

1 **Original Research Article**
2 **Excess Parameters of Binary Mixtures of 1, 2-**
3 **Dimethoxyethane-Propylene Carbonate and 2-**
4 **Methoxyethyl Ether-Propylene Carbonate**
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8 **ABSTRACT**
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The excess parameters associated with liquid mixtures were evaluated in order to ascertain the relative strength of intermolecular interactions in binary mixtures of 1,2-Dimethoxyethane-Propylene Carbonate (DME-PC) and 2-Methoxyethyl ether-Propylene Carbonate (DGM-PC). The density and viscosity of pure components of Propylene Carbonate (PC), 1,2-Dimethoxyethane (DME), 2-Methoxyethyl ether (DGM) and mixtures (DME-PC and DGM-PC) were measured within the composition range of 0 to 100 % at temperatures of 298.15, 308.15, 318.15, 328.15 and 338.15K. Experimental density and viscosity values decreased with increase in system temperature and mole fractions of DME and DGM. Mathematical operations were conducted from the density and viscosity data at 298.15 K to resolve the magnitude of excess molar volume (V_m^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (α). These parameters were mainly of negative value, which signified the dominance of dipole-dipole interactions within DME-PC and DGM-PC solvent systems. The existence of interactions between the components of the binary mixtures was also reflected by the non-zero result findings for values of excess parameters.

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11 *Keywords: Excess Volume, Excess Viscosity, Excess Gibbs free energy of activation of viscous flow,*
12 *Grunberg-Nissan parameter, dipole-dipole interaction.*
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15 **1. INTRODUCTION**
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17 Technically, the need to augment:

- 18 (i) ionic dissociation and conductivity
19 (ii) solubility and mobility of species
20 (iii) durability and thermal stability of cell
21 (iv) reduction in free energy of reaction or interaction (polar and non-polar)

22 are the fundamental reasons for deploying mixed solvents in electrochemical systems. This allows for
23 adjustment of properties of the medium of interest by varying proportions of the components of the
24 mixture. Ionic salts are characterized by large lattice energy and considerable energy expenditure is
25 required to separate the ions when they dissolve, giving solutions comprising of discrete anions and
26 cations dispersed in the solvent. Countless salts dissolve in water and in other polar non-aqueous
27 medium, indicating the favourable nature of interactions between solvent molecules and dissolved
28 ions. The introduction of ions into polar solvents is beneficial from the standpoint of ion but may
29 possibly not be from that of solvent. As a rule, solvents with pronounced intermolecular forces (dipolar
30 interactions and hydrogen bonding) are efficient ion solvates. In the solvation of ions, the solvent
31 structure is largely modified owing to strong commove of solvent-solvent interactions in the vicinity of
32 an ion. The knowledge of thermodynamic properties helps in formulating principles for the molecular
33 design of electrolytes utilized in high energy-density batteries. Denticity of coordinating solvent
34 molecules affect the stability of solvated complexes [1]. The ideal number of ligands result from
35 combination of factors namely: the consequence of the contest between attraction to ionic field, steric
36 repulsion forces between coordinating solvent groups and entropy effects of the ligands associated
37 with the metal ion [2]. Viscosity (transport property) and dielectric constant (bulk property of matter)
38 are indispensable parameters in the formulation of state-of-the-art conductive electrolytes for industrial
39 electrochemical processes [3, 4]. Earlier reports stated that the low viscosity property of solvent
40 supports to lessen resistance for ion transport in the solution, while high dielectric constant assists in
41 the reduction of energy of ionic dissociation [5, 6]. In studying thermodynamic properties, the
42 interpretation of excess parameters is obligatory to comprehend intermolecular interactions amid
43 components of the mixture. Intermolecular interactions can be established by the deviation of density,

