Turkish Journal of Science & Technology
16(2), 269-274, 2021

Research Paper

Investigation of Electrophoretic Mobility of Various Nanofibers in Ethanol or Water

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(Geliş/Received: 11/03/2020; Kabul/Accepted: 26/04/2021)

Abstract: In this study, the electrophoretic mobility of nanofibers in ethanol or in water was calculated by using both equations from zeta potential values and related to their measured diffusion coefficients. Results showed that all samples in ethanol had positive zeta potential values, whereas all samples in water, except sample 3 containing gelatin, had negative zeta potential values. The samples with PVA or PVA-alginate had the most stable suspensions in water compared to other samples, regarding zeta potential values. The electrophoretic mobilities calculated by using the Smoluchowski and Henry equations of samples showed similar charge characteristics as zeta potential values. Gelatin might have charged by applied voltage during the electrospinning process. When results were related to the diffusion coefficient values, it was observed that the higher electrophoretic mobility and zeta potential values resulted in lower diffusibility. Moreover, adding limonene to the structure decreased the electrophoretic mobility and zeta potential values, and increased the diffusion coefficient. The adding different polymers revealed that molecular structure and charging behavior of the polymers are some of the most important factors on the electrophoretic mobility and zeta potential of nanofibers.

Key words: Electrophoretic mobility, Zeta potential, Smoluchowski equation, Henry Equation, Electrospun nanofibers, Electrospinning.

Çeşitli Nanoliflerin Etanol veya Sudaki Elektroforetik Hareketliliğinin İncelenmesi

Öz: Bu çalışmada, etanolde veya suda bulunan nanoliflerin elektroforetik hareketliliği hem zeta potansiyel değerlerinden hem de ölçülen difüzyon katsayısı değerlerinden hesaplanmıştır. Etanoldeki bütün örneklerin zeta potansiyel değerleri pozitif bulunurken 3 numaralı örnek hariç sudaki bütün nanoliflerin zeta potansiyelleri negatiftir. Zeta potansiyel değerleri göz önüne alındığında suda bulunan PVA'lı veya PVA-aljinatlı nanolifler diğer örneklere göre daha stabil olarak değerlendirilmiştir. Smoluchowski ve Henry denklemleri hesaplanan elektroforetik hareketlilikler zeta potansiyel değerleri yle benzer yük karakteristikleri göstermiştir. Jelatin elektroeğirme sırasında uygulanan voltaj nedeniyle yüklenmiş olabilir. Elde edilen sonuçlar difüzyon katsayısı değerleriyle ilişkilendirildiğinde, yüksek elektroforetik hareketliliğe ve zeta potansiyel değerlerine sahip örneklerin difüzlenebilirliklerinin düşük olduğu belirlenmiştir. Buna ilave olarak nanolif yapısına limonen eklenmesinin elektroforetik hareketliliği ve zeta potansiyelini azalttığı, difüzyon katsayısını ise arttırdığı görülmüştür. Değişik polimerlerin ilavesiyle nanoliflerin elektroforetik hareketliliğine ve zeta potansiyeline etki eden en önemli faktörler polimerlerin moleküler yapısı ve yüklenme davranışıdır.

Anahtar kelimeler: Elektroforetik hareketlilik, Zeta potansiyeli, Smoluchowski denklemi, Henry denklemi, Elektroeğrilmiş nanolifler, Elektroeğirme

1. Introduction

Nanofibers electrospun from biomaterials has become important in many fields [1] such as filtration [2], smart packaging [3], scaffolds in tissue engineering [4], drug delivery [5], enzyme immobilization, biosensors, energy generation, functional textile products, affinity membrane and cosmetics [6-8].

The transport property of nanofibers and the quality of products with nanofibers are related to their dispersion and aggregation tendencies [9-10]. These properties depend on the surface charging characteristics [1; 11-14].

Monaghan & White [15] investigated the effect of proteins on electrophoretic mobility and sedimentation velocity of red cells. They reported that mobility of red cells was unchanged or only slightly decreased when bulk viscosity was increased by added protein is interpreted as indicating that the red cell surfaces are hydrated [15]. Then, electrophoretic mobility could have decreased due to red cells somehow absorbed water molecules (or hydrated) under some circumstances (in this case, added proteins).

The dispersion and aggregation of colloidal particles are based on the interaction energy between particles. This interaction energy represented by Derjaguin, Landau, Verwey and Overbeek (DLVO) theory is charging behavior and attractive van der Waals energy influence the sum of repulsive electrostatic interactions. However, electrospun nanofibers seem not to be agree with the DLVO theory [1; 16].

