



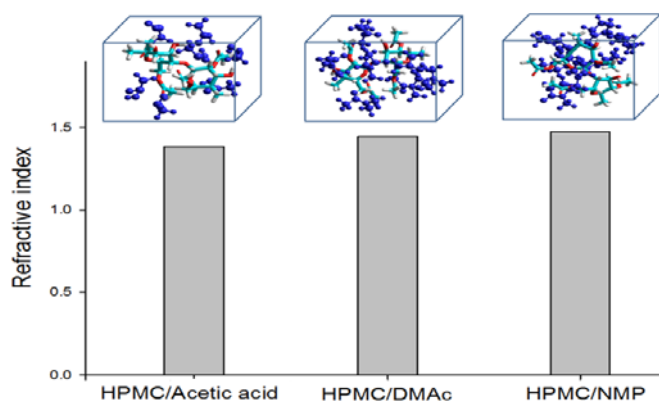
## MOLECULAR MODELING, SPECTRAL AND OPTICAL PROPERTIES OF HPMC IN DIFFERENT SOLVENTS

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Received February 8, 2021

Solutions of hydroxypropylmethyl cellulose (HPMC) were prepared in three distinct solvents. Molecular modeling was employed to attain a comprehensive image of the conformational changes in the solvent environment by means of quantum chemical parameters and interaction energy. UV-VIS spectra of the HPMC solutions were recorded, revealing distinct absorption features as a function of the solvent polarity. Also, the refractive index was determined in order to evaluate the solution density and in this way to probe the values of end-to-end chain distance obtained from simulations. These results are useful for understanding the effects of used solvents in HPMC processing and how they influence the spectral and optical properties.



### INTRODUCTION

Natural polymers, including cellulose derivatives, exhibit outstanding properties and their specific performances are impacted by the solvents types that are used in the preparation and processing stages.<sup>1</sup> Among cellulosic compounds, hydroxypropyl methylcellulose (HPMC) is a semi-synthetic cellulose ether, known for its good viscoelastic, biocompatible and biodegradable properties, which are of interest in many fields, ranging from flexible electronics<sup>2</sup> and pharmacology<sup>3</sup> to adhesives.<sup>4</sup> For such uses, HPMC needs to be processed under the form of gels, coatings or films, therefore the polymer powder must be dissolved in appropriate solvents. HPMC is soluble in water and many polar organic

solvents, enabling the work in both aqueous and non-aqueous media. This polymer presents unique solubility characteristics in cold or hot liquid environments. HPMC exhibits high organo-solubility and thermo-plasticity in regard to the rest of the methyl cellulose counterparts. The solvent employed for HPMC processability was shown to impact its shear flow features<sup>5</sup> and thereby other properties which are involved in the product performance.

Solvent environments could also determine different optical and spectral properties of polymers.<sup>6</sup> Analysis of light interaction with polymer solutions allows extraction of essential data related to electronic transitions and macromolecular coil characteristics in the fluid medium. The quality and polarity of the used

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solvent are determining specific arrangement of the macromolecular chains and implicitly of their constituent polar groups. These aspects are reflected in the polymer absorption/transmittance spectrum<sup>7</sup> and also in its refractive index.<sup>8</sup> Few studies deal with transparency and/or optical parameters of HPMC in combination with collagen<sup>9</sup> and polyvinyl alcohol.<sup>10</sup> From what we know, there are no scientific researches that investigate the effect that different solvents could have on the optical features of pure HPMC.

Based on this, our work aims to investigate the manner in which the solvent nature affects some spectral and optical features, namely transmittance, optical band-gap energy and refractive index. At the same time, molecular modeling was performed to gain comprehensive image of the optical features of this cellulose derivative. Such studies are useful for understanding the effects of solvents on the optical performance of polymer coatings used in optoelectronic domain. The advantage of cellulose derivatives arises from its biodegradable characteristics which enable low impact on the global environment after the device disposal and thereby preserves the quality of life.

## RESULTS AND DISCUSSION

### Molecular modeling of the HPMC/solvent interactions

Polymers behave differently in various liquid media since the solvent features are determining the strength and type of the interactions and through them the coil conformation. Molecular modeling enables facile understanding of these aspects prior to experiments. First, the HPMC and solvents molecules were computed to optimize their geometry and to calculate the total energy and interaction energy of the binary system. At this point, quantum chemical parameters, such as the highest occupied molecular orbital energy (E-HOMO) and lowest unoccupied molecular orbital energy (E-LUMO) were evaluated, providing data regarding the electronic transitions. The HOMO-LUMO energy gap (Eg) is linked to the compound stability, which is higher as Eg increases.<sup>11</sup> In Figure 1 are displayed the HOMO-LUMO graphs for HPMC structural unit (SU) surrounded by seven solvent molecules of either dimethylacetamide (DMAc), 1-methyl-2-pyrrolidone (NMP) or acetic acid. It is remarked that electron donating (E-HOMO) and accepting abilities (E-LUMO) of HPMC are slightly affected by the solvent type. The

higher polarity of NMP determines a better solubility of HPMC and a higher Eg value (higher stability in this environment) in contrast to acetic acid which has the lowest polarity.