viscosity and volume properties from ideality. Thermodynamic properties of binary mixtures find application in many chemical processing industries. Direct experimental measurements are frequently employed for studying non-ideal mixtures, requiring measurements performed over different composition range. By appraising thermodynamic properties and studying volume properties, we can construe the processes that occur in mixtures. The design of electrochemical and engineering processes comprising mass transfer, fluid flow and heat transfer require critical data provided by the excess molar volumes of component mixtures. New consequences resulting from mixing processes can influence volume behaviour such as structural changes of components of mixture and intermolecular attraction or repulsion between unlike molecules. Profound insight into transport properties can be achieved by studying viscosity behaviour of liquid mixtures. Viscosity and density data are extensively used in solution theory, equipment modelling and molecular dynamics. In coating and pharmaceutical industries, formulation processes require the benefit of viscosity data. Excess thermodynamics properties have been employed by researchers for studying the relative potency of intermolecular interaction in liquid mixtures [7]. The interactions at molecular level and its influence on the viscosity and density measurements in binary solvent systems of DME-PC and DGM-PC at various temperatures and compositions were considered in this case study. The glymes (DME and DGM) are aprotic saturated diethers that exhibit extreme solvency and stability in strong bases and moderate stability in acid solutions. DME and DGM efficiently solvate cations, surging anion reactivity and as such can upturn reaction rates. Their diether structures engender weak associations between the molecules, and this is responsible for the low viscosity and astounding wetting properties of these solvents. The structural feature of DME and DGM that contributes to their functionality relates to the format of oxygen atoms, as ether linkages at two-carbon intervals. This structural arrangement, analogous to that of crown ethers, gives these solvents the capacity to form complexes with myriad of cations. This study was carried out to investigate the deviation of liquid mixtures from ideality and to construe the relationship between molecular interaction and properties (density and viscosity) of the mixtures. The resultant inference will lay the groundwork for the formulation of electrolyte system with high density chemical source of current using DME-PC and DGM-PC as solvates.

2. MATERIAL AND METHODS

The sourced solvents for this research are DGM (99.5%) product of BASF Chemical Company England, DME (99.5%) and PC (99.5%) products of BDH Chemical Ltd. England and dry $Mg(BH_4)_2$ (95%) product of Sigma Aldrich. The Binary mixtures of DME & PC and DGM & PC were prepared in varying volume percent proportions of 0%, 15%, 25%, 50%, 75%, 85% and 100%. These were constituted by mixing appropriate volumes of the solvent components in standard flasks fitted with caps and the mass measurements were performed on HR-120 (A&D Japan) electronic balance with precision of $\pm 10^{-4}$ g. The mole fractions range from 0.125 to 1.000 (DME) and 0.095 to 1.000 (DGM). The density of the pure solvents and mixtures was determined with a single stem capillary pycnometer bottle at the temperatures 298.15, 308.15, 318.15K, 328.15K and 338.15K. The kinematic viscosity of the pure solvents and mixtures was determined using a suspended Ubbelohde viscometer tube ASTM D 446. Koehler electronic constant temperature water bath was used to maintain the experimental solvents and mixtures at the desired temperatures of 298.15, 308.15, 318.15, 328.15K and 338.15 ± 0.01 K. The flow time was determined electronically by using an electronic timer with precision of ± 0.01 s. The kinematic viscosity was calculated using the formula [8]:

$$V = kt \quad [1]$$

where V , k and t are the kinematic viscosity, viscometer constant and flow time respectively. The kinematic viscosity was converted into dynamic viscosities using the formula:

$$\eta = V\rho \quad [2]$$

where η and ρ are the dynamic viscosity and density of liquid respectively. The process was repeated until three successive determinations were obtained within ± 0.1 seconds.

The equations [9] for excess molar volume (V_m^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (\bar{a}) are as follows:

$$V_m^E = X_1 M_1 \left(\frac{1}{\rho_m} - \frac{1}{\rho_1} \right) + X_2 M_2 \left(\frac{1}{\rho_m} - \frac{1}{\rho_2} \right) \quad [3]$$

$$\eta^E = \eta_m - (X_1 \eta_1 + X_2 \eta_2) \quad [4]$$

where X_1 and X_2 are mole fractions of pure constituents 1 and 2 respectively, M_1 and M_2 are molar masses of pure constituents 1 and 2 respectively, ρ_1 and ρ_2 are densities of pure constituents 1 and 2

102 respectively, η_1 and η_2 are viscosities of pure constituents 1 and 2 respectively, ρ_m and η_m are density
 103 and viscosity of the mixture respectively.