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The Smoluchowski equation can be applied for large particles compared with the thickness of electric double layer [1]. It appears that the Smoluchowksi equation is mostly used for the calculation of zeta potential [13; 17-19]. On the other hand, the Smoluchowski equation can be inaccurate even for large spherical particles at low salt concentration due to the relaxation of the electric double layer [20-21]. Furthermore, Sato et al. [1] indicated that it is doubtful to apply the Smoluchowski neglects the effect of relaxation underestimating the zeta potential, therefore it is not valid for calculating the interaction energy and the capture efficiency. However, they used the equation for calculation electrophoretic mobilities of cellulose nanofibers in their study.

Electrophoretic mobility can also be expressed in terms of zeta potential [22]. The measured electrophoretic mobility (ue) is calculated from zeta potential (ζ) through Henry's equation which needs a constant called as the Henry function (F(κα) [19; 23]. This equation only applies for isolated particles of zeta potential less than around 25 mV and if F(κα)=1.5; it is known as the Smoluchowski equation that applies where κα is large (F(κα)= around 100) and the double layer is thinner than the particle radius [1; 24-25]. Delgado et al. [23] revealed that according to Henry's, the electrophoretic mobility is lower than that calculated from Smoluchowski equation and the theory fails for low-to-moderate zeta potentials due to neglecting concentration polarization which decreases the mobility for sufficiently high zeta potential values [23].

In this paper, the electrophoretic mobility of nanofiber encapsulation systems in ethanol or in water were calculated by using the Smoluchowski equation and Henry's equation. Then the results were related to the measured diffusion coefficients.

2. Materials and Methods

2.1. Materials

(+/-)-Limonene used in the study was purchased from Alfa Aesar Co. (Germany) and ethanol used in the study was purchased from Sigma-Aldrich Co. (Germany). Type B gelatin powder from bovine skin, PVA, Na-alginate E-401, lactalbumin and acetic acid used in the study were purchased from Sigma (Germany), ZAG (Turkey), Sigma (Germany), FMC-Biopolymer (US), Sigma (Germany) and Merck (US), respectively.

2.2. Methods

2.2.1. Electrospinning

The preparation of the feed solutions and electrospinning process were given by Dede and Altay [26]. The uniaxial electrospinning was performed by using an electrospinning equipment (Inovenso NE100, Turkey) at room temperature. The applied voltage, the feed rate and the distance to the collector plate were 25 kV, 0.5 ml/h and 10 cm, respectively. The diffusion coefficient measurements and morphological characterization of the samples were reported in Dede and Altay [26].

2.2.2. Dynamic light scattering measurements

The zeta potential measurements of dispersions containing electrospun nanofiber samples were carried out using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25 °C in triplicate. Ethanol or distilled water were used as dispersants and nanofibers were dispersed at 0.1% (w/v) [27].

2.2.3. Electrosphoretic mobility calculations

Electrophoretic mobilities were calculated from the zeta potential by using the Smoluchowski equation [1; 22]:

$$ue = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta} \quad (1)$$

where ue is the electrophoretic mobility (m2/V.s), ζ is the zeta potential (mV), η is the viscosity of the solution [1] or solvent [22], εr is the dielectric constant of the medium (for ethanol 24.3 and for water 80), εo is the permittivity of vacuum, (for ethanol 2.2x10-12 C/V.m and for water 8.85x10-12 C/V.m) [1; 22]. We used η is

the viscosity of the solvent (for ethanol 1,074 x10-3 Pa.s and for water 8,94x10-4 Pa.s) [22; 28]. The measured electrophoretic mobility (ue) was calculated from zeta potential (ζ) through Henry's equation:

$$ue = \frac{2\varepsilon \zeta F(\kappa a)}{3\eta} \quad (2)$$

where Ɛ is the dielectric constant of the dispersant, F(κα) is the Henry function and η is the viscosity [19; 23]. We acknowledged all assumptions made by Sato et al. [1] for nanofiber morphology and surface charge characteristics.

2.2.4. Statistical analysis

Excel 2016 (Microsoft, WA, USA) was employed for statistical analysis. The results of zeta potential, were evaluated by the two-way ANOVA (α=0.05). Significant differences among samples were determined by the least significant difference comparison by the Student's paired t-test and t-test probability limits of $p<0.05$ was used for two-sided testing in evaluation.

