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# London Dispersive and Polar Surface Properties of Styrene–Divinylbenzene Copolymer Modified by 5-Hydroxy-6-Methyluracil Using Inverse Gas Chromatography

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**Abstract:** The London dispersive and polar surface properties of solid materials are very important in many chemical processes, such as adsorption, coatings, catalysis, colloids, and mechanical engineering. One of materials such as styrene–divinylbenzene copolymer modified by 5-hydroxy-6-methyluracil at different percentages, was not deeply characterized in literature, and especially, it is very crucial to determine their London dispersive and polar properties. The new recent research in the inverse gas chromatography (IGC) technique allowed a full determination of the surface properties of styrene–divinylbenzene copolymer modified by 5-hydroxy-6-methyluracil by choosing well-known polar and non-polar organic solvents and varying the temperature. Applying the IGC technique at infinite dilution led to the retention volume of adsorbed molecules on styrene–divinylbenzene copolymer modified by 5-hydroxy-6-methyluracil at different percentages using the Hamieh thermal model and our new recent results on the separation of the two polar and the dispersive contribution of the free energy of interaction. The surface properties of these materials, such the surface free energy of adsorption, the polar acid and base surface energy, and the Lewis acid–base parameters were obtained as a function of temperature and for different percentages 5-hydroxy-6-methyluracil. The obtained results proved that the polar free energy of adsorption on styrene–divinylbenzene copolymer increased when the percentage of 5-hydroxy-6-methyluracil (HMU) increased. However, a decrease of the London dispersive surface energy of copolymer was observed for higher percentage of 5-hydroxy-6-methyluracil. A Lewis amphoteric character was shown for the copolymer with highest acidity, while the basicity linearly increased when the percentage HMU increased.

**Keywords:** Surfaces; interfaces; adsorption; Hamieh thermal model; London dispersive surface energy; Lewis acid–base parameters; polar acid–base surface energy; intermolecular separation distance

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## 1. Introduction

Styrene–divinylbenzene (S-DVB) copolymers are widely employed in various applications due to their chemical robustness, thermal stability, and tunable porosity. These crosslinked polymers serve as versatile platforms for ion exchange resins, adsorbents, and catalysts, particularly in fields such as water purification, chromatography, and catalysis [1–3]. However, the intrinsic hydrophobicity and limited functional diversity of the base S-DVB matrix often necessitate chemical modification to enhance selectivity, reactivity, and biocompatibility [4]. Incorporating biologically active or heterocyclic compounds into S-DVB matrices has proven effective in enhancing their physicochemical properties. Among such modifiers, 5-hydroxy-6-methyluracil (HMU)—a derivative of uracil—is of particular interest due to its hydrogen-bonding capability, antioxidant activity, and nucleobase-like structural features. These properties open avenues for molecular recognition, metal ion coordination, and biological interfacing [5–7]. The functionalization of S-DVB with HMU is expected to introduce hydrophilic groups and aromatic nitrogen heterocycles, thereby altering the surface chemistry and potentially the sorption characteristics, swelling behavior, and thermal stability of the polymer matrix. Previous work has shown that nucleobase-modified polymers exhibit enhanced metal-binding capacities and increased interaction with biomolecules [8,9], suggesting similar enhancements might be observed upon HMU grafting.

Other researches were interested in studying the two-dimensional network supramolecular structures [1–14]. The use of 5-hydroxy-6-methyluracil modifying the S-DVB copolymer at different percentage of the supported modifier is very important to constitute supramolecular network structures used for selective adsorption of several molecules [14–18].

Knowing that the surface properties of polymeric materials are of paramount importance in applications ranging from chromatography and sorption technologies to biomedical and catalytic systems, it is therefore crucial to determine these properties, such as the surface energy components, particularly the London dispersive ($\gamma^d$) and specific polar ($\gamma^s$) contributions, that govern a material's interactions with gases, liquids, and biological species. Precise characterization of these components is essential for understanding interfacial phenomena such as adhesion, wettability, sorption behavior, and chemical reactivity [19–24].

Inverse gas chromatography (IGC) has emerged as a powerful and sensitive technique for assessing the thermodynamic surface properties of solids, especially polymers, in their native dry state. Unlike traditional techniques such as contact angle measurements, IGC enables the evaluation of surface energy under well-controlled and reproducible gas–solid interaction conditions, even for porous, irregular, or finely powdered materials [25–27].

In this study, we investigated the London dispersive and specific polar components of the surface energy of a styrene–divinylbenzene (S-DVB) copolymer modified by 5-hydroxy-6-methyluracil at different percentages. Using inverse gas chromatography at infinite dilution (IGC-ID) by applying our new methodology [22–24,28–31], we determined the surface free energy parameters, assess the acid–base character of the surfaces, and examined how HMU grafting affects the thermodynamic affinity of the polymer toward various probe molecules. This analysis provided critical insight into the physicochemical transformation of S-DVB surfaces following functionalization and their potential suitability for selective adsorption, separation, or biomedical applications.

## 2. Materials and Methods

### *2.1. Adsorbent and Materials*

The styrene–divinylbenzene copolymer (Dowex L-285, from Dow Chemical, Midland, USA) used in this study was the same as that studied in a previous work [32]. S-DVB copolymer exhibited a specific surface area of 800 m²/g and the particle sizes varied from 250 µm to 500 µm. The chosen surface modifier was 5-hydroxy-6-methyluracil (from Vecton, St. Petersburg, Russia, 97%), varying the percentage mass from 1% to 10%, impregnated into the adsorbent surface by evaporation of aqueous solutions at 70 °C. Organic solvents with highest purity, such as *n*-hexane, *n*-heptane, *n*-octane, n-nonane, benzene, toluene, ethanol, *i*-propanol, *n*-butanol, *i*-butanol, i-pentanol, dichloromethane, and ethyl acetate (Chimreactivsnab, Russia) were used as the probes.

### *2.2. Inverse Gas Chromatography*

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The net retention time of adsorbed organic molecules on S-DVB copolymer modified by HMU was determined using inverse gas chromatography at infinite dilution with the help of a Chromos GC-1000 chromatograph (from Chromos, Russia) equipped with a flame ionization detector (FID). The solid particles were packed into stainless steel columns of 30 cm length and 3 mm internal diameter. The temperature of the column was 200 °C and the temperatures of the injector and detector were 280°C. The flow rate of the nitrogen carrier gas was 30 mL/min. The mass of the sorbent packed into the column was equal to 1 g. All chromatographic columns were conditioned overnight at 200 °C to remove any residual impurities. The probes in the vapor phase were injected with microsyringes at different temperatures to realize the infinite dilution and to satisfy Henry's law. The experiments were repeated three times and the error in the value of the retention volume did not exceed 2%.

### *2.3. Thermodynamic Methods*

#### 2.3.1. Dispersive and Polar Energies, and Lewis Acid–Base Parameters

The values of the free energy of adsorption $\Delta G_a^0$ of the adsorbed organic molecules on S-DVB/HMU system at different HMU percentages were obtained as a function of temperature using the following equation:

$$\Delta G_a^0(T) = -RT lnVn + C(T) \tag{1}$$

where $T$ is the absolute temperature, $R$ the perfect constant gas, and $C(T)$ a constant depending on the temperature and the solvent–sorbent interaction.

The free energy of adsorption $\Delta G_a^0(T)$ of organic solvents is composed by the summation of the London dispersive energy $\Delta G_a^d(T)$ and the free polar energy $\Delta G_a^{sp}(T)$ of adsorption for all temperatures:

$$\Delta G_a^0(T) = \Delta G_a^d(T) + \Delta G_a^p(T) \tag{2}$$

The separation of the two dispersive and polar contributions was obtained using our new methodology [30,31] giving the Expression (3) of London dispersion interaction energy:

$$\Delta G_a^d(T) = -\frac{\alpha_{0S}}{H^6}\left[\frac{3\mathcal{N}}{2(4\pi\varepsilon_0)^2}\left(\frac{\varepsilon_S\,\varepsilon_X}{(\varepsilon_S+\,\varepsilon_X)}\alpha_{0X}\right)\right] \tag{3}$$

where $\mathcal{N}$ is the Avogadro number, $\varepsilon_0$ the dielectric constant of vacuum, $\alpha_{0S}$ and $\alpha_{0X}$ are the respective deformation polarizabilities of the solid material denoted by S and the organic molecule denoted by X, separated by a distance $H$, and $\varepsilon_S$ and $\varepsilon_X$ are their corresponding ionization energies.