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$$V_m = \frac{X_1 M_1 + X_2 M_2}{\rho_m} \quad [5]$$

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$$G^E = RT[\ln \eta_m V_m - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \quad [6]$$

108
 109 where R is the Universal constant for gases, T is Absolute temperature, V_1 , V_2 and V_m are molar
 110 volumes of pure constituents 1, 2 and mixture respectively.

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$$a_i = \frac{\ln \eta_m - (X_1 \ln \eta_1 + X_2 \ln \eta_2)}{X_1 X_2} \quad [7]$$

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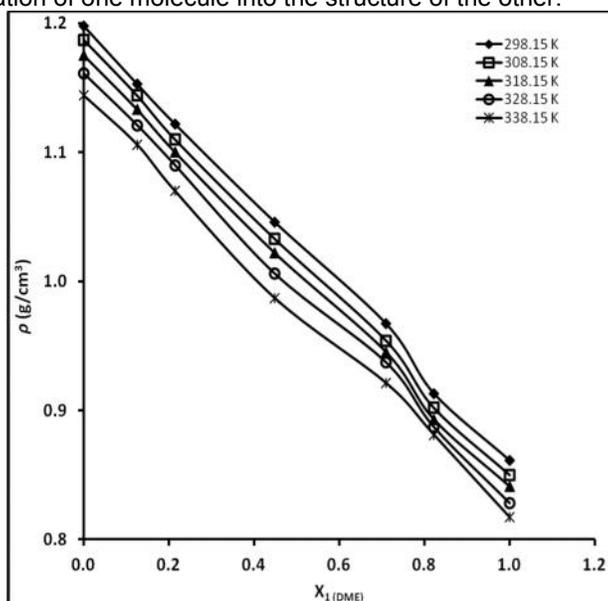
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116 **3. RESULTS AND DISCUSSION**

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118 **3.1 Density**

119 The density of the binary mixtures (DME-PC and DGM-PC) decreased as temperature increased
 120 (Figures 1 and 2). Increase in temperature disrupts the orientation of the electric dipoles of the solvent
 121 molecules when subjected to external electric field, with the negative end of dipole of one molecule
 122 facing the positive end of dipole of another molecule. This orientation of molecules accounts for
 123 elevated density and viscosity in liquids and mixtures. Also, the density of the binary mixtures
 124 decreased as the proportion of component 1 (DME and DGM) in the mixtures increased, which is
 125 credited to accommodation of one molecule into the structure of the other.

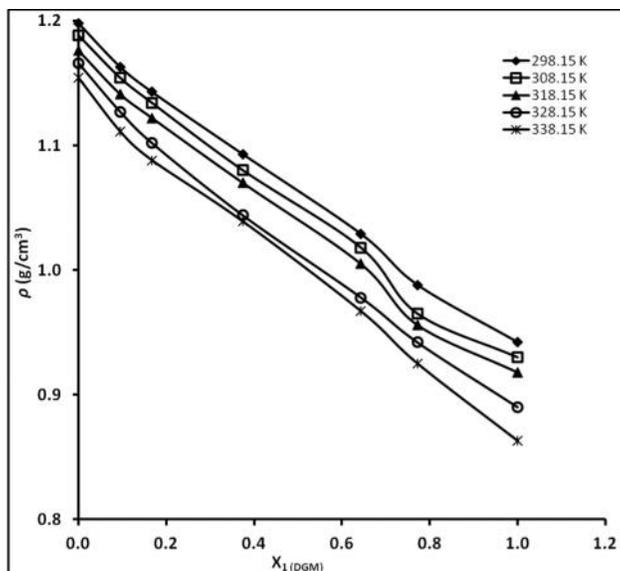


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Fig. 1. Plot of Density versus Mole Fraction (DME)

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Fig. 2. Plot of Density versus Mole Fraction (DGM)

