Electric Conductivity in Aqueous Solution of NaCl + Methanol Under External Microwave Field by Non-equilibrium Molecular Dynamics Simulation

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Nonequilibrium molecular dynamics simulations are performed to investigate the effects of an external microwave field on aqueous solution of NaCl + methanol at different temperatures. The microwave wave propagates in the z-axis direction with a frequency of 2.45 GHz and the intensity of the microwave field is 3×10^5 V/m. The results indicate that as the temperature of the electrolyte solution increased, the diffusion coefficient gradually decreased, but the electric conductivity gradually increased. In addition, all three will be increased, when the temperature increased. But the value of them will be reduced when microwave field is applied.

Key Words: Electrical conductivity, Sodium chloride, Methanol, Molecular dynamics simulation.

INTRODUCTION

Microwave heating has attracted interest in the chemical industry for its ability to provide targeted heating of liquids rapidly and uniformly[1,2]. For better application of microwaves in the chemical industry, the interaction between microwaves and the mixtures needs to be further studied.

Although some studies have reported the electric conductivity (EC) under the external electric field[3]. But for the external microwave field, there has been only a few studies[4] that analyzed the properties of NaCl methanol aqueous solutions. The distribution of the microwave field in the waveguide will be destroyed because the electrode can couple part of the microwave energy, when it inserts into the waveguide, lead to the measure of the electrical conductivity is not accurate. In recent years, molecular dynamics (MD) simulations have become an important tool in understanding the dynamics of electrolyte solution at the molecular level[5,6].

However, the molecular dynamics technique is expensive for electrolyte solutions because the multiplicity of components need very long run to get the correct ionic properties. Recently, dielectric relaxation, radial distribution functions and hydrogen bond statistics[7,8] have also been investigated for electrolyte solution. But more detailed dynamical aspects such as electrical conductivity dependent on external microwave field in NaCl methanol aqueous solutions have not been investigated before. This issue is of fundamental interest because of the significant role that electrolyte solutions play as reaction media in diverse chemical and biological processes. Therefore, in this paper

the nonequilibrium molecular dynamics (NMD) study of the effect of changing the temperature and temperature of NaCl methanol aqueous solutions on electrical conductivity, diffusion coefficient both the absence and presence of external microwave field was carried out.

EXPERIMENTAL

In all the simulations, the water molecules were characterized by the SPC/E model and the OPLS-AA model for methanol. All ions were represented by a point charge having a Lennard-Jones (LJ) center on it. The potential parameters for ion-water and water-water interactions in this model, collected from the work of Lee[9].

The simulations involved a total of 500 water molecules and 10 Na$^+$, 10 Cl$^-$ ions contained within an isotropic simulation box and considered two different methanol solution concentrations, *i.e.*, 1:1 and 1:2 (molality), corresponding to 250 CH$_3$OH molecules and 500 CH$_3$OH molecules, respectively. The Nosé-Hoover thermostat was used to maintain the equilibrium temperature at 283, 298 and 313 K and periodic boundary conditions were imposed in all three dimensions.

The trajectories of the atoms during the equilibration process were calculated using the Verlet velocity algorithm. To make sure the pressure of two systems is the same at 1 bar, the NPT ensemble was carried out in the pre-equilibrium process. The microwave field was applied in the NVT ensemble to isolate the field effects from the thermal effects and hence the simulations were effectively nonequilibrium NVT (NNVT) simulations. External microwave fields were applied to those

models10, all of the fields were of frequency $\nu = 2.45$ GHz and the root-mean-square (RMS) electric field intensities were $E_{RMS} = 3.0 \times 10^5$ V/m, respectively.

During the molecular dynamics simulation, a time step of 1 fs was used in all simulations; a period of 50 ps was allowed for equilibration (NPT ensemble). Following the equilibration process, a microwave field of the specified frequency and intensity were applied for 100 ps. The generated trajectories were stored every 50 fs.

RESULTS AND DISCUSSION

Diffusion coefficient: Diffusion coefficient (D) is a factor of proportionality representing the amount of substance diffusing across a unit area through a unit temperature gradient in unit time. In this paper, we use the Einstein relation[11]:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} < | r(t) - r(0) |^2 > \qquad (1)$$

where r(t) is the position of the geometric center of a molecule at time t, to determine the diffusion coefficient D of the ions from the mean-squared displacement (MSD) with or without the external microwave field.

The diffusion coefficient (D) calculated from the mean-squared displacement of the ions is listed in Table-1. It is found that the diffusion coefficient increase with the temperature increase but decrease when the electrolyte solution under the external microwave field due to the presence of ion atmosphere friction. It is also found that the friction of ion pairs increases with increasing ion temperature and this will lead to decrease the value of diffusion coefficient.