The combination of Equations (1) and (3) allowed writing Equation (4):

$$RT lnVn = \frac{\alpha_{0S}}{H^6}\left[\frac{3\mathcal{N}}{2(4\pi\varepsilon_0)^2}\left(\frac{\varepsilon_S\,\varepsilon_X}{(\varepsilon_S+\,\varepsilon_X)}\alpha_{0X}\right)\right] - \Delta G_a^p(T) + C(T) \tag{4}$$

The interaction parameter $\mathcal{P}_{SX}$ used as chromatographic index was given by Equation (5):

$$\mathcal{P}_{SX} = \frac{\varepsilon_S\,\varepsilon_X}{(\varepsilon_S+\,\varepsilon_X)}\alpha_{0X} \tag{5}$$

For n-alkanes, $RT lnVn$ can be written as:

$$\begin{cases} RT lnVn(n-alkane) = A\left[\dfrac{3\mathcal{N}}{2(4\pi\varepsilon_0)^2}\mathcal{P}_{SX}(nn-alkane)\right] + C(T) \\ A = \dfrac{\alpha_{0S}}{H^6} \end{cases} \tag{6}$$

where $A$ is the slope of the n-alkane straight line de pending on $\alpha_{0S}$ and $H$.

The determination of the free polar energy $\Delta G_a^p(polar)$ of an adsorbed polar molecule was obtained by taking the distance between the representative point of a polar molecule and the hypothetical point $X_{n.p.}$ located on the straight line of n-alkanes (Equation 7):

$$\Delta G_a^p(T,polar) = RTlnVn\,(T,polar) - ARTlnVn\,\left(T,X_{n.p.}\right) \tag{7}$$

While, the polar enthalpy $\left(-\Delta H_a^p\right)$ and entropy $\left(-\Delta S_a^p\right)$ of adsorption of polar probes was deduced from Relation (8) when the linearity of $\Delta G_a^p(T)$ was confirmed:

$$\Delta G_a^p(T) = \Delta H_a^p - T\Delta S_a^p \tag{8}$$

The following equations (9) allowed obtaining the Lewis enthalpic ($K_A$, $K_D$) and entropic ($\omega_A$, $\omega_D$) Lewis acid–base constants:

$$\begin{cases} \left(-\Delta H^p\right) = K_A \times DN' + K_D \times AN' \\ \left(-\Delta S_a^p\right) = \omega_A \times DN' + \omega_D \times AN' \end{cases} \tag{9}$$

where $DN'$ and $AN'$ are, respectively, the corrected electron donor and acceptor numbers of the polar molecule [33,34].

### 2.3.2. London Dispersive Surface Energy, and Lewis Acid–Base Surface Energies

The Fowkes relation [35] and the Hamieh thermal model [22–24,28–31] were applied to determine the London dispersive surface energy $\gamma_s^d(T)$ of the modified copolymer using the following relation:

$$RTlnV_n = 2\mathcal{N}a(T)\left[\gamma_l^d(T)\gamma_s^d(T)\right]^{1/2} + \beta(T) \tag{10}$$

Where $a(T)$ is the surface area of organic molecules given by Hamieh [22] as a function of the temperature, $\gamma_l^d(T)$ the London dispersive component of the surface energy of the solvent, and $\beta(T)$ a constant depending only on the temperature and the solid material.

Supposing $\gamma_s^p$ the total polar (or acid–base) contribution of the surface energy, Equation (11) can then give the total surface energy $\gamma_s$ of the copolymer.

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{11}$$

where $\gamma_s^p$ represents the total polar (or acid–base) contribution of the surface energy.

The determination of $\gamma_s^p$ and the Lewis acid $\gamma_s^+$, and base $\gamma_s^-$ surface energies of the different materials was performed using Van Oss et al.'s method [36], considering two monopolar solvents such as ethyl acetate ($B$) and dichloromethane ($A$), and applying the following expression of the polar free energy $\Delta G_a^p(T)$ of solvents:

$$\Delta G_a^p(T) = 2\mathcal{N}a(T)\left(\sqrt{\gamma_l^-\gamma_s^+} + \sqrt{\gamma_l^+\gamma_s^-}\right) \tag{12}$$

This allowed obtaining the polar (or acid–base) surface energy $\gamma_s^{AB}$ and the total surface energy $\gamma_s^{tot.}$ of the modified copolymers using Equation (15):

$$\gamma_s^{AB} = \gamma_s^p = 2\sqrt{\gamma_s^+\gamma_s^-} \tag{13}$$

## 3. Results

### *3.1. Variations of the Free Energy of Adsorption*

The evolution of the free energy or $RTlnV_n(T)$ of different adsorbed organic solvents at various temperatures for different percentages of 5-hydroxy-6-methyluracil modifying the styrene–divinylbenzene copolymer, was represented in Figure 1.

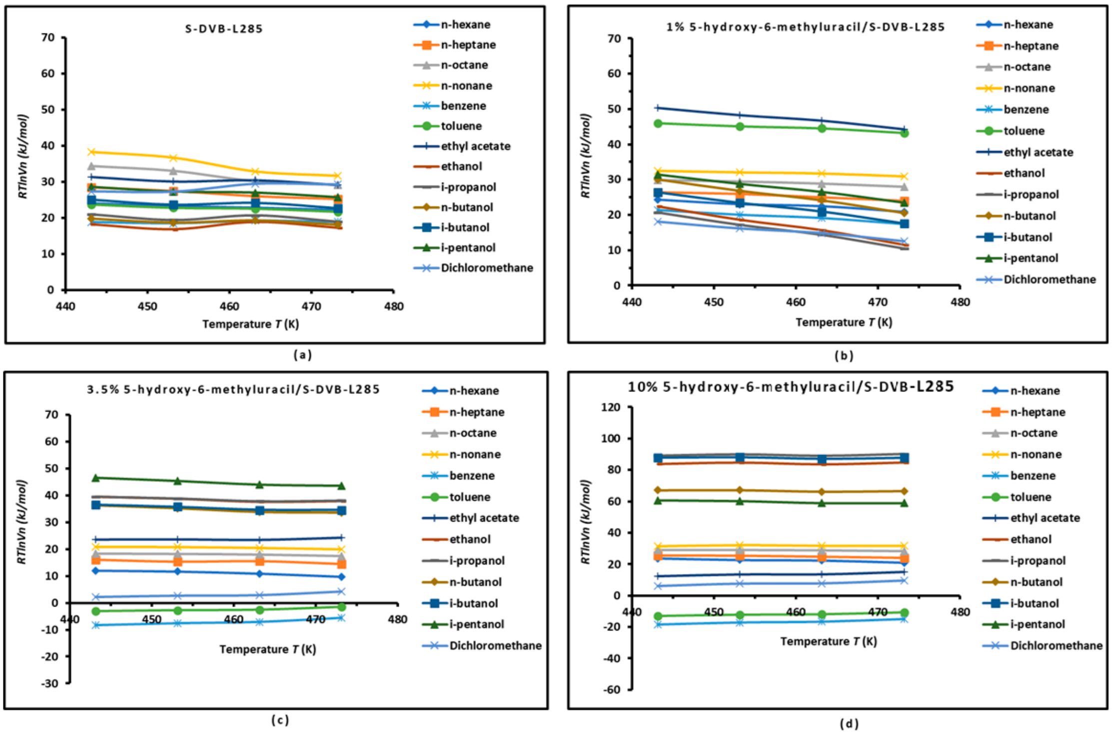


**Figure 1.** Effect of the percentage of 5-hydroxy-6-methyluracil modifying the styrene–divinylbenzene copolymer, on the values of $RTlnV_n(T)$ of different adsorbed organic solvents at various temperatures: porous copolymer S-DVB-L-285 (a), 1% of 5-hydroxy-6-methyluracil (b), 3.5% of 5-hydroxy-6-methyluracil (c), and 10% of 5-hydroxy-6-methyluracil (d).

