Original Research Article

DIELECTRIC PROPERTIES OF 1-ETHYL-3-METHYL-IMIDAZOLIUM TETRAFLUOROBORATE (EMIM-BF4) USING COLE-COLE RELAXATION MODEL.

ABSTRACT

The Cole-Cole relaxation equations were derived from the Debye equation. The dielectric constant ε' and loss factor ε'' of EMIM-BF4 were fitted using the derived equations at temperature range of $5℃\ to\ 65℃$ and frequency range of 0.1GHz to 10GHz. The result obtained shows that the dielectric constant and loss factor of EMIM-BF4 were higher at low frequency (i.e. $f = 0.1GHz$) and decrease as the frequency increases. The dielectric constant also increase with increase in the temperature except at 0.1GHz. At 15°C there was a sudden increase in the dielectric constant especially as the frequency increase beyond 5GHz. This sudden increase in the dielectric constant of EMIM-BF4 may be due to the phase change of EMIM-BF4. The loss factor of EMIM-BF4 was generally small for all frequencies and temperatures. This may be due to the fact that EMIM-BF4 consumed less energy when subjected to an applied field.

INTRODUCTION

The last decade has witnessed an upsurge in research activities focusing on replacing the abundant used volatile organic solvents (VOC) with a more environmental friendly one. Several alternative methods have been developed and recently ionic liquids have emerged as “green” and environmental friendly solvents. Ionic liquids are a new class of purely ionic, salt-like materials that are liquid at ambient temperatures. In broad sense, this term includes all the molten salts, for instance, sodium chloride at temperatures higher than $800℃$ [1]. Today however, the term “ionic liquids” is used for the salts whose melting point is relatively low (below$100℃$) [2]. A typical ionic liquid (IL) has a bulky organic cation (e.g N-alkylpyridinium, N-N-dialkylimidazolium) that is weakly coordinated to an organic and inorganic anions, such as $BF_4^-, Cl^-, I^-, CF_3SO_3^-, and\ AlCl_4^-$. The big difference in the size of a bulky cation and a small anion does not allow packing of lattice, which happens in many organic salts; instead, the anions are disorganized [3]. Ionic liquids have several advantages compared to commercial organic solvents or electrolyte liquids [4-5]. They are characterised by their non-combustible, non-flammable, display wide electrochemical windows, high inherent conductivity and lack of reactivity in various electrochemical or industrial applications etc. [6-10].

Because their properties, ionic liquids have attracted great attention in many fields, including organic chemistry, electrochemistry, physical chemistry, industrial physics and engineering generally. Today ionic liquids have been thought to be more safe electrolytes materials for electrochemical and energy storing devices, such as lithium batteries for cellular phones, batteries for vehicles, fuel cells, super capacitors, solar cells etc. [11-14].

Due to the special characteristics of ILs, such as wide electrochemical windows, high inherent conductivities, high thermal and electrochemical stability, tuneable physicochemical properties, etc., they are potentially excellent candidates for environmentally sound, green electrolytes in batteries. In order to predict their success in a specific application, it is essential to gain information about their dielectric properties.

In this work, attempt have been made to study the dielectric properties of 1-Ethyl-3-methyl-imidazolium tetrafluoroburate (EMIM-BF4) because of its high ionic conductivity and low viscosity. Therefore, EMIM-BF4 is expected to be a good electrolyte candidate for lithium batteries when compared to organic solvent electrolytes and other ionic liquids.

MATHEMATICAL DERIVATION OF COLE-COLE EQUATIONS

The Debye equations can be expressed more concisely as

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (1)$$

But polar dielectrics that have more than one relaxation time do not satisfy Debye equations. An empirical equation for the complex dielectric constant has been suggested as:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau_{c-c})^{1-\alpha}}; \quad 0 \le \alpha \le 1 \quad (2)$$

$\alpha = 0$ for Debye relaxation, τ_{c-c} is the mean relaxation time and α is a constant for a given material.

