

Article

Polysaccharides-Reinforced Bitumens: Specificities and Universality of Rheological Behavior

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Abstract: The rheological properties of bitumens can be modified by the addition of specific chemical additives. Taking into account the molecular complex aggregation pattern, we hypothesized that macromolecules characterized by long, flexible, and hydrophilic chains can establish soft bridges connecting the different polar aggregates of asphaltenes, strengthening their overall hierarchical supra-structures, and consequently increasing rheological performance at higher temperatures. Here, we propose the use of low cost and high availability polysaccharides as chemical additives to improve the rheological characteristics of a bitumen and to strengthen its thermal resistance. Fourteen different low-cost and high-availability polysaccharides, (flours, gums, and extracts from vegetable products) have been tested. While algae *euchemae* have proved to be the most effective additive, corn and 00 flours are the least effective. Attempts to explain their differences have been made considering their chemical interactions with the polar molecules of asphaltenes within the complex framework of their supramolecular hierarchical structures. Through Arrhenius analysis, a correlation between activation energy and preexponential factor has been found, which can be useful for practical purposes, together with an unexpected consistency with the behavior of simple liquids, despite the striking differences in structure. Furthermore, a qualitative model has been suggested. The added value of this work is the focus on polysaccharides constituting low-cost, high availability materials which are sometimes even found as waste in industrial processes, all factors which, together with the environmental issues connected with their use, can be considered for large-scale applications.

Keywords: bitumen; asphaltene; network; polysaccharides; Arrhenius; viscosity

1. Introduction

Asphalts are used throughout the world for road pavement. They are biphasic materials with the major phase made by macro-meter sized inorganic particles (93–96% *w/w*) held together by the minor phase, an organic high viscosity viscoelastic material called bitumen, which acts as the binding agent among the inorganic particles, thus conferring to the final material the required plasticity, rigidity, and stability. Despite its minor presence in the overall material, bitumen plays a pivotal role in determining rheological characteristics, which must fulfill the desired need for ductility, resistance to stress, and thermal stability.

The properties of a bitumen are the overall consequence of its structure: it is characterized by the presence of assemblies of small (few nm) stacks of polar molecules (asphaltenes) stabilized by

amphiphilic resins and dispersed in the apolar matrix phase of paraffins and aromatic oils (maltene) [1,2]. Recently, it has been unveiled by X-Ray scattering [3] that the structure is even more complex, with the asphaltene clusters organized in hierarchical structures of different length scales (up to hundreds of nanometers and even to micro-scales with the so called “bee-structures” [4]).

In this framework, an additive can therefore exert its action through various mechanisms: for example, an additive tuning the red-ox state of the polar molecules can hinder oxidation-induced degradation, an adhesion promotion (acting on the inorganic/organic interfacial tension) can better disperse the inorganic particles among the bitumen matrix, and an amphiphilic additive like lecithin can help in avoiding ageing [5] stabilizing the asphaltene clusters due to their well-known capability of keeping dispersed nanoparticles of polar substances, both organic [6,7] and inorganic [8,9]. In this ambit, it has been recently observed that some additives can form a polymeric network (e.g., poly phosphoric acid) increasing the rigidity [10]. Furthermore, additives with rejuvenating actions (reducing viscosity and restoring the plastic behavior of a freshly prepared bitumen) have been discovered [11].

In evaluating the rheological performances of such a complex material, an empirical approach is always followed within a chosen temperature range [12,13] for convenient use [14,15]. Among the various methods for bitumen characterization [16], however, small amplitude oscillatory rheometry is considered one of the most effective. It uses specific specimen geometries and instruments and allows systematic and mathematical interpretation of the results. Moreover, rheometry, as a scientifically rigorous (non-empirical) method, has the advantage to give data that can be rationalized in terms of the real complex structure possessed by the bitumen. A review offering perspectives of bitumen characterization is the recent review by Loise et al. [11].