The curves given in Figure 1 show an important effect of the organic solvents as a function of temperature and also a large effect of the percentage of 5-hydroxy-6-methyluracil on the porous copolymer S-DVB-L285. Figure 1 also showed a linear decrease of $RTlnV_n(T)$ when the temperature increases. The highest values of $RTlnV_n(T)$ were obtained for 10% of 5-hydroxy-6-methyluracil. Therefore, the increase of the modifier percentage led to the increase of the free energy of adsorption.

To better describe the dispersive and polar interactions, it is important to determine the London dispersive surface energy and the surface acid-base interactions, because the variations of the free energy of interaction versus the temperature cannot alone give the required information. This will be developed in the next sections.

### *3.2. London Dispersive Surface Energy of the System S-DVB-L285 with Different Percentages 5-hydroxy-6-methyluracil Percentages*

The Hamieh thermal model [22,24] gave the variations of the surface area $a(T)$ of organic molecules. Equation (10) was used to draw the variations of $RTlnV_n(T)$ of n-alkanes adsorbed on S-DVB-L285 for different percentages of 5-hydroxy-6-methyluracil, as a function of $2\mathcal{N}a(T)\left(\gamma_l^d\right)^{1/2}$ (the expressions of $\gamma_l^d(T)$ of n-alkanes were taken from the Hamieh works [22–24]). The London dispersive surface energy $\gamma_s^d(T)$ of the various porous copolymers for different temperatures was obtained from the slope of $RTlnV_n(T)$ of n-alkane-straight-lines.

Figure 2 gave the variations of $\gamma_s^d(T)$ of different copolymer surfaces as a function of the temperature (Figure 2.a) and the percentage of 5-hydroxy-6-methyluracil (Figure 2b). An excellent linearity in $\gamma_s^d(T)$ was shown with a decrease of $\gamma_s^d(T)$ when the temperature increased (Figure 2a). However, a slight increase in the London dispersive surface energy was observed for 1% of 5-hydroxy-6-methyluracil followed by an important decrease in $\gamma_s^d(T)$ when the modifier percentage increased for all temperatures (Figure 2.b).

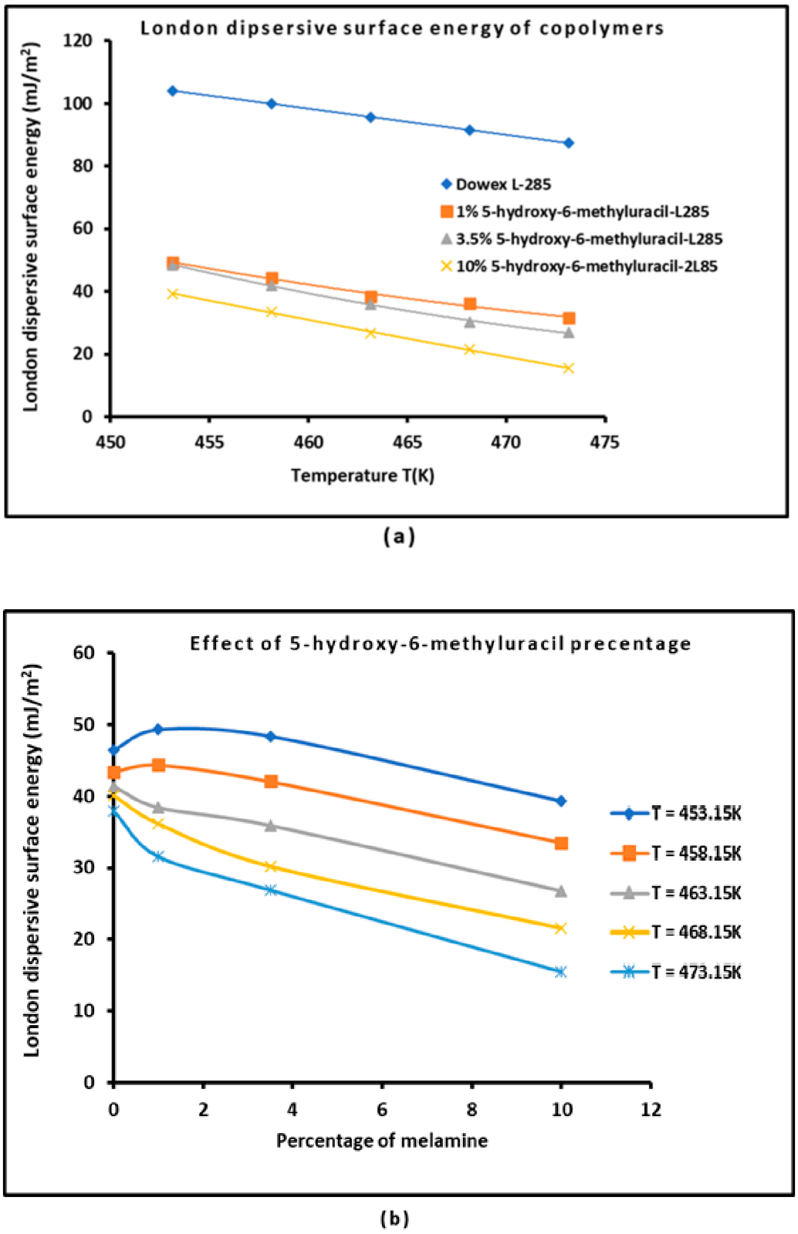


**Figure 2.** Variations in the London dispersive surface energy of materials as a function of the temperature (a) and the percentage of 5-hydroxy-6-methyluracil (b).

To better understand the thermodynamic behavior difference in the modified copolymers, Table 1 was resumed the different values of $\gamma_s^d(T)$ of S-DVB-L-285 modified by 5-hydroxy-6-methyluracil percentages, including the London dispersive surface entropy $\varepsilon_s^d$, the extrapolated values of London dispersive surface energy at 0 K and at 298.15 K, and the temperature maximum $T_{Max}$ of surfaces.

**Table 1.** Linear expressions of $\gamma_s^d(T)$ of S-DVB-L-285 modified by different percentages of 5-hydroxy-6-methyluracil, regression coefficients, London dispersive surface entropy $\varepsilon_s^d$, extrapolated values of London dispersive surface energy at 0 K and 298.15 K, and the temperature maximum $T_{Max}$, using the Hamieh thermal model.

| Copolymer | $\gamma_s^d(T)$ (mJ/m²) | R² | $\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m⁻² K⁻¹) | $\gamma_s^d(T=0K)$ (mJ/m²) | $\gamma_s^d(T = 298.15K)$ (mJ/m²) | $T_{Max}$ (K) |
|---|---|---|---|---|---|---|
| S-DVB-L-285 | $\gamma_s^d(T)$ = -0.835 T + 482.43 | 0.9980 | -0.835 | 482.43 | 233.47 | 577.8 |
| 1% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = -0.874 T + 444.68 | 0.9837 | -0.874 | 444.68 | 184.16 | 508.9 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3.5% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = -1.096 T + 544.23 | 0.9886 | -1.096 | 544.23 | 217.52 | 496.7 |
| 10% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = -1.198 T + 582.13 | 0.9973 | -1.198 | 582.13 | 224.95 | 485.9 |

Table 1 showed that the different values of -$\varepsilon_s^d$, $\gamma_s^d(T = 0\text{ K})$, and $\gamma_s^d(T = 298.15\text{ K})$, increased when the percentage of 5-hydroxy-6-methyluracil increased. This also showed an important effect of the surface groups of the copolymer on the London dispersive surface parameters. However, a decrease was observed in the values of $T_{Max}$ when the modifier percentage increased certainly due to the decrease of $\gamma_s^d(T)$ for higher temperatures.