To determine the geometrical interpretation of equation (2), we substitute $1 - \alpha = n$ and rewrite it as

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau_{c-c})^n(cos\,\frac{n\pi}{2} + jsin\frac{n\pi}{2})};\quad 0 \le \alpha \le 1 \qquad (3)$$

Where $j^n = cos\,\frac{n\pi}{2} + jsin\frac{n\pi}{2}$ and $\varepsilon^* = \varepsilon' - j\varepsilon''$

Multiply equation (3) by $\frac{1+((\omega\tau_{c-c})^n(cos\,\frac{n\pi}{2} - jsin\frac{n\pi}{2})}{1+((\omega\tau_{c-c})^n(cos\,\frac{n\pi}{2} - jsin\frac{n\pi}{2})}$

i.e $\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau_{c-c})^n\left(\cos\frac{n\pi}{2} + jsin\frac{n\pi}{2}\right)} \times \frac{1+((\omega\tau_{c-c})^n(cos\,\frac{n\pi}{2} - jsin\frac{n\pi}{2})}{1+((\omega\tau_{c-c})^n(cos\,\frac{n\pi}{2} - jsin\frac{n\pi}{2})}$

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty[1+((\omega\tau_{c-c})^n(\cos\frac{n\pi}{2} - jsin\frac{n\pi}{2})}{1+2(\omega\tau_{c-c})^n\cos\left(\frac{n\pi}{2}\right)+(\omega\tau_{c-c})^{2n}} \qquad (4)$$

Equating the real and imaginary part, we have

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1+((\omega\tau_{c-c})^n\cos\,(\frac{n\pi}{2})}{1+2(\omega\tau_{c-c})^n\cos\left(\frac{n\pi}{2}\right)+(\omega\tau_{c-c})^{2n}} \qquad (5)$$

$$-j\varepsilon'' = \varepsilon_s - \varepsilon_\infty\frac{1+((\omega\tau_{c-c})^n(-jsin\frac{n\pi}{2})}{1+2(\omega\tau_{c-c})^n\cos\left(\frac{n\pi}{2}\right)+(\omega\tau_{c-c})^{2n}}$$

$$\therefore\ \varepsilon'' = \varepsilon_s - \varepsilon_\infty\frac{1+((\omega\tau_{c-c})^n(\,sin\frac{n\pi}{2})}{1+2(\omega\tau_{c-c})^n\cos\left(\frac{n\pi}{2}\right)+(\omega\tau_{c-c})^{2n}} \qquad (6)$$

METHODS

Equations (5) & (6) are called the real and imaginary parts of the Cole-Cole relaxation model. The real part (ε') represents the dielectric constant while the imaginary part (ε'') represents the loss factor. An algorithms was written using Maple-13 and the dielectric constant ε' and the loss factor ε'' of 1-ethyl-3-methylimidazolium tetraflouroborate $[EMIM][BF_4]$ were generated (see tables 1 and 3 below). The computations were done within frequency range of 0.1GHz to 10GHz and the temperatures between 5°C and 65°C. The results generated in our computations are discussed below:

RESULTS AND DISCUSSION

The dielectric constant and the loss factor of ionic liquids were computed using Cole-Cole relaxation method. The dielectric constant ε' and the loss factor ε'' of EMIM-BF4 were computed within the temperature range of

5°C *to* 65°C and the frequency of 0.1GHz to 10GHz. The results have been discussed based on the existing theories.

DIELECTRIC CONSTANT

The effect of frequency on the dielectric constant, its variation as a function of temperature at different frequencies of EMIM-BF4 is shown graphically below:

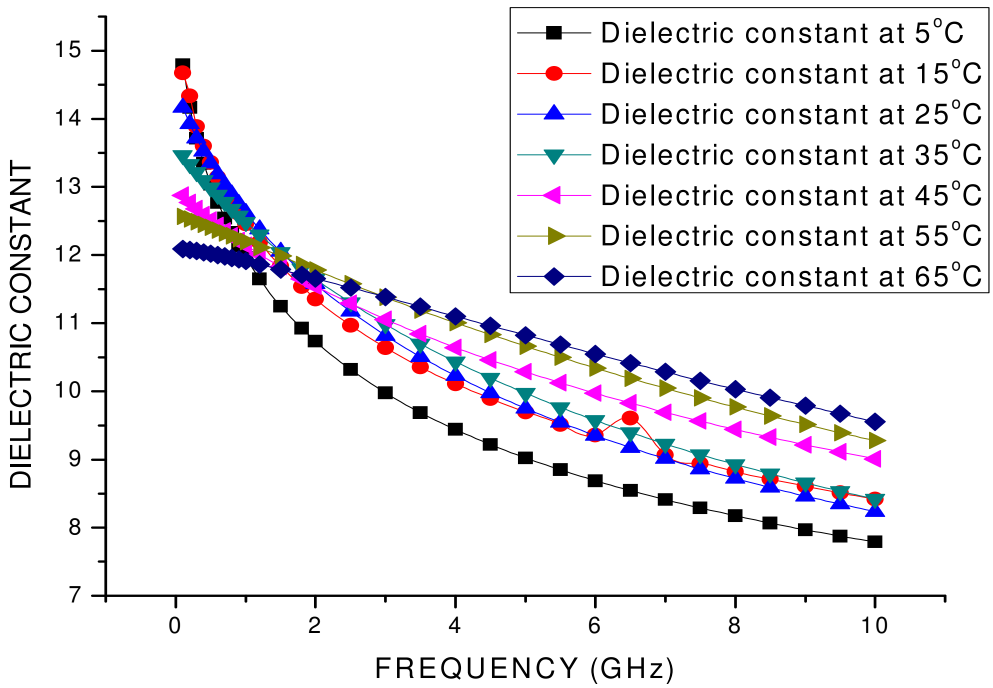

Fig.1: The graph of dielectric constant against the frequency.

The dielectric constant of EMIM-BF4 decrease with increase in the temperature at frequency 0.1GHz (i.e. 14.733 to 12.090 for 5°C and 65°C respectively). However, as the frequency increase beyond 0.1GHz the dielectric constant increases with increased in the temperature (see fig.1 above).

DISCUSSION

The dielectric constant ε' and loss factor of EMIM-BF4 has been studied using Cole-Cole relaxation model. The results revealed that at frequency 0.1GHz the dielectric constant decrease with increase in temperature. This decrease in the dielectric constant as a result of the increase in the temperature at that particular frequency may be due to the relaxation time which has been found to be fast at high temperature and increases dramatically at low temperatures, suggesting a freezing of electric dipole at low temperature [15-17].

The dielectric constant of EMIM-BF4 was also high at lower frequencies. The higher value of dielectric constant ε' at low frequency may be due to the effect of ionic conductivity which is inversely proportional to frequency or maybe because of the overall conductivity which consists of different conduction mechanism. The most prevalent one in moist materials is the ionic conductivity [16].

The graph of dielectric constant against frequency in gigahertz (GHz) at various temperatures revealed that the dielectric constant $\varepsilon'$of EMIM-BF4 have high values at low frequency then decreased sharply with increased in the frequency. The decrease of dielectric constant at higher frequency range for EMIM-BF4 may be due to the fact that the dipole cannot follow up the applied field. The higher values of dielectric constant ε' and loss factor ε'' at lower frequencies may be due to the contribution from all the four types of polarization (i.e the space charge, dipole, ionic and electronic polarization) [18]. It is observed that at higher frequencies, only the ionic and electronic polarizations contribute. The decrease in the dielectric constant and loss factor as the result of increased in the frequency may also means that the response of the permanent dipole decreases as the frequency increases and the contribution of the charge carriers (ions) toward the dielectric constant decreases [16,19]. It is also observed that at temperature $15°\mathrm{C}$ and between the frequencies range 5GHz to 7GHz there was a sudden increased in the dielectric constant of EMIM-BF4 (see fig.1 above). The sudden increase in the dielectric constant of EMIM-BF4 at that particular temperature may be due to the structure changes in a phase change of EMIM-BF4 [20]. This is because the dielectric constant strongly dependent on the structure of materials [21].