Then, the scientific idea behind this work takes into account for the spatial distribution of the asphaltene-based polar domains, and the microscopic mechanism of viscosity involved in such systems: to use a soft (i.e. flexible) and long molecule characterized by hydrophilic functional groups which can bridge the different polar stacks/aggregates of asphaltenes by formation of a network connecting them and reinforcing the overall structure. The idea is somehow not new: Król et al. [17] and Somé et al. [18], used vegetable oils and the corresponding methyl esters for obtaining environment-friendly bitumen fluxes by oxypolymerization-based polymerization, which crosslinks the structural units. This allowed for the viscosity increase of the stock, and contributed to its hardening and drying. The principle of using additives susceptible to oxypolymerization has been recently exploited to prepare additives able to increase the bitumen viscosity [19] and resembles the well-known effect of poly-phosphoric acid of stiffening the bitumen [20]. However, here the scientific idea is more articulated: given the complex framework of asphaltene stacks hierarchically organized in assemblies with different length-scales, it can be reasonably hypothesized that the interactions at longer length scales must be of lower intensity than those at shorter length-scales. Therefore, in order to better accommodate both (i) small and strongly interacting asphaltene stacks, and (ii) bigger and less interacting asphaltene assemblies of clusters, “softer”, long and flexible molecules with interacting polar groups disseminated along their chain would be needed.

The flexibility would allow for the additive to better adapt its conformational state to the long-range structure, whereas the presence of polar functional groups along the chain, together with its length, can allow for effective and disseminated interactions. The mutual interactions between the additive molecules (polysaccharides are well known in increasing the viscosity even at low concentrations) should complete the job. The additive can therefore be considered as a “softly interacting” species, not establishing a rigid network, which would bring brittleness, but, rather the high number of soft interactions would allow for a marked final effect in increasing the viscosity without causing brittleness. To test this hypothesis several polysaccharides have been used as additives in comparable conditions (same concentrations, same operating temperatures) and the data of small amplitude oscillatory rheometry have been used to gain insight on their effects. It must be noted that the choice of polysaccharides has been dictated by the will of exploring highly commercially available, low-cost, and environmentally friendly chemicals, which are aspects worthy of attention for large-scale applications.

This constitutes, besides the original scientific idea connected to the hypothesized mechanism, further added value of this work. Finally, an unexpected behavior upon temperature change, resembling that of simple liquids, will be found, and a qualitative model will be suggested.

2. Experimental Part

2.1. Materials

The bitumen, kindly supplied by Loprete Costruzioni Stradali—Terranova Sappo Minulio—Calabria—Italy, had penetration grade, measured by the usual standardized procedure (ASTM D946) [21], (50/70). By the S.A.R.A. method [22], the concentrations (*w/w* %) of the four different portions (Saturates, Aromatics, Resins and Asphaltenes) [23] were found to be 3.8, 51.3, 21.5, and 23.4 respectively. The asphaltenes amount is typical of 50/70 grade bitumens. It is called hereafter “ref” (standing for “reference”).

The additives were collected in powder form from the local supermarket given the applicative purpose of the work. They were: algae *euchemae*, carob seeds flour, orange skin, 00 flour, agar, carragenine, carboxymethylcellulose (CMC), pectin, arabic gum, cellulose, corn flour, starch, guar gum, xantam gum. The particle size in all the powders was characterized by optical microscopy and the analysis is reported in Supplementary Table S1. The small size of the particles (micrometer range) and the thermal treatment required for sample preparation (see below) allow for complete additive/bitumen homogenization.

2.2. Methods

A weighted amount of additive (1 g of additive in 20 g of bitumen, giving a final content of 4.76% *w/w*), was added separately to a fully flowing hot bitumen (150 ± 10 °C) and stirred at 500–700 rpm by a mechanical stirrer (IKA RW20, Königswinter, Germany) for 30 min at the same temperature to allow homogenization of the blend. Our previous studies showed that such conditions assure the preparation of homogeneous samples: at lower rpm, sample homogenization is not effective, while above 700 rpm the bitumen can become oxidized with a consequent change in the rheological properties. This method is quite standard and also other authors use analogous procedure [24].

After mixing, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber at 25 °C to retain the desired morphology. Due to the sensitivity of such kinds of material to the annealing time [5], and due to the comparative spirit of our work, we took care that all our samples had the same temperature cooling rate (5 °C min^{-1}) and annealing time (15 min).

A standard additive-free bitumen sample was used as a reference, hereafter labeled as “ref”.

2.3. Rheological Tests

The complex shear modulus $G^* = G' + i \cdot G''$ was measured in the regime of small-amplitude oscillatory shear at 1Hz as a function of temperature (temperature controlled by a Peltier element, uncertainty ± 0.1 °C) by dynamic stress-controlled rheometer (SR5, Rheometric Scientific, Piscataway, NJ, USA) equipped with a parallel plate geometry (gap 2 mm, diameter 25 mm). Conditions were chosen after preliminary stress-sweep tests to guarantee linear viscoelastic conditions in all measurements. The real and imaginary parts define the in-phase (storage, measure of the reversible elastic energy) and the out-of-phase (loss, irreversible viscous dissipation of the mechanical energy) moduli, respectively. Their ratio is related to the phase angle δ according to $\tan \delta = G''/G'$.

