decades ago for gas chromatographic applications [13]; however, the use of monolithic columns in GC is still very limited [14–16] compared to the enormous development of monoliths

for LC applications [17]. Basically, monolithic stationary phases are of two main types, inorganic silicates and organic polymers formed as a one piece material of a continuous interconnected network of pores [18]. Inorganic silica-based monoliths are known to have the advantage of separating small molecules, in contrast to organic monoliths, which were originally designed to separate macromolecules. The introduction of a nano- or micro-particles within the polymeric mixture to form a monolithic composite stationary phase is a successful trend to enhance the separation ability of organic monoliths toward small molecules; for this purpose, various particles were tested [19–30].

Metal-organic frameworks (MOFs) of micro- and nano-particles comprise one of the most interesting materials incorporated with monoliths [17,31]. The unique properties of MOF materials provided the monolithic matrix with a further high surface area, micro- and nano-pores, as well as a specific chemical nature, including chiral selectors. MOFs are highly ordered crystalline porous materials with superior properties concerning their high surface area, chemical and physical stability, unlimited diversity and easy manipulation through the precise selection of its primary precursors and preparation conditions [32].

Recently, our research group published the first contribution of MOF-monolith composite in gas chromatography [29]. The effect

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of incorporation of different percentages of zeolitic imidazolate framework-8 (ZIF-8) micro-particles into a butyl methacrylate-co-ethylene dimethacrylate (BuMA-co-EDMA) monolith has been explored and compared to a neat monolith as well as an open tubular commercial column, giving a surprisingly higher efficiency and fast separation. From a chromatographic perspective, the mentioned composite (ZIF-8-(BuMA-co-EDMA)) combines the advantages of both MOF high surface area and monolithic matrix permeability; however, such columns require more in-depth studies. In the current work, we performed an extensive IGC study of a ZIF-8-(BuMA-co-EDMA) composite column to achieve a deeper understanding of its superiority.

Inverse gas chromatographic studies for monoliths in their crosslinked monolithic form are very rare [33,34]. The weight, morphology, heterogeneity and defects of stationary phases were reported to have an obvious effect on its thermodynamic properties [35,36]. Thus, performing IGC studies using the monolithic columns instead of using a packed column with the grinded material has a relative advantage. The Kurganov group investigated the effect of different degrees of crosslinking in methacrylate and styrene based monolithic columns by means of IGC [33]. They used gaseous light alkanes for the study (ethane, propane, and *n*-butane) and a modified gas chromatograph for high-pressure separation (up to 10 MPa). The enthalpy-entropy compensation effect was discussed in another publication by the same research group for three monoliths with different polarities and for five different carrier gases under high pressure [34]. The hydrophilic monolith based on a methacrylate polymer showed a stronger interaction toward the light hydrocarbons than the hydrophobic monolith. They also concluded that the high-pressure separation has no strong effect on the separation process.

The present work is considered as complementary research to the previously published work on the zeolitic imidazolate framework-8-butyl methacrylate-co-ethylene dimethacrylate composite monolith for GC applications. Butyl methacrylate-co-ethylene dimethacrylate (neat monolith) and ZIF-8-butyl methacrylate-co-ethylene dimethacrylate (composite monolith) monoliths were prepared and investigated via a classical low-pressure gas chromatograph. At infinite dilution, a series of linear alkanes (pentane, hexane, heptane, octane, and nonane), alkylbenzenes (benzene, toluene, ethylbenzene, propylbenzene, and butyl benzene), and a group of polar probes, (diethyl ether (DEE), acetone (Acet.), dichloromethane (DCM), tetrahydrofuran (THF), chloroform (CHL), and ethyl acetate (EtAc.)) have been utilized to calculate various thermodynamic parameters. The free energy of adsorption (ΔG_A), enthalpy of adsorption (ΔH_A), entropy of adsorption (ΔS_A), dispersive component of surface energy (γ_S^D), acid-base characteristics and Flory-Huggins (χ) parameters were determined at constant pressure (1 MPa) over a temperature range of 110–150 °C.