CONCLUSION

The Cole-Cole equation and its derivatives have been used to compute the dielectric constant and loss factor of EMIM-BF4. The dielectric constant and loss factor of EMIM-BF4 was higher at lower frequencies and decrease as the frequency increases. The dielectric constant however, increase with increase in the temperature for all frequencies except those at 0.1GHz (see tables 1 and 2 below).

The loss factor of EMIM-BF4 was relatively small for all temperatures studied in this work. This implies that the imaginary part of EMIM-BF4 does not absorb too much heat from alternating field (see tables1 and 2 below)

Table 1. The dielectric constant ε' and loss factor ε'' of ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate) within the temperature range of 5°C and 35°C.

F(GHz)	5°C		15°C		25°C		35°C	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
0.1	14.7932	0.0459	14.6717	0.0523	14.1658	0.0753	13.4608	0.0870
0.2	14.1668	0.0410	14.3346	0.0481	13.9239	0.0719	13.3343	0.0847
0.3	13.7120	0.0376	13.8837	0.0450	13.7136	0.0689	13.2141	0.0825
0.4	13.3457	0.0350	13.6012	0.0462	13.5236	0.0663	13.0989	0.0805
0.5	13.0409	0.0329	13.3575	0.0405	13.3487	0.0640	12.9879	0.0785
0.6	12.7752	0.0311	13.1419	0.0387	13.1859	0.0618	12.8806	0.0766
0.7	12.5404	0.0295	12.9479	0.0372	13.0331	0.0598	12.7767	0.0748
0.8	12.3297	0.0282	12.7712	0.0357	12.8890	0.0580	12.6759	0.0731
0.9	12.1387	0.0270	12.6088	0.0345	12.7523	0.0563	12.5780	0.0714
1.0	11.9635	0.0259	12.4584	0.0333	12.6223	0.0547	12.4827	0.0699
1.2	11.6524	0.0241	12.1868	0.0313	12.3794	0.0517	12.2998	0.0668
1.5	11.2490	0.0218	11.8361	0.0288	12.0510	0.0478	12.0423	0.0627
1.8	10.9291	0.0200	11.5357	0.0267	11.7571	0.0445	11.8027	0.0590
2.0	10.7356	0.0190	11.3570	0.0255	11.5771	0.0425	11.6518	0.0567
2.5	10.3210	0.0169	10.9675	0.0230	11.1723	0.0382	11.3017	0.0516
3.0	9.9791	0.0153	10.6400	0.0209	10.8197	0.0347	10.9855	0.0472
3.5	9.6894	0.0140	10.3581	0.0193	10.5082	0.0317	10.6980	0.0434
4.0	9.4390	0.0129	10.1112	0.0179	10.2301	0.0292	10.4352	0.0400
4.5	9.2191	0.0120	9.8920	0.0167	9.9794	0.0269	10.1938	0.0370
5.0	9.0237	0.0112	9.6954	0.0156	9.7519	0.0250	9.9712	0.0344
5.5	8.8482	0.0105	9.5174	0.0147	9.5440	0.0233	9.7652	0.0320
6.0	8.6893	0.0099	9.3551	0.0139	9.3532	0.0218	9.5739	0.0299
6.5	8.5445	0.0093	9.6062	0.0132	9.1771	0.0205	9.3956	0.0280
7.0	8.4115	0.0089	9.0688	0.0125	9.0139	0.0192	9.2292	0.0263
7.5	8.2889	0.0084	8.9414	0.0120	8.8622	0.0181	9.0734	0.0247
8.0	8.1753	0.0081	8.8229	0.0114	8.7207	0.0172	8.9272	0.0233
8.5	8.0696	0.0077	8.7121	0.0109	8.5882	0.0162	8.7896	0.0220
9.0	7.9709	0.0074	8.6083	0.0105	8.4639	0.0154	8.6600	0.0208
9.5	7.8784	0.0071	8.5107	0.0100	8.3470	0.0147	8.5377	0.0197
10.0	7.7915	0.0068	8.4186	0.0097	8.2368	0.0140	8.4219	0.0187

Table 2. The dielectric constant ε' and loss factor ε'' of ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate) within the temperature range of $45℃\ and\ 65℃$.