3. Results and Discussion

The data obtained during a small amplitude oscillatory rheometry test include the complex modulus G^* , which is a measure of the total energy required to deform the specimen, and is defined as:

$$|G^*|^2 = G'^2 + G''^2 \quad (1)$$

where G' is the elastic modulus (or storage modulus), a measure of the energy stored in the material during an oscillation, and G'' is the viscous modulus (or loss modulus), a measure of the energy dissipated as heat.

The temperature dependence of the experimental G' and G'' measured at 1 Hz can give several information.

3.1. G' @50 °C and T^*

First of all, the value of G' at 50 °C (G' @50 °C) can be immediately derived and is representative of the mechanical property (rigidity) of the material. The temperature of 50 °C was chosen as representative of the normal temperature under usage conditions. On the other hand, the idea of considering the rigidity at temperatures higher than room temperature is sometimes adopted in the literature so the use of G' at 50 °C in the present work allows comparison with those papers [18]. The value of G' @50 °C is expected to change in the presence of additives as a consequence of the additive (reinforcing) effect on the bitumen microstructure.

The effect of temperature is reported in Figure 1 where the behavior of G' and G'' as a function of temperature is shown for the neat bitumen chosen as representative. When temperature is increased, the material becomes progressively softer with G' monotonously decreasing.

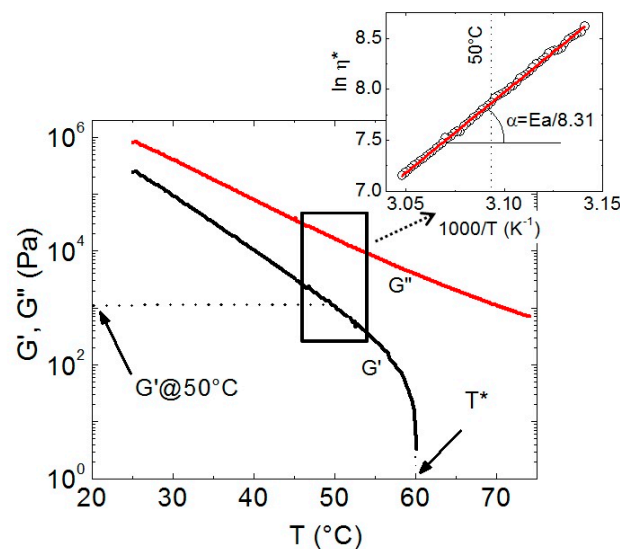


Figure 1. Plot of G' and G'' as a function of temperature for a representative sample (neat bitumen). The meaning of the extracted values of G' @50 °C and T^* is shown by the pointing arrows. From the values of G' and G'' around 50 °C the Arrhenius plot of η^* is built and reported in the inset which also shows how to extract the activation energy (E_a). In the inset the red line is the linear regression of the experimental data (circles).

This fact, together with the fact that $G' < G''$ always holds, shows that the samples have a pseudoplastic fluid behavior and allows to consider that the investigated temperatures are all at higher values than the glass temperature, usually slightly below 0 °C [3], at which G'' should have a maximum.

Upon increasing temperature, at a certain point, G' suddenly drops. The temperature at which G' drops (T^*) is taken as that temperature at which $G''/G' > 1000$. T^* has the meaning of being that temperature at which the binder can be considered almost as a Newtonian fluid. From the microscopic point of view, it can be intended as the temperature at which the thermal motion is sufficiently high to completely destroy the interacting network made by the above described complex structure. Consequently, at T^* no storage of energy can be afforded by the sample so the storage modulus G' drops. The sudden drop of G' is shown in the same Figure 1 together with the easy way to extract the

corresponding T^* . Like $G'@50\text{ }^\circ\text{C}$, and for the same reason, T^* is also expected to change according to the additive added to the bitumen.

The values of $G'@50\text{ }^\circ\text{C}$ and T^* are reported in Table 1 for the various samples.

Table 1. $G'@50\text{ }^\circ\text{C}$, T^* and E_a values for bitumen modified with various additives.