Electric conductivity: The most popular model for describing the transport of anion under the influence of temperature and electric potential gradients is derived using the following chain of arguments. The electric conductivity (σ) can be obtained by Nernst-Planck law and Fick's law[12] as:

$$\sigma = \frac{F^2 | Z |^2 C(D_+ + D_-)}{RT} \qquad (2)$$

Now, assuming that the sample is placed in an electric circuit, Fick's law should be modified to account for the effect of the resulting electric field. Where Z is the valence, F is Faraday's constant, R is the ideal gas constant, T is the absolute temperature and φ is the electric potential. For two given monovalent (Cl⁻ and Na⁺ with |Z| = 1) and $C_+ = C_-$.

This Fig. 1 illustrates the effects of the microwave field on the electrical conductivity in the electrolyte solution with different temperature. When the microwave field has a high intensity of $E_{rms} = 3 \times 10^5$ V/m. According to the Debye-Hückel
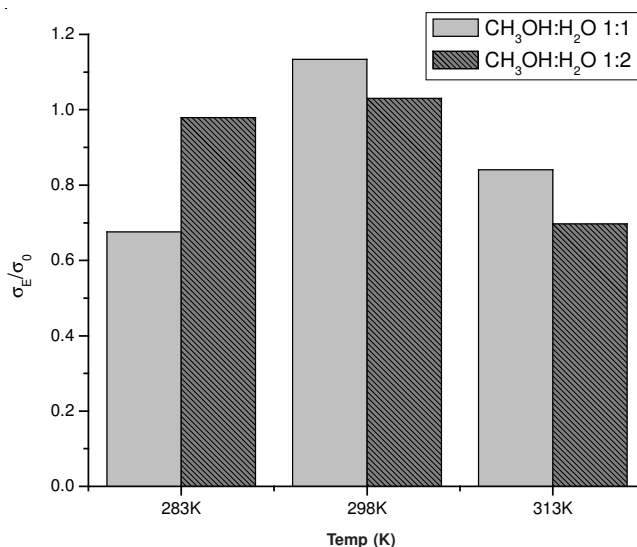

Fig. 1. Calculation value of electrical conductivity: (a) with the external E/M field; (b) without external E/M field

theory, the ion-ion interaction can be described as a formation of an oppositely charged ionic atmosphere surrounding the central ions. This ionic atmosphere lowers the electric potential of the ions and thus retards the drift velocity. Under the action of an external microwave field, the ionic interaction will result in two different effects:

(1) The relaxation effect, which is the distortion of the ionic clouds when the central ions move towards the electrode. This distortion produces a relaxation field, which produces a relaxation force acting on the central ions.

(2) The electrophoretic effect, which arise because the motion of a central ion does not occur in an immobile medium but in a medium moving in the opposite direction to this ion. The ionic atmosphere will rubbing past each other, when the external microwave field present, thus enhancing the viscous drag and lowering the kinetic energy. The two forces both relate to the temperature of the electrolyte and to the intensity of the external microwave field. Further, electrophoretic effect is temperature dependent. The two different effects will both induces a decrease in the electrical conductivity.

Conclusion

In this paper, nonequilibrium molecular dynamics simulations of the electrolyte solution were performed at different temperatures (283, 298 and 313 K) in both the absence and presence of external microwave field, to investigate the influence of an external microwave field on the diffusion coefficient of aqueous solutions. The results have shown that the diffusion

TABLE-1
DIFFUSION COEFFICIENT D ($\times 10^{-9}$ m²/s) FOR Na⁺ AND Cl⁻ IONS AT DIFFERENT
TEMPERATURE WITH OR WITHOUT THE EXTERNAL MICROWAVE FIELD

Temp. (K)	CH₃OH:H₂O 1:1				CH₃OH:H₂O 1:2			
	Na⁺		Cl⁻		Na⁺		Cl⁻	
	E_1*	E_2	E_1	E_2	E_1	E_2	E_1	E_2
283	0.241065	0.35478	0.11808	0.176555	0.148598	0.170783	0.297137	0.284485
298	0.268968	0.361653	0.377098	0.208252	0.262263	0.271725	0.345748	0.31842
303	0.151555	0.531723	0.634823	0.403138	0.248258	0.343215	0.162795	0.246793

*$E_1 = 3 \times 10^5$ V/m, $E_2 = 0$.

coefficient as well as electrical conductivity of the electrolyte solution increase, when the temperature of the electrolyte solution increases. When the external microwave field is applied, electrical conductivity and diffusion coefficient are decrease due to the relaxation effect and the electrophoretic effect.

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