Based on the HOMO and LUMO energies, it was further possible to estimate some chemical reactivity descriptors.<sup>11</sup> The obtained values for HPMC/solvent samples are depicted in Table 1. The ionization potential (IP) and electron affinity (EA) are essential for estimation of the chemical hardness (CH), which denotes reactivity and stability of a chemical system. For the studied HPMC solutions, CH is ranging as follows: NMP > DMAc > Acetic acid. Also, chemical potential (CP), which describes the half of gap energy, presents small variations for the studied samples. Electrophilicity index (EPh) indicates the capacity of a substance to accept electrons and is higher for HPMC in acetic acid medium.

The next simulation step relies on assessment of the HPMC energy of interaction with these three solvents. Determination of the interaction energy ( $\Delta E$ ) of the binary systems is made using equation (1):

$$\Delta E = E_{\text{complex}} - (E_{\text{HPMC}} + E_{\text{solvent}}) \quad (1)$$

where  $E_{\text{complex}}$  is the total energy of polymer/ solvent system,  $E_{\text{HPMC}}$  is the polymer total energy and  $E_{\text{solvent}}$  is the solvent total energy.

Figure 2 illustrates the computed conformation of HPMC enclosed by seven solvent molecules subjected to geometry optimization routine. The chain end-to-end distance measured with modeling software is ranging in the following order: 11.54 Å (NMP) > 11.07 Å (DMAc) > 10.41 Å (Acetic acid). This shows that NMP can be considered “good” solvent for HPMC and facilitates polymer–solvent interactions, so the macromolecules in this medium assume a somewhat extended shape.

The total energy of HPMC structural unit and those of molecules pertaining to each of the used solvents were obtained using parametric model 3 approach combined with Restricted Hartree Fock mechanism (see Table 2). To extract the total energy, the fully-optimized geometries of HPMC and of the solvent cage were used. These values were further inserted in equation (1) to deduce the interaction polymer/solvent energy. The magnitude of the interaction energy describes the cellulosic polymer affinity towards the solvent molecules, denoting the stability of the formed complex. Analyzing the  $\Delta E$  data from Table 2, one may observe that the stability of HPMC/solvent system is varying in the next order: NMP > DMAc > Acetic acid.