Additive	$G'@50\text{ }^\circ\text{C}$ (kPa)	T^* ($^\circ\text{C}$)	E_a (kJ/mol)
ref	1.0	60.2	132
Algae <i>euchemae</i>	13.0	75.0	130
carobs	10.5	72.0	139
orange skin	5.4	68.5	123
flour 00	1.4	61.8	132
agar	1.9	63.2	132
carragenine	6.0	70.3	127
carboxymethylcellulose	7.8	70.5	140
pectin	1.7	62.7	139
arabic gum	1.4	62.2	131
cellulose	1.7	63.1	133
Corn flour	1.1	60.4	134
starch	1.6	62.6	131
guar gum	5.3	68.4	135
xantam gum	2.4	64.2	138

It is interesting to notice that the $G'@50\text{ }^\circ\text{C}$ is correlated with T^* as shown in Figure 2. The goodness of this result is supported by the observed R-squared value (0.985). Although this may be expectable, it must be noticed that $G'@50\text{ }^\circ\text{C}$ refers to the Y-value of the G' plot in Figure 1, whereas T^* refers to the X-value at which the curve drops, i.e., two independent, in principle, parameters. The observed correlation therefore confirms that the reinforcing effect caused by the network-type interactions between the additive and the asphaltene clusters and their aggregates takes place at all temperatures shifting T^* to higher values: this means that the rigidity at temperatures under usage conditions and the maximum possible operational temperatures can be seen as different aspects of the same microscopic phenomenon. This observation is in accordance with that observed by Oliviero Rossi et al. [3], who investigated the rheological effect of some additives. They found in that paper that some additives with almost apolar nature, like organosilane, oleic acid, and octadecylamine, are preferentially solubilized within the maltene phase, giving weak interactions with asphaltenes and their cluster, and consequently not being able to reinforce the overall structure. In this situation, T^* decreases, as well as $G'@50\text{ }^\circ\text{C}$, which seemed correlated. On the contrary, a more polar additive like polyphosphoric acid was able to reinforce the structure, stiffening the bitumen, and increasing T^* .

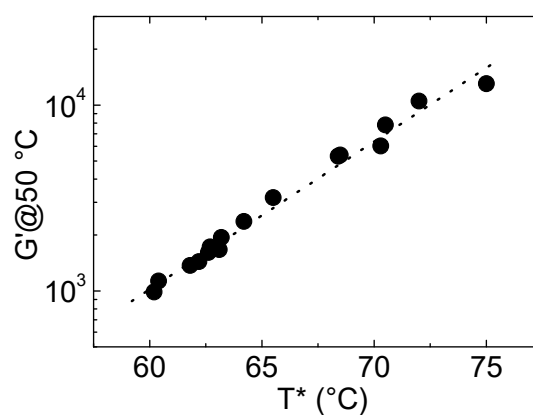


Figure 2. Correlation between the values of $G'@50\text{ }^\circ\text{C}$ and T^* . The dotted line is a guide for the eye.

In our case, the additives are long molecules/polymers characterized by the presence of numerous polar groups. They would be able, in fact, to establish interactions with the asphaltene molecules and their clusters and this is confirmed by the fact that all additives tend to bring both G' @50 °C and T^* to higher values. This can be ascribed by the presence of numerous polar groups that are able to establish interactions with the asphaltene molecules and their clusters. There are some differences among the various polysaccharides in the extent of G' @50 °C and T^* increase: the most prominent effect is exerted by algae *euchemae*, followed by carob seeds flour, with the least effect by 00 and corn flours. These differences can be ascribed to their specific molecular structure. The most soluble additives, like those rich in starch, i.e., 00 and potato flours, have little influence on the bitumen properties. They can bind asphaltenes but are not of sufficient length or strength to connect the hierarchical structures made of asphaltenes clusters at longer length scales. Fibers instead, (recognizable by their lower solubility in water) like carboxymethylcellulose or algae *euchemae*, have the proper characteristics to do this. The remaining small differences among the various polysaccharides should be interpreted going deeper into their specific interactions with all the molecules involved in such complex systems, for which more challenging experiment would be required. The present data however, represent a good starting point for experimentalists and theoreticians.