3. Results

Zeta potentials of electrospun samples in ethanol or in water were given in Table 1. All samples in ethanol had positive zeta potential values, whereas all samples in water, except sample 3 containing gelatin, had negative zeta potential values. The zeta potentials of sample 1 and sample 2 in water were closer to -25 mV compared to the zeta potential values of other samples in water. The zeta potentials lower than -25 mV or higher than +25 mV indicate stability for a given suspension [29]. The samples with PVA or PVA-alginate had the most stable suspensions in water compared to other samples. The zeta potential values of the rest of electrospun samples were not different from each other.

Table 1. Zeta potentials of electrospun samples in ethanol or in water

Sample no	Electrospun Sample	Samples in ethanol (E) or in water (W)	Zeta potential (mV)*	Diffusion Coefficient (μm2/s)**	Calculated electrophoretic mobility, u_e (m^2/V.s) via Smoluchowski equation	Calculated electrophoretic mobility, u_e (m^2/V.s) via Henry's equation
1	PVA + Limonene	**E**	**+2.71±0.07a**	**0.15±0.01bcd**	**+1.4x10^{-8}**	**+61**
		W	-12.60±2.32b	1.37±0.03a	-1.0x10^{-8}	-1008
2	PVA + Alginate + Limonene	**E**	**+1.18±0.26a**	**0.49±0.01bc**	**+0.6x10^{-8}**	**+27**
		W	-10.4±0.9b	1.91±0.04a	-0.8x10^{-8}	-832
3	Gelatin + Limonene	**E**	**+1.86±0.39a**	**0.69±0.01b**	**+0.9x10^{-8}**	**+42**
		W	+1.31±0.05a	1.12±0.10ab	+0.1x10^{-8}	+105
4	Gelatin + Alginate + Limonene	**E**	**+3.57±0.07a**	**0.25±0.00bcd**	**+1.8x10^{-8}**	**+81**
		W	-6.38±0.49ab	1.02±0.07ab	-0.5x10^{-8}	-510
5	Gelatin + Lactalbumin + Limonene	**E**	**+6.35±0.41a**	**0.28±0.07bcd**	**+3.2x10^{-8}**	**+144**
		W	-0.27±0.07a	0.77±0.21b	-0.2x10^{-9}	-22
6	Only Gelatin***	**E**	**-0.52±0.47**	**0.02±0.00**	**-0.3x10^{-8}**	**-12**
7	Gelatin Nanofiber 2***	**E**	**+3.79±0.75**	**0.31±0.41**	**1.9x10^{-8}**	**+86**
8	Gelatin Nanofiber 7***	**E**	**+21.90±0.10**	**1.19±0.08**	**10.9x10^{-8}**	**+496**

*Means±SD (n=3); values within each group followed by the same letter (in column, sample number and samples in ethanol or water) are not significantly different ($p\leq0.05$)
**Means±SD (n=3); values within each group followed by the same letter (in column, sample number and samples in ethanol or water) are not significantly different ($p\leq0.05$) and Reference: Dede and Altay, [8].
***Reference: Okutan et al. [27].

In this study, zeta potential values were used for calculating electrophoretic mobilities of electrospun nanofibers via Smoluchowski and Henry's equations (Table 1). While calculated electrophoretic mobility values of all samples in ethanol via Smoluchowski equation were founded positive, all samples except sample 3 (containing gelatin) in water was negative as similar as zeta potential values of samples. The same trend was true for the results of Henry's equation. In addition, the results of electrophoretic mobility calculations via Henry's for samples in water were founded $9.9x10^{-12}$ times to those samples calculation of Smoluchowski equation, the results of Henry's equation for samples in ethanol were founded as $2.2x10^{-10}$ times to that samples' calculated via Smoluchowski equation. Furthermore, zeta potentials of electrospun samples in ethanol were higher than samples in water except sample 4 (containing gelatin and alginate). Gao et al. [30] reported that the zeta potential values were directly proportional with ethanol proportion in the solvent. Delgado et al. [23] revealed that positive electrophoretic mobility values were consequences of positive zeta potential values.