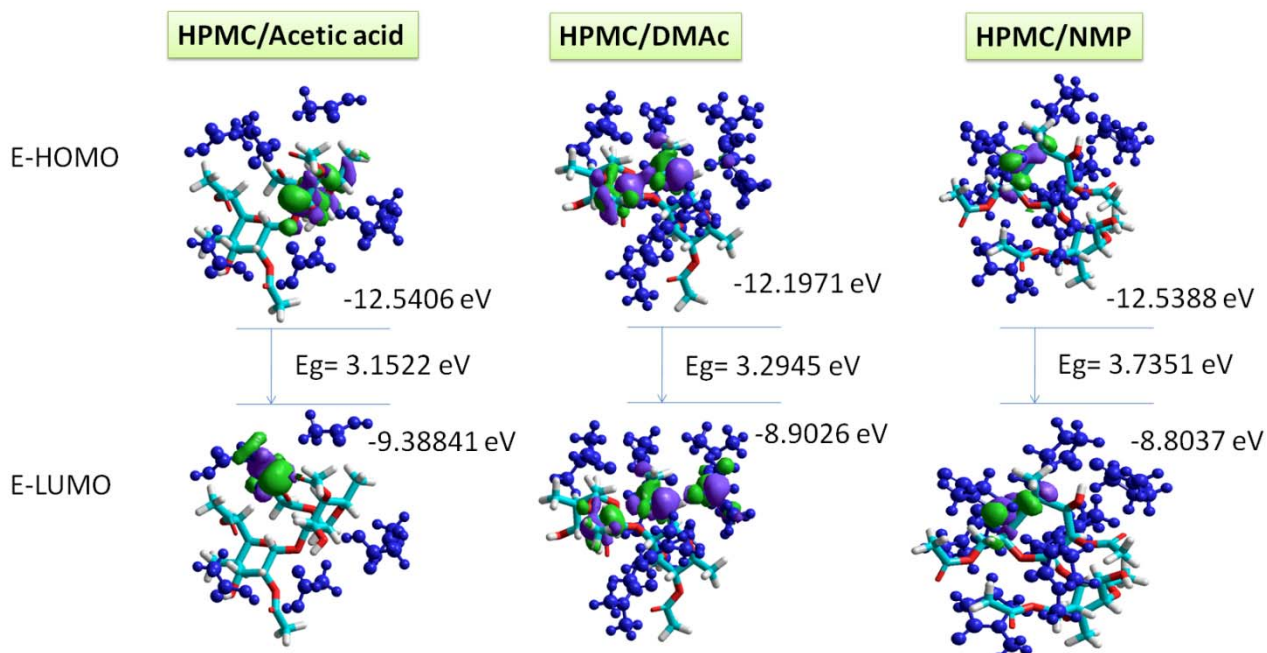


Fig. 1 – Images of the HOMO-LUMO plots for HPMC in various solvents.

Table 1

Computed data of the chemical reactivity descriptors (in eV): ionization potential (IP), electron affinity (EA), electronegativity (EN), chemical potential (CP), chemical hardness (CH), and electrophilicity (EPh)

System	IP	EA	EN	CP	CH	EPh
HPMC/Acetic Acid	12.541	9.388	10.965	-10.965	1.576	38.139
HPMC/DMAc	12.197	8.903	10.549	-10.549	1.647	33.784
HPMC/NMP	12.539	8.804	10.671	-10.671	1.868	30.488

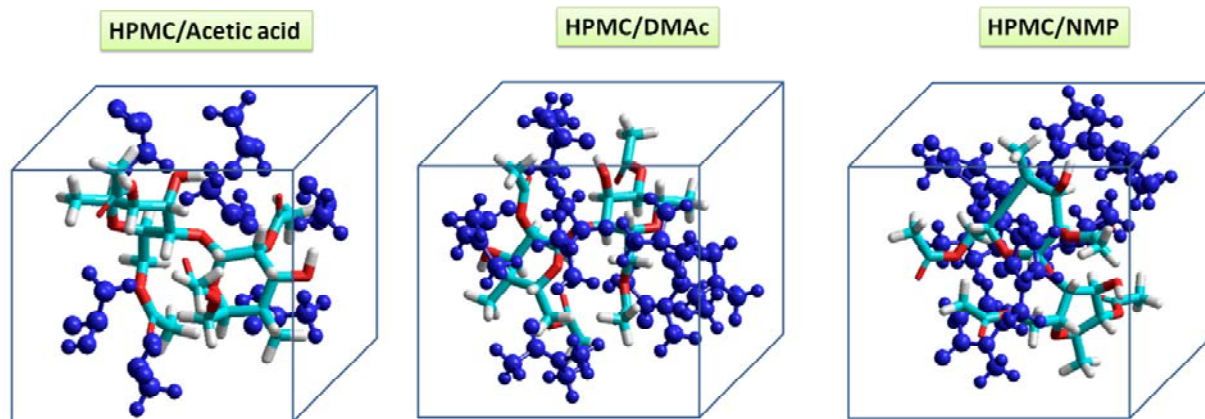


Fig. 2 – Molecular modeling of optimized HPMC conformation enclosed by seven solvent molecules.

Table 2

Computed data of total energy and interaction of the studied molecules and systems

System	E-TOT, kcal/mol	Interaction energy, kcal/mol
HPMC	-160227.82	-
Acetic acid	-20448.42	-
DMAc	-24635.92	-
NMP	-27389.78	-
HPMC /DMAc	-184870.77	-7.03
HPMC /NMP	-187625.99	-8.39
HPMC /Acetic acid	-180681.32	-5.08

### Optical properties of the HPMC solutions

Transmittance spectra of HPMC solutions were recorded in the UV-VIS spectral range. Figure 3 shows that the used solvents are affecting the absorption/transmittance of HPMC. The obtained data are presenting differences, especially in the 260-330 nm interval of wavelengths. The magnitude of the cut-off wavelength ( $\lambda_c$ ), attributed to a transmittance less than 1%, is depicting the influence of the polymer/solvent interactions. Examining the obtained spectra, it can be noted that the  $\lambda_c$  values are: 281 nm, 289 nm and 316 nm for HPMC/NMP, HPMC/DMAc and HPMC /Acetic acid, respectively. Starting with 400 nm, one may see that all prepared solutions have a transmittance above 90%. The absorption edge allows to evaluate band gap energy ( $\sim 1240/\lambda_c$ ), which is 4.41 eV, 4.29 eV and 3.92 eV for HPMC/NMP, HPMC/DMAc and HPMC /Acetic acid, respectively. The band gap values determined from spectral data are ranging in the same order as those achieved from molecular modeling.