3.2. Viscosity (η) as a Function of Temperature (T)—Arrhenius Model

The temperature dependence of both G' and G'' allows further analysis. To do so, a more synthetic indicator has been derived: the complex viscosity (η^*). It is the ratio of G^* to angular frequency ω , i.e., [25]:

$$\eta^* = \frac{G^*}{\omega} = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad (2)$$

Here, η^* has been considered because it is a synthetic indicator. In fact, differently from G' and G'' , which give separate information on the energy absorbed by the system in elastic (G') and dissipating (G'') form, η^* instead synthetically yields information on the *total* amount of energy that the system absorbs. In addition, besides being more synthetic, η^* has the physical meaning of representing the resistance to flow under oscillatory shear conditions.

The temperature dependence of η^* is reported in the inset of Figure 1 as $\ln \eta^*$ vs. $1000/T$ (Arrhenius plot).

The choice of the Arrhenius plot, far from following usual habits to show the temperature dependence of viscosity, is instead the result of our approach based on the molecular interpretation of the macroscopic properties (an approach we are keen on) which lead to the following observations and considerations. From the microscopic point of view, in fact, the complex viscosity modulus is determined ultimately by the force field between the molecules, i.e., the strength of the interactions involved in the intermolecular network in bitumen. The theoretical description is quite complex [26], and several approaches have been developed, both theoretical [27–29] and numerical as based on molecular dynamic simulations [30]. On the other hand, for a simple analytical description of the temperature dependence of viscosity, several forms have been derived. The most common is the Arrhenius model, but other models are also present, like the Vogel-Tamman-Fulcher (VTF) equation, the polynomial expansion [31] and other formulas taking into account for eventual tunneling [32]. These forms are nicely commented in [30] and [31]. Basically, as some authors shown [31], the main distinction lies on the linearity of the $\ln \eta^*$ vs. $1/T$ trend (Arrhenian behavior). The trend is usually linear for simple liquids, which follows the basic two-wells potential model. If the trend is not linear then other equations must be used according to the reason of non-linearity: if cooperative effects are present, as occurring for example for strongly interacting fluids like ionic liquids, heavy oils and fuels, polymers, melting salts, and glasses, then, the VTF can be used. It is usually used, indeed, for glass, with the phenomenological description of the glass forming behavior close to T_g . If tunneling is present, then the Nakamura-Takayanagi-Sato (NTS) or Aquilanti-Sanches-Coutinho-Carvalho (ASCC) formulas can be considered. Other approaches, like a polynomial expansion, with interpolation of

experimental data, can be used. Further details of these aspects can be found in many academic and specialized textbooks so the eager reader is redirected to those readings. Here, this preliminary distinction will be used to justify the choice of Arrhenius model. As can be seen by the Arrhenius plot (inset in Figure 1), the linear trend of the data is pretty well observed in an adequate interval around the temperature chosen as representative of the working condition (50 °C). It has been also observed that:

1. this behavior is observed for all the investigated samples;
2. the same linear trend is observed also in a wider interval including lower temperatures;
3. the effect of network breakdown at higher temperatures (G' drop at $T = T^*$), which represents however a strong structural modification, does not exert its effects in the temperature range considered, preserving the linear trend in the Arrhenius plot.

These observations suggest that the choice the Arrhenius model is the most adequate. There is no reason, in fact, to use the VTF equation since the temperatures considered are significantly higher than the T_g (in this case the VTS would reduce to the Arrhenius giving $T_0 = 0$) and since a polynomial expression would get rid of the physics behind the Arrhenius model (see later) to simply take into account for the numerical interpolation of experimental data. In fact, although the Arrhenius model has been derived from the reaction kinetics in the gas phase, a favored theoretical base for the interpretation of viscosity has been provided by the application of the transition-state-theory [33] (TST) by Eyring of Arrhenius chemical kinetics to transport phenomena [34]. In this framework, E_a represents the activation energy to overcome for flowing to occur. It can be easily derived from the slope of the best fit line in the Arrhenius plot (as shown in the inset of Figure 1) according to the logarithmic form

$$\ln \eta^*(T) = \ln A_s + \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

where η^* is the complex viscosity (Equation (2)), R is the gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and A_s is the pre-exponential (entropic) factor.

In the same framework, the logarithm of pre-exponential factor ($\ln A_s$) can be derived as the intercept of the best fit linear regression of the experimental data. A_s has been generally dealt with a “frequency factor”, representing the fraction of effective collisions which are able to turn into the flow process. In the context of TST, $\ln A_s$ represents the entropic change when passing from the initial state to the transition state typically formed during the hopping between one potential well to the other in the shearing process.