F(GHz)	45^0C		55^0C		65^0C	
	ε'	ε''	ε'	ε''	ε'	ε''
0.1	12.8747	0.0765	12.5661	0.1020	12.0899	01191
0.2	12.7733	0.0748	12.5278	0.1011	12.0756	0.1186
0.3	12.6805	0.0732	12.4880	0.1002	12.0590	0.1182
0.4	12.5935	0.0718	12.4472	0.0993	12.0409	0.1177
0.5	12.5109	0.0705	12.4058	0.0984	12.0216	0.1171
0.6	12.4319	0.0692	12.3640	0.0975	12.0012	0.1165
0.7	12.3559	0.0680	12.3220	0.0965	11.9799	0.1159
0.8	12.2826	0.0667	12.2798	0.0956	11.9580	0.1153
0.9	12.2117	0.0658	12.2375	0.0946	11.9353	0.1147
1.0	12.1429	0.0647	12.1951	0.0937	11.9120	0.1140
1.2	12.0111	0.0627	12.1105	0.0919	11.8640	0.1127
1.5	11.8259	0.0599	11.9843	0.0892	11.7890	0.1106
1.8	11.6531	0.0574	11.8595	0.0865	11.7110	0.1084
2.0	11.5440	0.0559	11.7772	0.0848	11.6579	0.1070
2.5	11.2894	0.0522	11.5755	0.0806	11.5218	0.1033
3.0	11.0567	0.0490	11.3799	0.0767	11.3830	0.0996
3.5	10.8426	0.0462	11.1908	0.0730	11.2427	0.0960
4.0	10.6442	0.0436	11.0083	0.0695	11.1021	0.0924
4.5	10.4595	0.0413	10.8323	0.0662	10.9620	0.0889
5.0	10.2869	0.0392	10.6629	0.0632	10.8229	0.0855
5.5	10.1250	0.0373	10.4997	0.0603	10.6854	0.0822
6.0	9.9727	0.0356	10.3426	0.0575	10.5498	0.0790
6.5	9.8290	0.0339	10.1913	0.0550	10.4164	0.0759
7.0	9.6931	0.0324	10.0457	0.0525	10.2855	0.0729
7.5	9.5643	0.0310	9.9055	0.0503	10.1571	0.0701
8.0	9.4420	0.0298	9.7705	0.0481	10.0324	0.0673
8.5	9.3257	0.0286	9.6404	0.0461	9.9085	0.0647
9.0	9.2149	0.0274	9.5150	0.0442	9.7884	0.0622
9.5	9.1091	0.0264	9.3941	0.0424	9.6712	0.0598
10.0	9.0080	0.0254	9.2776	0.0407	9.5568	0.0575

REFERENCES

[1]. Laus G, Bentivoglio G, Schottenberger H, Kahlenberg V, Kopacka, H, Roder T, Sixta H. (2005) Ionic liquids: current developments, potential and drawbacks for industrial applications. *Journal Lenzinger Berichte*. 84:71-85.

[2]. Hagiwara R, Ito Y. (2000). Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *Journal of Fluorine Chem*. 105(2):221-227.

[3]. Seddon K.R.(1996). Room temperature ionic liquids: Neoteric solvents for clean catalysis. *Journal of Kinetics and Catalysis*.37 (5):693-697

[4]. Mutelet, F and Jaubert, J.N. (2006). Accurate Measurements of thermodynamics Properties of Solutes in Ionic Liquids using gas Chromatograghy. Journal of Chromatograghy. A1102, 1(2): 256-267; 00219673.