The above results obtained using the Hamieh thermal model are very different from those obtained by applying the classical Dorris-Gray method [37]. Indeed Dorris and Gray determined the London dispersive component of the surface energy of a solid by defining the increment $\Delta G^0_{-CH2-}$(Relation 14):

$$\Delta G^0_{-CH2-} = \Delta G^0\left(C_{n+1}H_{2(n+2)}\right) - \Delta G^0\left(C_nH_{2(n+1)}\right) \qquad (14)$$

where $C_nH_{2(n+1)}$ and $C_nH_{2(n+1)}$ represents the general formula of two consecutive n-alkanes. $\gamma_s^d(T)$ was determined by Equation (15):

$$\gamma_s^d = \frac{\left[RT\ln\left[\frac{V_n\left(C_{n+1}H_{2(n+2)}\right)}{V_n\left(C_nH_{2(n+1)}\right)}\right]\right]^2}{4\mathcal{N}^2\, a_{-CH2-}^2\, \gamma_{-CH2-}} \qquad (15)$$

Dorris and Gray [85] supposed the surface area of methylene group $a_{-CH2-}$ equal to 6 Å$^2$ and the surface energy of $-CH2-$ given by Equation (16)

$$\gamma_{-CH2-}(\text{in mJ/m}^2) = 52.603 - 0.058\, T\ (in\ K) \qquad (16)$$

Applying the Dorris-Gray method, it was possible to give the results in Table 2.

**Table 2.** Linear expressions of $\gamma_s^d(T)$ of S-DVB-L-285 modified by different percentages of 5-hydroxy-6-methyluracil, regression coefficients, London dispersive surface entropy $\varepsilon_s^d$, extrapolated values of London dispersive surface energy at 0 K and 298.15 K, and the temperature maximum $T_{Max}$, using the Dorris-Gray method.

| Copolymer | $\gamma_s^d(T)$ (mJ/m$^2$) | R$^2$ | $\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m$^{-2}$ K$^{-1}$) | $\gamma_s^d(T = 0K)$ (mJ/m$^2$) | $\gamma_s^d(T = 298.15K)$ (mJ/m$^2$) | $T_{Max}$ (K) |
|---|---|---|---|---|---|---|
| S-DVB-L-285 | $\gamma_s^d(T)$ = 3.250 T + 1610.5 | 0.9037 | -3.25 | 1610.5 | 641.51 | 495.54 |
| 1% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = 1.065 T - 416.4 | 0.9855 | 1.065 | -416.4 | -98.87 | 390.99 |
| 3.5% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = 1.091 T - 421.2 | 0.9493 | 1.091 | -421.2 | -95.92 | 386.07 |
| 10% HOMU/ S-DVB-L-285 | $\gamma_s^d(T)$ = 1.474 T - 600.3 | 0.9413 | 1.474 | -600.3 | -160.83 | 407.26 |

The comparison between Tables 1 and 2 clearly showed the superiority of the Hamieh thermal model relative to the Dorris-Gray method. Indeed, the Dorris-Gray method was based on the hypothesis supposing the surface area of the methylene group did not depend on the temperature, while Hamieh recently proved that this surface area strongly depended on the temperature. This explained the errors obtained by the Dorris-Gray method that showed negative values in the extrapolated London dispersive surface energy at room temperature and at 0 K. The thermal model was proved to be the most accurate method and corrected the errors in the values of $\gamma_s^d(T)$ committed by Dorris-Gray method that exceeded 100% in several cases.

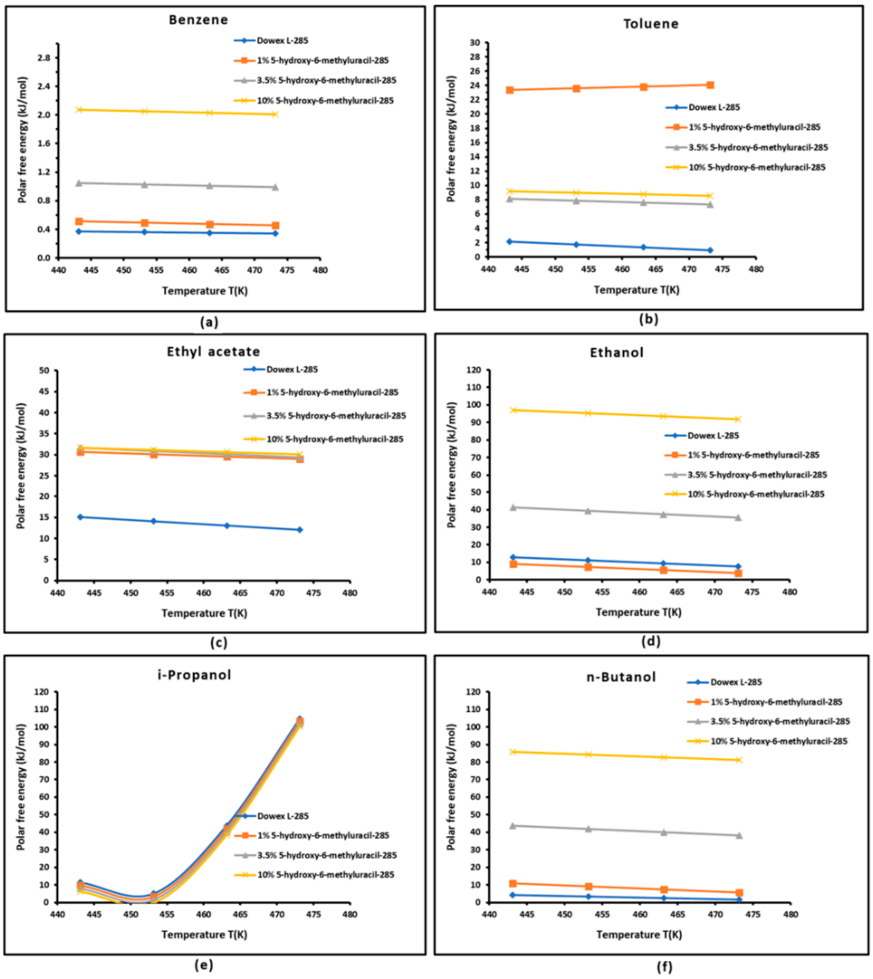
### *3.3. Polar Free Interaction Energy of Dowex L-285 Modified by 5-hydroxy-6-methyluracil with the Polar Probes*

Applying Equations (4) to (7), it was easy to determine the free polar energy $-\Delta G_a^p(T)$ of adsorption of polar organic probes adsorbed on the copolymer surfaces as a function of temperature. The obtained values were given in Table S1.