Let's now use these physical quantities to interpret the observed data (reported in Table 1). The E_a values are consistent with the value observed for other additivated bitumens [3] lying in the range 120–140 kJ/mol. In addition, while all additives cause a more or less marked increase in the G' @50 °C, they do not uniquely affect E_a . Some additives in fact cause an increase in E_a , like carob seeds flour, xanthan gum, pectin and carboxymethylcellulose, whereas some other compounds affect the bitumen in the opposite way causing a decrease of E_a , like oranges skins and carragenines. This observation suggests prudence in interpreting the two parameters (rigidity—or G' —and E_a) in the same terms. They should be treated, instead, as independent and sometimes different aspects of the phenomenon. Indeed, as shown in Figure 3, lack of correlation has been found between E_a and G' @50 °C (or T^* , given the correlation between T^* and G' @50 °C shown in Figure 2). Similar behavior has been found in other papers as, for example, the polyphosphoric acid-additivated bitumen in [31], which showed higher rigidity with respect to the neat bitumen but lower activation energy of the viscosity.

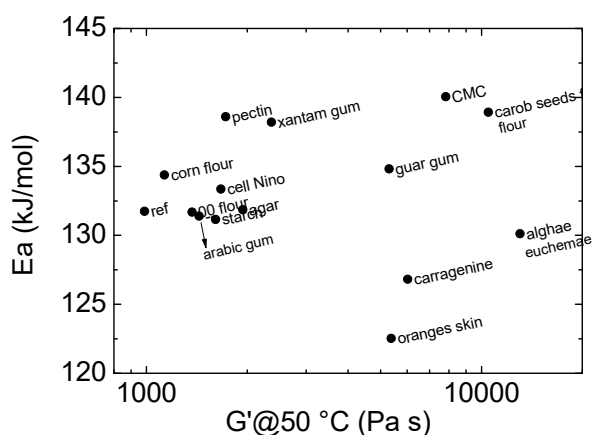


Figure 3. Plot of E_a vs. $G'@50\text{ }^{\circ}\text{C}$ showing lack of correlation.

As for the pre-exponential factor, it can be observed that $\ln A_s$ is always negative, independently of the additive used. Remaining in the same theoretical model considering the formation of a transition state during flow (TST model), this would indicate a positive entropy of formation of the activated state during flow. This means that the mechanism of flowing is mediated by the formation of a *disaggregated* transition state. This is typical for viscosity, since during flow the chemical species must find the room for their sliding one over the other: they must somehow pass over a situation where some displacement is required in order to make locally room for a chemical species to be able to finally slip over the remaining neighbors thus determining the flow. We like the description given by Byran et al. [35] so we report their own words: “For any one molecule to move, other surrounding molecules must first give way and move into vacant lattice sites or “holes” to create a space for the molecule to enter”. Beyond the TST theory, and considering A_s as a frequency factor, its low value would indicate a low number of effective molecular collisions which are able to turn into the flowing process, in agreement with the complex structure of the bitumen, the presence of high molecular mass molecules, and the low viscosity.

When considering the effect of temperature, the microscopic interpretation becomes more complex since the various additives differently affect the force field among the molecules in the systems. In our opinion, during bitumen flowing, the disaggregative step bringing to the intermediate step (“activated complex”) must be affected by the conformational re-adaptability of the additive connecting the various asphaltene clusters and their clusters. However, further investigations, both theoretical and experimental, are needed to validate this hypothesis.

3.3. Correlation between Activation Energy (E_a) and Pre-Exponential Factor (A_s)

Before rationalizing the specific effect of the various additives on the activation energy and the pre-exponential factor, it must be unveiled another interesting observation: the activation energies are correlated with the pre-exponential factors (Figure 4). The goodness of this result is supported by the observed R-squared value (0.93) and the mean squared errors (MES) value of less than 0.2. Although the R-squared value may seem to be not strikingly high, it must be considered that the pre-exponential factor, as derived by the Arrhenius model, is an extrapolation to the Y-axis of the data in the Arrhenius plot, i.e., at infinite temperature, which is an un-physical situation. Moreover, it must be considered that the determination of viscosity in bitumens is problematic for several reasons. As an example, it can be considered that measurements from different laboratories on carefully collected samples of the same bitumen have given values differing even of a factor of two [36]. After these considerations, and given the statistically significant number of the samples (fifteen samples, including the reference) of the present work, in our opinion the correlation seems safe and deserves attention.