2. Experimental

2.1. Reagents and materials

Basolite®Z1200 [2-methylimidazole zinc salt (ZIF-8)] was obtained from Sigma-Aldrich (St. Louis, MO, USA). Fused silica capillaries with internal diameter of 250 μm were purchased from Restek (Bellefonte, USA). The initiator azobisisobutyronitrile (AIBN) and the spacer 3-(trimethoxysilyl) propyl methacrylate (TMSM) were obtained from Fluka (Buchs, Switzerland). The monomer Butyl methacrylate (BuMA) and the crosslinker ethylene dimethacrylate (EDMA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). High-purity grade (99.9999%) gases (air, helium, hydrogen, nitrogen and methane), were purchased from SIGAS (Riyadh, Saudi Arabia). *n*-Alkanes (pentane, hexane, heptane,

octane, and nonane), alkylbenzenes (benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene) as well as polar probes (diethyl ether, dichloromethane, tetrahydrofuran, chloroform, and ethyl acetate) all of the highest purity grade, were obtained from Merck (Darmstadt, Germany).

2.2. Instrumentation

All GC separations were performed on a conventional chromatographic system (Trace GC Ultra, Thermo Scientific, USA) consisting of split/splitless injector, an oven with a temperature range of 50–400 °C and a flame ionization detector (FID). All the experiments were performed at constant pressure (1 MPa) and over a temperature range of 110–150 °C. Both the injector and the detector were adjusted to 190 °C. The carrier gas was dry, high-purity helium. Data acquisition and processing were performed using the Chrom-Card data handling software package.

2.3. Preparation of monolithic capillary columns

Two batches of columns were prepared to examine the effect of adding ZIF-8 on the thermodynamic properties of the monolith; one batch contains only the neat (BuMA-co-EDMA) monolith, and the other batch was loaded with a composite monolith containing 10 mg mL⁻¹ of ZIF-8 [29]. The polymerization mixture consisting of 21% BuMA, 9% EDMA, 35% 1-propanol and 35% 1,4-butandiol. ZIF-8 was dispersed and homogenized in the polymerization mixture and then purged with nitrogen for 5 min. The empty fused silica capillaries (250 μm i.d) were activated and modified with 10% 3-(trimethoxysilyl) propyl methacrylate (TMSM) in toluene solution for 10 min, as described in a previous work [16]. After activation, 33.5 cm long \times 250 μm i.d. empty capillaries were filled with the polymerization mixture and then thermally polymerized using AIBN as an initiator at 60 °C for 16 h. Finally, the prepared columns washed with acetonitrile over night to remove the unreacted materials and porogenic solvents.

2.4. Inverse gas chromatography (IGC)

At infinite dilution (zero surface coverage), where the adsorbate-adsorbate interactions could be neglected and Henry's law is obeyed, the net retention volume, V_N (Table S1), is the fundamental parameter that is directly linked to the thermodynamic interactions with the studied surfaces. In these conditions the net retention volume is expressed by Eq. (1) [1]:

$$V_N = (t_R - t_M) F_a \frac{T}{T_a} J \quad (1)$$

where t_R is the retention time (Table S2), t_M is the dead time (determined experimentally using methane), F_a is the volumetric flow rate ($\text{cm}^3 \text{min}^{-1}$) determined practically using bubble flowmeter, T and T_a are the column temperature (K) and the ambient temperature (K) respectively and J is the James-Martin gas compressibility correction factor that elucidates the pressure drop along the chromatographic column [37] and is determined according to the following Eq. (2):

$$J = \frac{3(P^2 - 1)}{2(P^3 - 1)} \quad (2)$$

with P being P_i/P_o , Where P_i is the inlet pressure (at the column pressure), and P_o is the outlet pressure (at atmospheric pressure).

The specific retention volumes, V_g (Table S3), is calculated from the net retention volume, Eq. (3) [38]:

$$V_g = \frac{V_N 273.15}{wT} \quad (3)$$

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