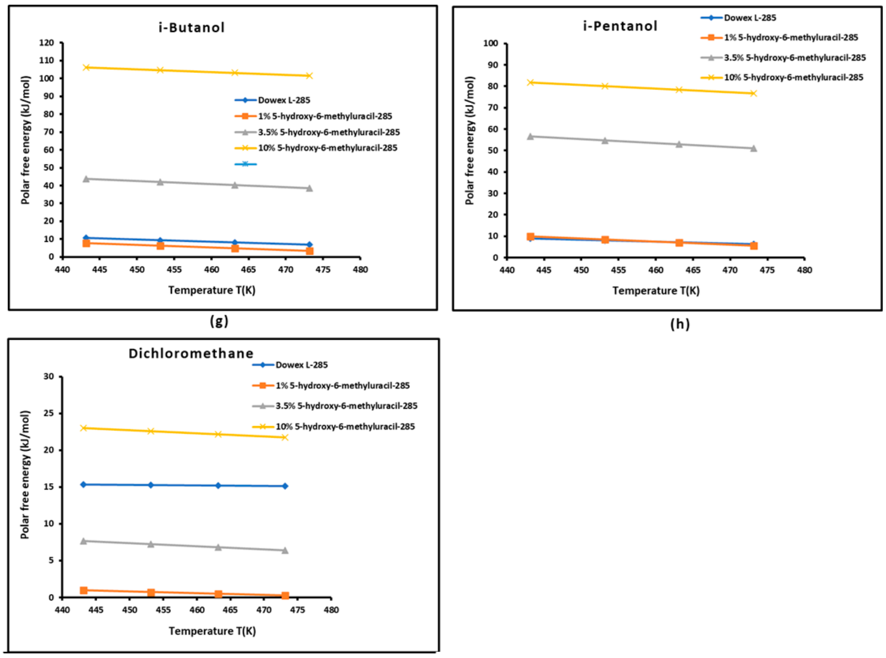
The variations of $-\Delta G_a^p(T)$ of the various polar solvents adsorbed on the copolymer surfaces were plotted in Figure 3 as a function of temperature for various 5-hydroxy-6-methyluracil percentages. Linear variations were obtained allowing giving the values of polar enthalpy $(-\Delta H_a^p)$ and entropy $(-\Delta S_a^p)$ of adsorption. Table S1 and Figure 3 showed that the highest interaction was obtained with the highest percentage of 5-hydroxy-6-methyluracil (10%) showing that the polar free energy increased with the modifier percentage for all polar solvents. whereas, the lowest interaction was obtained with the S-DVB copolymer meaning that the addition of 5-hydroxy-6-methyluracil on the copolymer certainly increased the interaction capacity of the copolymer with the polar molecules. It can be also deduced that the lowest interaction for all materials was obtained with benzene and toluene solvents, whereas, the highest adsorption was shown in Table S1 and Figure 3 for i-pentanol and i-butanol solvents thus proving the highest effect of the hydroxyl group on the free polar interaction.

These conclusions can be obviously shown by Figure 4 giving the variations of $-\Delta G_a^p$ presented as a function of the percentage of 5-hydroxy-6-methyluracil on the copolymer. at different temperatures, where the maximum of the free interaction energy is shown for all polar solvents. The effect of the modifier percentage showed in Figure 4 non-linear variations in the polar free energy of adsorption, with an evident increase of the polar interaction with the 5-hydroxy-6-methyluracil percentage increased.

The determination of the polar enthalpy and entropy of adsorption for the different copolymers was obtained using Equation (8). The obtained results allowed determining the surface polar enthalpy and the entropy of adsorption, as well as the Lewis acid–base constants of the solid materials, as it was shown in the next section.



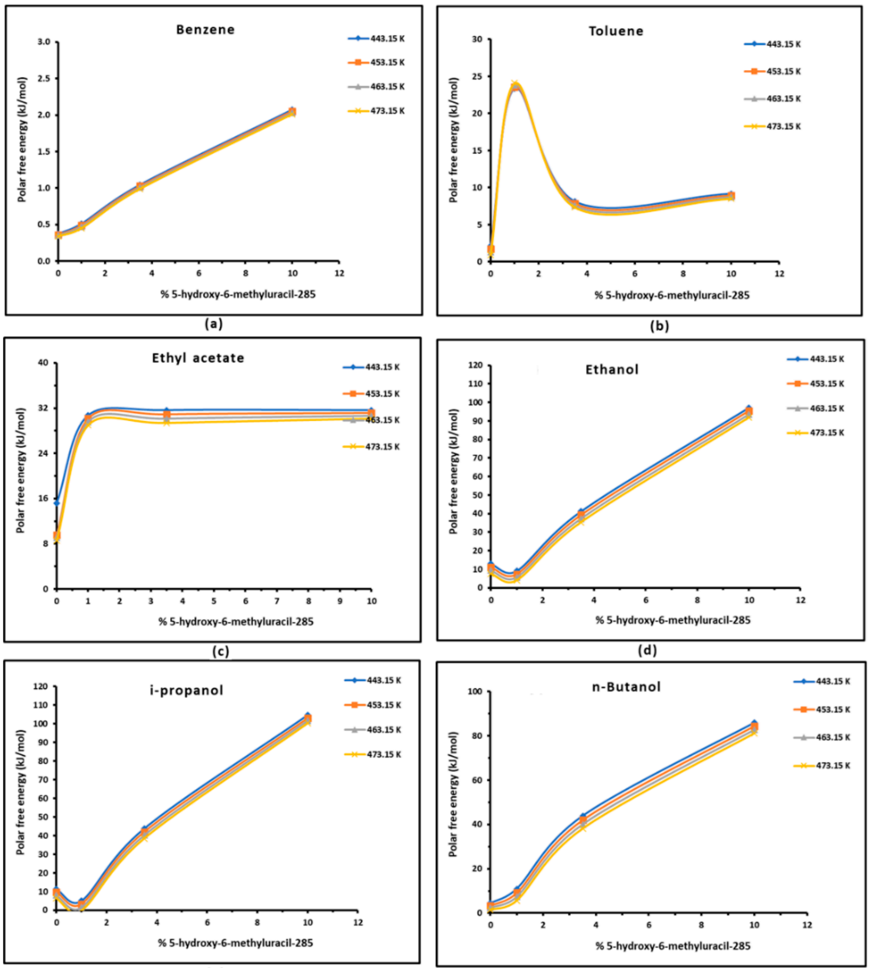
(a) (b) (c) (d) (e) (f)



(g) (h)

(i)

**Figure 3.** Evolution of the free polar energy $\left[-\Delta G_a^p(T)\right]$ of the various polar organic probes adsorbed on the different solid materials as a function of temperature for different 5-hydroxy-6-methyluracil percentages. (a) Dichloromethane, (b) cyclohexane, (c) benzene, (d) toluene, (e) ethyl acetate, (f) ethanol, (g) *n*-propanol, (h) *i*-propanol, (i) *n*-butanol, and (j) *i*-butanol.



(a) (b)

(c) (d)

(e) (f)

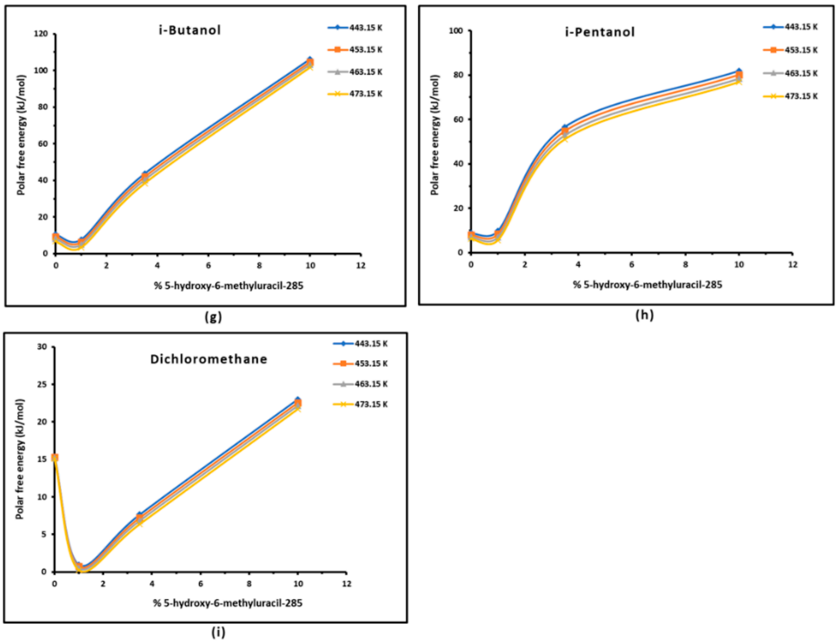


**Figure 4.** Variations in the free polar energy $[-\Delta G_a^p(T)]$ of polar organic probes adsorbed on the different solid materials as a function of 5-hydroxy-6-methyluracil percentage on Dowex L-285 at various temperatures. (a) Dichloromethane, (b) cyclohexane, (c) benzene, (d) toluene, (e) ethyl acetate, (f) ethanol, (g) *n*-propanol, (h) *i*-propanol, (i) *n*-butanol, and (j) *i*-butanol.