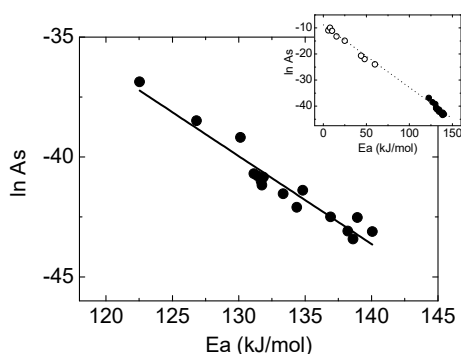


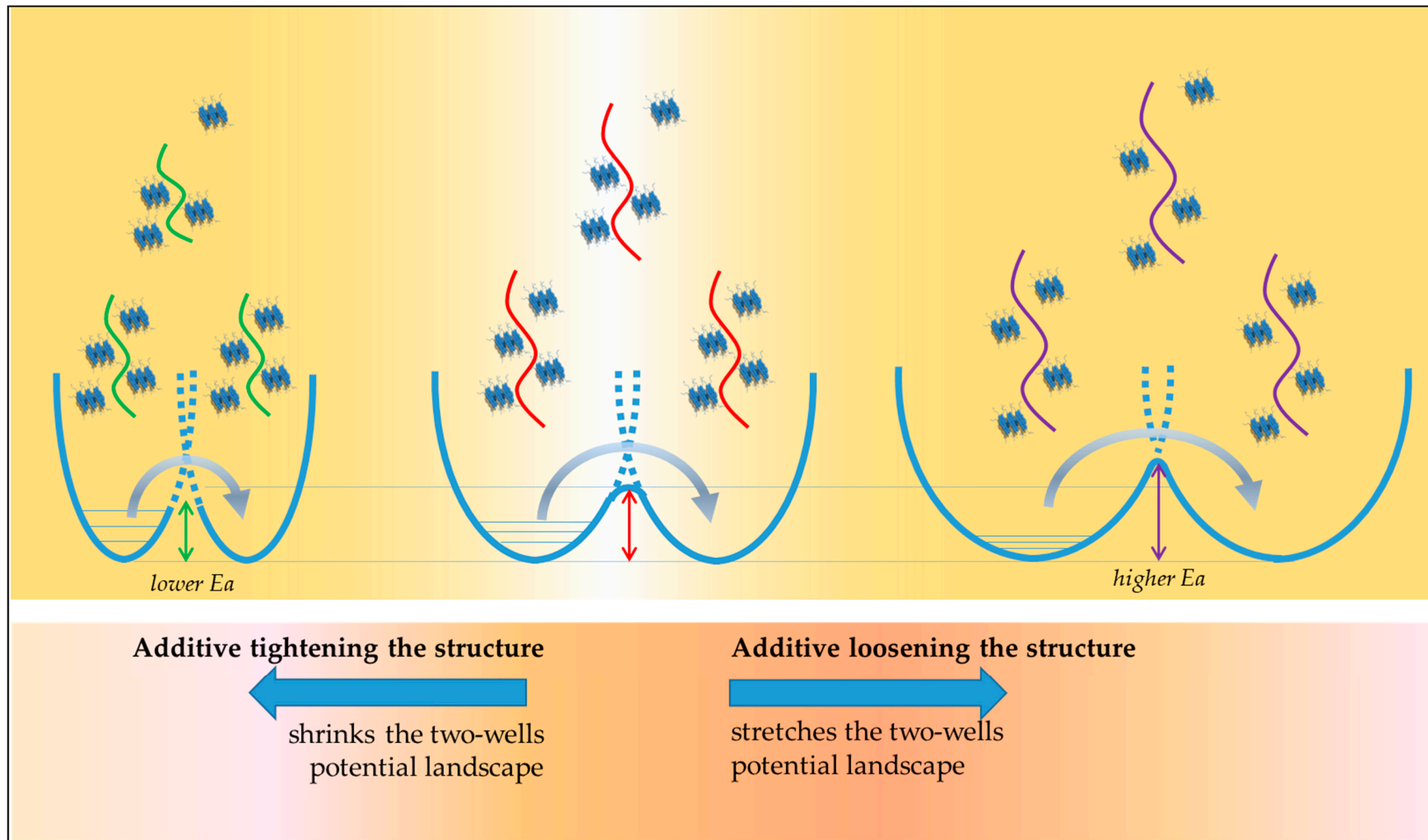
Figure 4. Correlation between the pre-exponential factor A and the activation energy E_a . The line is the linear regression of the experimental data. In the inset the data of the present paper (closed symbols) are shown together with those taken from biography (open symbols). In the inset the dotted line is only a guide for the eye.