Okutan et al. [27] determined zeta potentials of electrospun gelatin nanofibers in ethanol to characterize them and found the values between 3.79±0.75 and 21.90±0.10 as consequences of applied voltage (28-35kV), concentration of gelatin (7-20%, w/v) and feed rate (0.1-1mL/h). Calculating the electrophoretic mobility of electrospun gelatin nanofibers in ethanol result as between $+1.9x10^{-8}$ and $+1.1x10^{-7}$ m2/V.s for Smoluchowski equation and between +85.75 and +495.50 m2/V.s for Henry's equation. They also determined the zeta potential of only gelatin in ethanol and found it as -0.52±0.47 [27] which its electrophoretic mobility results as $-2.6x10^{-9}$ $m^2/V.s$ for Smoluchowski equation and -11.77 $m^2/V.s$ for Henry's equation. When compared to our gelatin containing samples (3, 4 and 5) to those electrospun gelatin nanofibers from Okutan et al. [27], our zeta potential values and electrophoretic mobility values were lower than those of Okutan et al. [27]. Besides all electrospun gelatin nanofibers from Okutan et al. [27] values were positive as ours. However, both zeta potential [27] and electrophoretic mobility values of gelatin in ethanol were negative. Gelatin electrospun nanofibers charged positively resulting in the zeta potentials and the mobilities as positive because of applied voltage during electrospinning. After all, sample 3 in our study has the only positive values of both zeta potential and electrophoretic mobility in water. It's thought that the applied voltage charged the electrospun gelatin nanofibers positively if used as only one polymer (gelatin) in the jet.

Results showed that higher electrophoretic mobility and zeta potential values mean lower diffusibility. When the results obtained related to the diffusion coefficient values of same samples, on the one hand, diffusion coefficient of solely gelatin in ethanol was found 0.02±0.00, after gelatin electrospun as nanofiber charged positively, both zeta potential (-0.52±0.47 to +3.79±0.75) and electrophoretic mobility ($-2.6x10^{-9}$ to $1.9x10^{-8}$ for Smoluchowski equation and -11.77 to +85.75 for Henry's equation) values increased with diffusion coefficient (0.31±0.41). When added limonene to the structure, zeta potential (+3.79±0.75 to +1.86±0.39) and electrophoretic mobility ($1.9x10^{-8}$ to $9.3x10^{-9}$ for Smoluchowski equation and +85.75 to +42.08 for Henry's equation) values decreased, but diffusion coefficient increased (0.69±0.01) due to the limonene's being highly unstable and hydrophobic, is difficult to incorporate in aqueous food, beverage, fragrance, and cosmetic systems [31]. Then gelatin was electrospun with other polymers (alginate or lactalbumin) zeta potential (+1.86±0.39 to +3.57±0.07) and electrophoretic mobility ($9.3x10^{-9}$ to $1.8x10^{-8}$ for Smoluchowski equation and +42.08 to +80.77 for Henry's equation) values increased, while diffusion coefficients (0.25 for sample containing gelatin + alginate and 0.28 for sample containing gelatin + lactalbumin) decreased closely. These polymers (alginate and lactalbumin) were thought to both decrease zeta potential and electrophoretic mobility values and increase diffusion coefficient values (Table 1).

On the other hand, using alginate with PVA electrospun nanofibers in ethanol decreased both zeta potential (+2.71±0.07 to +1.18±0.26) and electrophoretic mobility ($1.4x10^{-8}$ to $5.9x10^{-9}$ for Smoluchowski's equation and +61.32 to +26.70 for Henry's equation) values and increased diffusion coefficient value (0.15±0.01 to 0.49±0.01) as same as alginate did for the sample containing gelatin + alginate + limonene (Table 1).

Same results can be seen for the samples in water (Table 1). Using alginate with PVA electrospun nanofibers in water decreased both zeta potential (-12.60±2.32 to -10.4±0.9) and electrophoretic mobility ($-1.0x10^{-8}$ to $-8.2x10^{-9}$ for Smoluchowski equation and -1008 to -832 for Henry's equation) values and increased diffusion coefficient value (1.37±0.03 to 1.91±0.04) as same as alginate did for the sample containing gelatin + alginate + limonene (Table 1). Furthermore, lactalbumin added gelatin electrospun nanofiber sample in water gave opposite results for zeta potential (decreased from +1.31±0.05 to -0.27±0.07), electrophoretic mobility (decreased from $+1.04x10^{-9}$ to $-5.1x10^{-9}$ for Smoluchowski equation and +104.8 to -510.4 for Henry's equation) and diffusion coefficient (1.12±0.10 to 0.77±0.21) (Table 1).

4. Conclusions

The electrophoretic mobility of nanofibers in ethanol or in water was calculated by using zeta potential values via the Smoluchowksi equation and the Henry equation. Calculations via both equations showed similar charging characteristics as zeta potentials. The effects of the molecular structure, charging behavior, viscosity and the dielectric constants of the polymers are very important factors in the calculation of the electrophoretic mobility. Moreover, results showed that higher electrophoretic mobility and zeta potential values mean lower diffusibility and diffusion coefficient values.

Acknowledgement

Mr. Dede thanks Mrs. Okutan and Mrs. Bakır for their help on dynamic light scattering measurements at Dr. Altay's nanofiber characterization lab.

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