### *3.4. Polar Enthalpy and Entropy of Adsorption, and Lewis Acid–Base Parameters of Dowex L-285 Modified by 5-hydroxy-6-methyluracil*

The linear variations of $-\Delta G_a^p(T)$ giving in Table S1 and Figure 3 as a function of temperature allowed giving the values of the polar enthalpy $(-\Delta H_a^p)$ and entropy $(-\Delta S_a^p)$ of the adsorbed polar solvents for the different modifier percentages, using Equation (9). The representation of the variations of $\left(\frac{-\Delta H_a^p}{AN'}\right)$ and $\left(\frac{-\Delta S_a^p}{AN'}\right)$ versus $\left(\frac{DN'}{AN'}\right)$ of the polar solvents adsorbed on the different surfaces led to the values of the Lewis enthalpic $K_A$ and $K_D$ and entropic $\omega_A$ and $\omega_D$ acid–base constants of S-DVB-L-285 with different 5-hydroxy-6-methyluracil percentages (from 1% to 10%). The obtained values were given in Table 3. The results proved the amphoteric character of the different copolymers. A stronger Lewis acidity than the Lewis basicity was observed in the case of the S-DVB copolymer and for a modifier percentage equal to 1%. However, this tendency was inversed for a HMU percentage higher than 3% where the Lewis basicity was shown to be two times higher than their Lewis acidity.

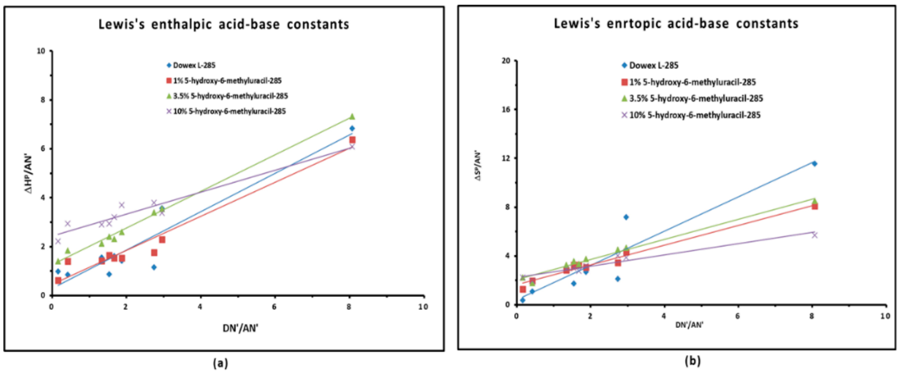


**Figure 5.** Variations in $\left(\frac{-\Delta H_a^p}{AN'}\right)$ and $\left(\frac{-\Delta S_a^p}{AN'}\right)$ against $\left(\frac{DN'}{AN'}\right)$ of polar solvents adsorbed on S-DVB-L-285 modified by different percentages of 5-hydroxy-6-methyluracil (HMU).

**Table 3.** Values of the Lewis acid–base constants $K_A$, $K_D$, $\omega_A$, and $\omega_D$; the acid–base ratios; and the linear regression coefficient $R^2$ relative to S-DVB-L-285, modified by different HMU percentages with the corresponding parameters $S_K = K_A + K_D$ and $S'_K = \omega_A + \omega_D$.

| Material | $K_D$ | $K_A$ | $K_D/K_A$ | $K_A + K_D$ | R² | $10^{-3}\omega_D$ | $10^{-3}\omega_A$ | $\omega_D/\omega_A$ | $10^{-3}(\omega_A + \omega_D)$ | R² |
|---|---|---|---|---|---|---|---|---|---|---|
| S-DVB-L-285 | 0.283 | 0.786 | 0.36 | 1.069 | 0.886 | 0.43 | 1.41 | 0.30 | 1.83 | 0.871 |
| 1% HMU on S-DVB-L-285 | 0.459 | 0.696 | 0.66 | 1.155 | 0.9561 | 1.64 | 0.81 | 2.02 | 2.45 | 0.975 |
| 3.5% HMU on S-DVB-L-285 | 1.265 | 0.75 | 1.69 | 2.015 | 0.994 | 2.07 | 0.82 | 2.52 | 2.89 | 0.9806 |
| 10% HMU on S-DVB-L-285 | 2.425 | 0.451 | 5.38 | 2.876 | 0.9397 | 2.25 | 0.46 | 4.89 | 2.71 | 0.9277 |

Table 3 clearly showed that the basicity of the copolymer linearly increased with the HMU percentage from $K_D = 0.28$ to $K_D = 0.24$ (about 10 times higher for 10% HMU on the copolymer). However, the acidity of S-DVB-copolymer gradually decreased from $K_A = 0.79$ to $K_A = 0.45$ showing a decrease of about 60% for 10% HMU on S-DVB copolymer. The same conclusions were confirmed for the entropic Lewis acid-base parameters $\omega_A$ *and* $\omega_D$. Table 3 showed that total Lewis acid-base parameters $S_K$ and $S'_K$ highlighted an important increase when the HMU percentage increased also confirming the previous conclusion relative to the stronger polar interaction for higher HMU percentage.

The previous results allowed to give in Table 4 the different equations of Lewis acid-base parameters as a function of HMU percentage with the linear regression coefficients.

The excellent linear regression coefficients given in Table 4 and shown in Figure 6 highlighted the important effect of the HMU percentage on the Lewis acid-base character of the copolymer.

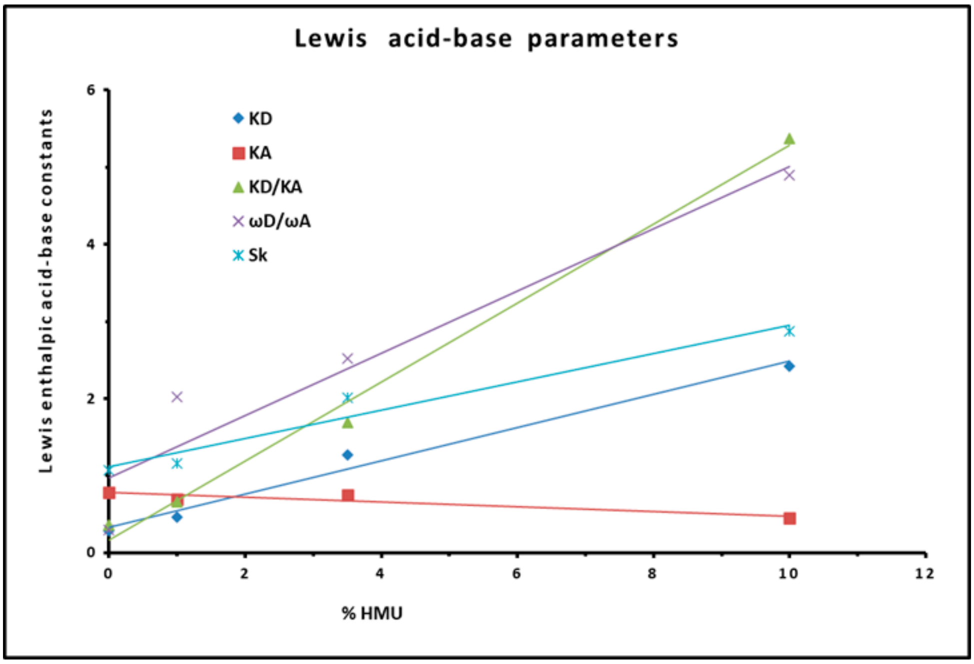


**Figure 6.** Curves of the Lewis acid–base parameters $K_A$, $K_D$, $K_D/K_A$, $\omega_D/\omega_A$, and the parameters $S_K = K_A + K_D$ as a function of 5-hydroxy-6-methyluracil percentage (%HMU).