The correlation between E_a and $\ln A_s$ has been already observed for simple liquids [31]. This is an important aspect also for applicative purposes. In fact, if this correlation holds, then the temperature dependence of the viscosity of liquids can be expressed through one parameter only (the only one known, E_a or A_s). This would have the advantage to allow for the viscosity description even if only one parameter is known, since the other can be derived from it. Although there is not a theory explaining such correlation [31] this can be helpful for practical uses. The data presented in that paper are reported in the inset of Figure 4 (open circles) together with the data of the present work. It must be noted that the viscosity calculated for our data refers to a region quite far from the T_g (generally occurring around 0°C) and where the contribution of the elastic response is negligible (G' is lower than G'' by two orders of magnitude) so it can be approximated to the zero-shear viscosity. For this reason, the comparison with the literature data shown in the inset of Figure 4 can be considered at first approximation as safe. Interestingly, we found a nice consistency between the two sets of data, despite they greatly differ in:

- I. viscosity (the viscosity of our samples is several orders of magnitudes higher);
- II. activation energies (E_a of our samples is from 2 to 20 times higher);
- III. pre-exponential factor (our samples have pre-exponential factors several orders of magnitude lower);
- IV. structure (bitumens are highly complex materials—see introduction - contrasting the structure of simple liquids).

The data in the present work, despite these big differences, extend the number and types of systems for which this linear correlation holds, suggesting a quite universal behavior although some difference in the slope is still (reasonably) present. The data of the present paper open a door for a more general view of fluids, based on a deeper understanding of the key ingredients dictating their behavior. For this reason, we hope that our data can be precious for further theoretical investigation in order to model such a universal behavior.

This correlation lets us to schematically depict the additive effect on the microstructure as a more or less pronounced “shrinking” or “stretching” of the structure and, consequently, of the microscopic energetic landscape that the system has to explore in the flowing process. This principle is represented in Scheme 1. If the additive gets closer the microscopic molecular structures involved in the flowing, then the energetic landscape is shrunk, and so the two potential wells are shrunk and brought closer. So, a more pronounced overlap of the two potential curves can be expected. This would result in a lowering of the activation energy as well as a neat increase of the entropy change during the disaggregative formation of the activated state. This makes sense, since in a compressed and tighter structure an increased entropy change is expected to pull away a chemical species from its original location. On the contrary, if the additive stretched the two-potential well landscapes, the opposite effect is observed. Of course this hypothesis needs to be verified with further experiments and investigations.



Scheme 1. Scheme of the additive hypothesized effect on the microscopic structure of a bitumen with consequent modification of the two wells potential.

4. Conclusions

We showed that the addition of commercially available polysaccharides can increase the rigidity in bitumens and their resistance to temperatures. This has been attributed to the high number of polar groups able to bind the polar clusters of asphaltene and their supra assembled aggregates, forming an interconnected network. Algae *euchemae* and carob seeds flour exert a more marked effect. Viscosity follows an Arrhenian behavior, showing, despite what one would expect, an activation energy uncorrelated with the rigidity. Interestingly, the activation energy is correlated with the pre-exponential factor, an effect already observed in simple liquids/solvents. An interpretation of the Arrhenius model in terms of Eyring transition state theory (TST) highlights a disaggregative process as the necessary step in allowing the hopping from one potential well to the successive for flowing to occurs.

The effect of the additive has been therefore interpreted in terms of shrinking or stretching of the structure and consequently of the microscopic energetic landscape that the system has to explore in the flowing process. The low cost and availability of the additive used, their big rheological effect, and their eco-friendly nature, make their use of added value. The rheological characteristics of bitumens reinforced with those materials have been shown. The observed correlation between activation energy and pre-exponential factor deserves attention for practical purposes since it allows for the description of the rheological behavior from only one of these two parameters, since the other can be derived. Finally, the microscopic interpretation of the observed outcome presents new opportunities in the comprehension of the rheological effect of additives for the future piloted design of ever performing additives.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/9/24/5564/s1>, Table S1: range size (min-max) and average size of the grains making the additives.

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