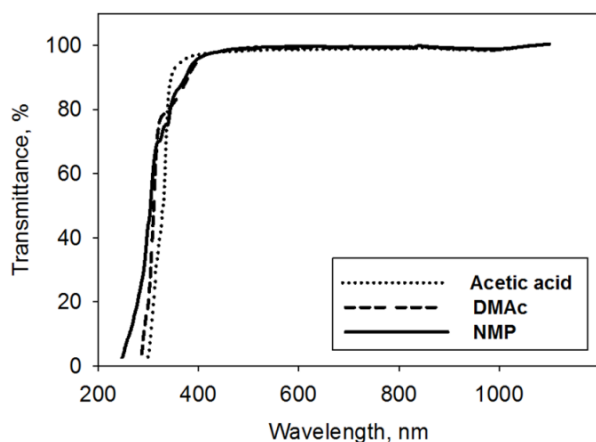


Fig. 3 – UV-VIS spectra of the HPMC solutions.

The refractive index of HPMC samples was attained by theoretical and experimental procedures. First, the theoretical refractive index ( $n_{th}$ ) of the solutions was calculated using additivity rule, described by equation (2):

$$n_{th} = n_{solvent} \phi_{solvent} + n_{polym} \phi_{polym} \quad (2)$$

where  $n_{solvent}$  is the refractive index of the solvent,  $\phi_{solvent}$  is volume fraction of the solvent,  $n_{polym}$  is the refractive index of the polymer and  $\phi_{polym}$  is volume fraction of the polymer.

The refractive index values of each solvent were taken from provider's data as being 1.470 for NMP, 1.437 for DMAc and 1.371 for acetic acid. For HPMC, refractive index was estimated based on group contribution theory that involves addition of the molar refraction and molar volume increments - known in the literature.<sup>12</sup> This led to a refractive index for HPMC of 1.520, which is in agreement with the report of Curtis-Fisk *et al.*<sup>13</sup> The values of theoretical refractive index of the HPMC solutions are presented in Table 3. Secondly, experiments were conducted on an Abbe refractometer and the attained values ( $n_{exp}$ ) are listed in Table 3. There are small differences that can be noted between the theoretical and the experimental data, but overall the refractive index is highest for the polymer solutions in NMP and lowest for acetic acid. These results can be explained by considering the variations in the solvent's polarity. The dielectric constants of the solvents, reflecting their relative polarity, are: 6.2 for acetic acid, 21 for DMAc and 32 for NMP. Acetic acid which has a less polar character has a weaker power to penetrate among the HPMC chains than the other two solvents, thus the coils density in solution is smaller and light travels faster leading to a smaller refractive index. Regarding NMP samples, the result could be ascribed to the good solvent nature, which expands the macromolecular chains. In turn, this affects the solution density so that the light speed is lower in this sample environment. Such spectral and optical results could be useful for optoelectronic purposes, including in display devices,<sup>14</sup> where cellulose derivatives are desired for fabrication of "green" device components with minimal impact on the environment.

Table 3

The experimental and theoretical values of the refractive index of HPMC solutions

System	$n_{th}$	$n_{exp}$
HPMC/Acetic Acid	1.386	1.390
HPMC/DMAc	1.445	1.446
HPMC/NMP	1.475	1.479

### EXPERIMENTAL

Hydroxypropyl methylcellulose (40-60 cP, 2% in water), dimethylacetamide (anhydrous, 99.8%), 1-methyl-2-pyrrolidone (anhydrous, 99.5%) and acetic acid (glacial,  $\geq 99.7\%$ ) were achieved from Sigma-Aldrich.

Molecular modeling of the interactions of the cellulose derivative with certain solvents was done using Hyperchem8

(Demo version). The examined compounds were geometrically optimized by employing molecular mechanics (MM) based on BIO+(CHARMM) force field. Then, semi-empirical quantum chemical with parametric method 3 (PM3) routine was employed to determine chemical reactivity descriptors. This approach allowed obtaining of some parameters that included the energy of the highest occupied molecular orbital (E-HOMO), the energy of the lowest unoccupied molecular orbital (E-LUMO), and the total energy (E-TOT).

UV-VIS spectra of the 10% HPMC solutions were collected on SPECORD 210 PLUS Analytik Jena. Refractive index of HPMC solutions was measured on a Abbe refractometer at room temperature.

## CONCLUSIONS

The effect of the solvent nature on polymer solutions structural, spectral and optical properties are analyzed. The quality of the solvent affects the conformational properties of HPMC as indicated by the values of the chemical reactivity descriptors, total energy and interaction energy. Solvent features determine various degrees of HPMC coil expansion in solution and therefore different properties. The high transparency and low refractive index values recommend the samples for realization of “green” components used in displays or other optoelectronic devices.

*Acknowledgments.* This work was performed with the support of Roumanian Academy Projects “Polymer materials. Correlations of structure, morphology, optical and electrical properties” (P8.3)

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