**Table 4.** Equations of Lewis acid-base parameters as a function of %HMU with the corresponding linear regression coefficients.

| Parameter | Equation | R² |
|---|---|---|
| Acid constant $K_A$ | $K_A = 0.22\ \%\mathrm{HMU} + 0.33$ | 0.9839 |

| | | |
|---|---|---|
| Basic constant $K_D$ | $K_D$ = -0.031 %HMU + 0.79 | 0.8638 |
| Ratio $K_D/K_A$ | $K_D/K_A$ = 0.51 %HMU + 0.17 | 0.9926 |
| Ratio $\omega_D/\omega_A$ | $\omega_D/\omega_A$ = 0.40 %HMU + 0.97 | 0.9165 |
| Parameter $S_K$ | $S_K$ = 0.18 %HMU + 1.11 | 0.9561 |

### *3.5. Polar Acid–Base Surface Energies of S-DVB Copolymer Modified by HMU*

Using Equations (11) to (13), the polar acid $\gamma_s^+$ and base $\gamma_s^-$ surface energies of S-DVB copolymer modified by 5-hydroxy-6-methyluracil for different percentages were determined with the help of the values of the free polar energy $-\Delta G_a^{sp}(T)$ of dichloromethane and ethyl acetate polar solvents given in Table 5.

**Table 5.** Values of $-\Delta G_a^p(T)$ (in kJ/mol) for dichloromethane and ethyl acetate adsorbed on Dowex L-285 modified with different 5-hydroxy-6-methyluracil percentages at different temperatures.

| Dichloromethane | | | | |
|---|---|---|---|---|
| T(K) | Dowex L-285 | 3.5% HOMU/Dowex L-285 | 1% HOMU/Dowex L-285 | 10% HOMU/Dowex L-285 |
| 453.15 | 15.274 | 15.609 | 24.349 | 9.737 |
| 458.15 | 15.239 | 15.559 | 24.294 | 9.352 |
| 463.15 | 15.204 | 15.509 | 24.239 | 8.967 |
| 468.15 | 15.169 | 15.459 | 24.184 | 8.582 |
| Ethyl Acetate | | | | |
| T(K) | Dowex L-285 | 3.5% HOMU/Dowex L-285 | 1% HOMU/Dowex L-285 | 10% HOMU/Dowex L-285 |
| 453.15 | 10.106 | 8.503 | 9.667 | 10.567 |
| 458.15 | 9.593 | 8.378 | 9.507 | 10.314 |
| 463.15 | 9.079 | 8.253 | 9.347 | 10.06 |
| 468.15 | 8.566 | 8.128 | 9.187 | 9.807 |

The obtained results were plotted in Figure 7.

The polar acid–base surface energy $\gamma_s^p$ was obtained using Equation (11), while the total surface energy $\gamma_s^{tot.}$ was determined from Equation (13) as a function of temperature. The values of the different surface polar parameters such as $\gamma_s^+(T)$, $\gamma_s^-(T)$, $\gamma_s^{AB}(T)$, $\gamma_s^d(T)$, and $\gamma_s^{tot.}(T)$ of modified copolymer were given in Table S2. The variations of the different surface polar parameters were plotted in Figure 7 as a function of temperature. Linear variations of the different polar surface energy versus the temperature were shown in Figure 7. The results show that the highest polar surface energy values were obtained for the highest HMU percentage again confirming the important role of the modifier in increasing the polarity of the copolymer and consequently its use in many industrial applications such as catalysis and selective adsorption of several organic molecules.

The results given in Table S3 and Figure 7 allowed drawing in Figure 8 the polar surface energy of the adsorbed polar probes against the temperature using the Fowkes relation and the Hamieh thermal model. It seems that the adsorbed ethanol and i-propanol polar solvents the highest values of the polar surface energy, while the lowest values were obtained in the case of adsorption of toluene and benzene. Identical results were obtained when the S-DVB copolymer was modified by melamine in a previous study [32].

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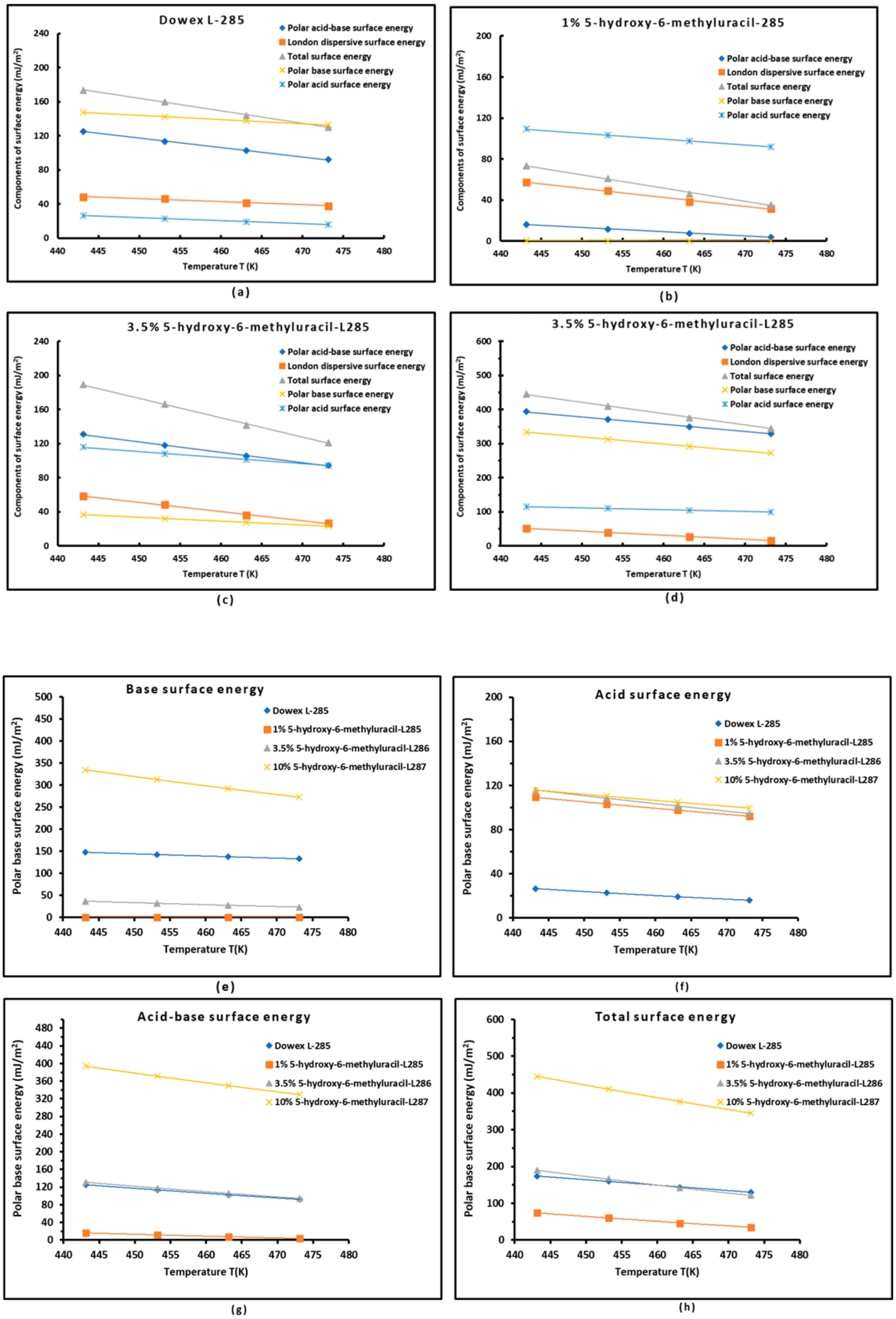
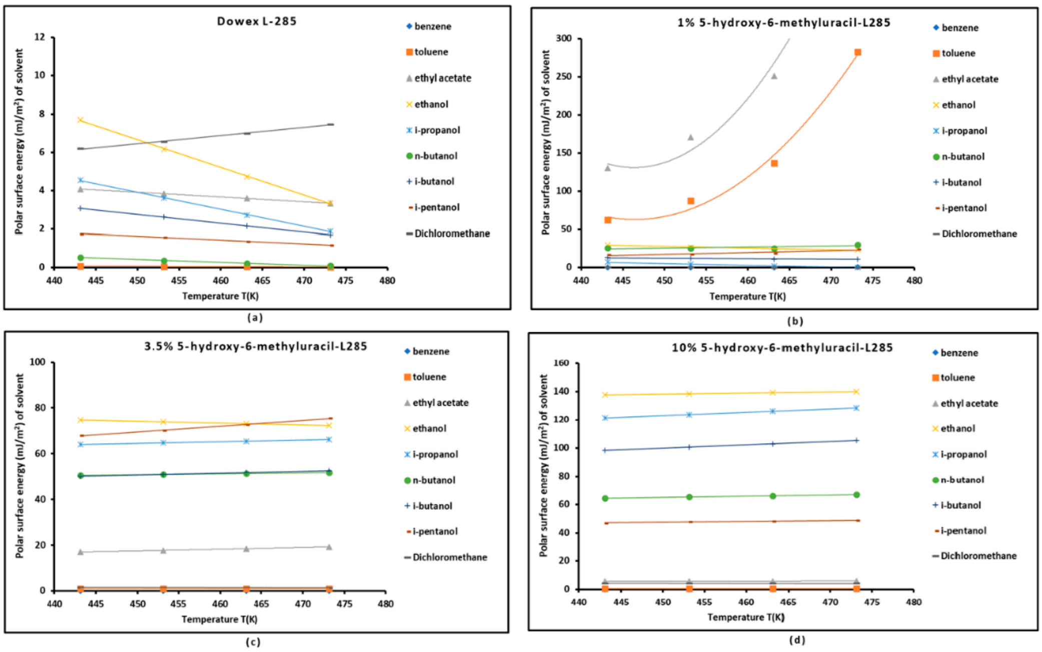