[5]. Plechkova, N.V and Seddon, K.R. (2008). Applications of Ionic Liquids in the Chemical Industry. Chemical Society Reviews. 37(1): 123-150; 0306-0012.

[6]. Mastumoto, H., Sakaebe, H. and Tatsumi,K. (2005). Preparation of room temperature ionic liquids based on aliphatic onium cations and asymmetric amide anions and their electrochemical properties as a lithium battery electrolyte. *Journal of Power Sources*, 146. 1(2): 45-50., 0378-7753.

[7]. Saruwatari,H., Kuboki, T., Kishi, T., Mikoshiba. S. and Takami, N. (2010). Imidazolium Ionic Liquids containing LiBOB electrolyte for lithium battery. *Journal of Power Sources*, 195, 5: 1495-1499., 0378-7753.

[8]. Giroud, N.M., Rouault, H. Chainet, E., Poignet, J.C. (2008). Ionic Liquids based electrolytes for lithium ion battery. ECS *Meeting Abstrats*, 802, 3044: 1091-8213.

[9]. Stracke, M.P., Migliorini, M.V., Lissner, E., Schrekker, H.S., Dupont, J., and Goncalves, R.S. (2009). Imidazolium ionic liquids as electrolytes for manganese dioxide free Leclanche batteries. *Applied Energy*, 86, 9:1512-1516, 0306-2619

[10]. Seddon, K.R. (2003). Ionic liquids: A taste of the future. *Nature Materials*. 2, 6: 363-365, 1476-1122.

[11]. Sakaebe, H., Matsumoto, H. and Tatsumi, K. (2007). Application of room temperature ionic liquids to Li batteries. *Electrochimica Acta*. 53(3): 1048- 1058, 0013-4686.

[12]. Ohno, H. (2005). *Electrochemical Aspects of Ionic Liquids,* 2nd Ed., John Wiley and Sons, Inc., ISBN:978-0-471-64851-2, Hoboken, New Jesey, USA.

[13]. Sato, T., Masuda, G. and Takagi, K. (2004). Electrochemical Properties of novel ionic liquids for electric double layer capacitor applications. *Electrochimica Acta,* 49: 21, 3603-3611.

[14]. Stathatos, E. Lianos, P. Jovanovski, V and Orel, B. (2005). Dye-sensitized Photoelectrochemical Solar cells based on nano-composite organic- ionorganic materials. *Journal of Photochemistry and Photobiology A*: Chemistry, 169, 1: 57-61.

[15]. Ahmad, M.M, Yamada, K. (2007).Superionic $PbSnF_4$: A giant dielectric constant material. *Appl. Phys. Lett*.19(5):052912-3.

[16]. Onimisi, M.Y., Ikyumbur, T.J., Abdu, S.G. and Hemba, E.C. (2016b). Frequency and Temperature Effect on Dielectric Properties of Acetone and Dimethylformamide. *Physical Science International Journal*. 11(4): 1-8, 2348-0130.

[17]. Graca M, Valente M.A, Ferreira da Silva M.G. (2003). Electrical Properties of Lithium nobium silicate glasses. *J. Non-Cryst. Solids*. 325(1-3):267-274.

[18]. Salman F, Khalil R, Hazaa H. (2014) Dielectric studies and Cole-Cole plot analysis of silver-ion conduction glasses. *Adv. J. Phys. Sc*. 3(1):1-9.

[19]. Bergo P, Pontuschka W.M, and Prison J.M. (2007).Dielectric properties of $P_2O_5 - Na_2O - Li_2O$ glasses containing WO_3, C_oO or Fe_2O_3. *Solid state communications*. 141(10):545-547.

[20]. Onimisi M.Y, Ikyumbur T.J.(2016a) Dielectric study of pure propan-1-ol and propan-2-ol using Debye Relaxation Model. *American Chemical Science Journal*. 10(1):1-12.

[21]. Agilent (2006). Basics of Measuring the Dielectric Properties. http://www3.imperial.ac.uk/pls/portallive/docs/1/11949698.PDF