(a) (b) (c) (d) (e) (f) (g) (h)

**Figure 7.** Variations in acid and base surface energy components, and total energy (in mJ/m$^2$) of Dowex L-285 modified by different 5-hydroxy-6-methyluracil percentages as a function of temperature: Dowex L-285 copolymer (a), 1% HMU (b), 3.5% HMU (c), 10% HMU (d), base surface energy (e), acid surface energy (f), acid–base surface energy (g), and total surface energy (h).



(a) (b) (c) (d)

**Figure 8.** Variations in polar surface energy (in mJ/m$^2$) of the different polar solvents adsorbed on Dowex L-285 modified by varying the HMU percentage as a function of temperature: Dowex L-285 (a), 1% HMU (b), 3.5% HMU (c), and 10% HMU (d).

### 3.6. Determination of the Average Separation Distance H

Our new methodology was applied to determine the separation distance $H$ between the organic molecules and the modified copolymer as a function of the temperature. The results were represented in Figure 9. It was showed a certain effect the HMU percentage on the separation distance between solvents and copolymer. A net difference in the values of *H* between the S-DVB copolymer and the corresponding modified copolymer.

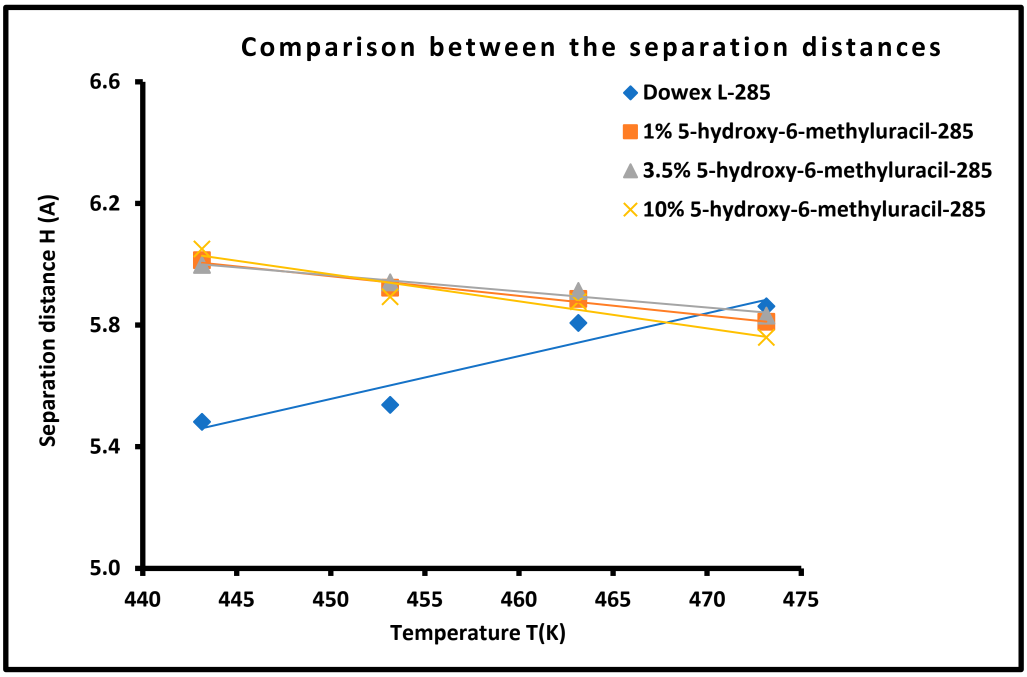


**Figure 9.** Evolution of the separation distance $H(T)$ (in Å) between the organic solvents and Dowex L-285, modified by HMU, as a function of the temperature.

## 4. Conclusions

This study constituted a new contribution on the determination of the London dispersive surface energy, the polar surface energy and Lewis acid-base properties of styrene–divinylbenzene copolymer (Dowex L-285) modified by 5-hydroxy-6-methyluracil at different percentages from 1% to 10%, using the inverse gas chromatography technique at infinite dilution and applying our new methodology allowing a net separation between the dispersive and polar contributions of the interaction between the polar solvents and the copolymer. The determination of the London dispersive surface energy of the different surfaces showed a linear decrease of $\gamma_s^d(T)$ when the temperature increased and proved that the modification of the copolymer by 5-hydroxy-6-methyluracil led to a net decrease in the values of $\gamma_s^d$. The application of the Hamieh thermal model using the London dispersion interaction allowed an accurate determination of the Lewis acid–base parameters of the modified copolymer. An amphoteric character of the different copolymers was highlighted with more acidic character for the copolymer and for 1%HMU and a stronger basicity when the percentage of the modifier is higher than 3%. The highest basicity was observed for 10%HMU. An important effect of the modifier percentage on the dispersive and polar surface energy of the styrene–divinylbenzene copolymer was highlighted with highest values of the different surface parameters for the copolymer modified by 10% of 5-hydroxy-6-methyluracil.

**Supplementary Materials:** The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Table S1. Variations in $\Delta G_a^p(T)\ (kJ/mol)$ of different polar solvents adsorbed on Dowex L-285 and various 5-hydroxy-6-methyluracil percentages as a function of temperature. Table S2. Values of $\gamma_s^+(T)$, $\gamma_s^-(T)$, $\gamma_s^{AB}(T)$, $\gamma_s^d\ (T)$, and $\gamma_s^{tot.}(T)$ of Dowex L-285 and the different percentages of 5-hydroxy-6-methyluracil on the copolymer.

**Author Contributions:** Conceptualization, T.H. and V.Y.G.; methodology, T.H.; software, T.H.; validation, T.H. and V.Y.G.; formal analysis, T.H. and V.Y.G.; investigation, T.H. and V.Y.G.; resources, V.Y.G.; data curation, V.Y.G.; writing—original draft preparation, T.H.; writing—review and editing, T.H.; visualization, T.H. and V.Y.G.; project administration, T.H. and V.Y.G.; funding acquisition, V.Y.G. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data presented in this study are available in the article and Supplementary Materials.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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