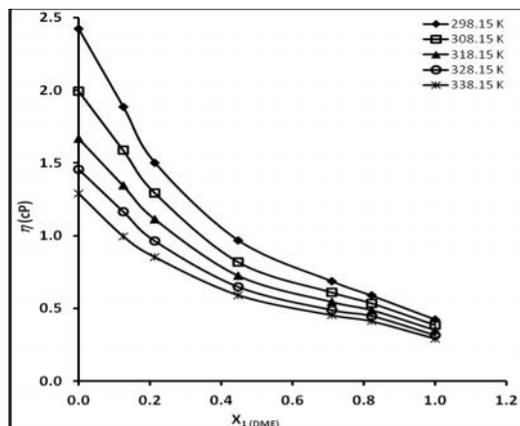
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132 3.2 Viscosity

133 Increase in the temperature of the binary mixtures (DME-PC and DGM-PC), increased the average
 134 speed of molecules, leading to decrease in the amount of time spent in contact with neighbouring
 135 molecules. As temperature increased, the average intermolecular forces decreased and thus,
 136 accounts for the observed decrease in viscosity of the mixtures (DME-PC and DGM-PC) with
 137 temperature increase (Figure 3 and 4). The viscosity of the binary mixture also decreased as the ratio
 138 of DME or DGM in the mixture increased, due to the lower viscosity of the solvents. Furthermore, the
 139 measured values of viscosity for DME-PC were lower than those of DGM-PC at all experimental
 140 temperatures. This is likely due to the higher steric influence experienced as a result of the structurally
 141 longer DGM molecule on interaction with PC as compared to that of the relatively shorter chain length
 142 of DME.

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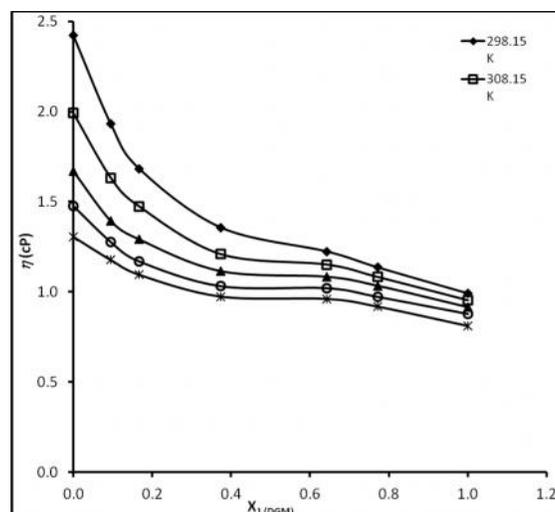
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Fig. 3. Plot of Viscosity versus Mole Fraction (DME)



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Fig. 4. Plot of Viscosity versus Mole Fraction (DGM)

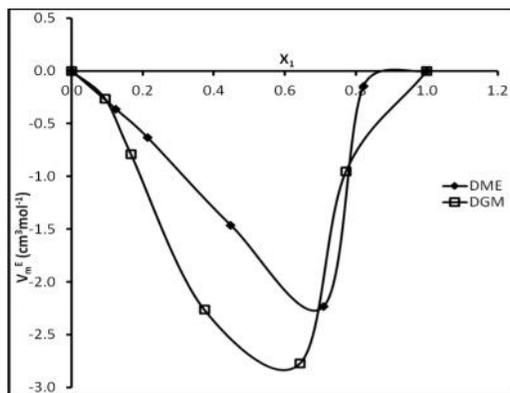
149 3.3 Excess Parameters

150 The measure of variation between the values of property of solution thermodynamics and that for an
 151 ideal solution under parallel conditions of temperature and composition is termed the excess property.
 152 This level of variation represents the positive or negative excess of solution thermodynamics, relative
 153 to the ideal solution as reference [10]. Excess parameters have zero value for ideal mixing. The
 154 negative or positive values of excess parameters indicate non-ideal behavior in mixtures, signifying
 155 the existence of specific interactions between the mixtures of DME-PC and DGM-PC. The positive
 156 values of excess volume are attributed to dispersive forces, while negative values are attributed to
 157 dipole-dipole interactions and formation of hydrogen bonds [11]. Negative values of excess volume
 158 result from strong interactions between unlike molecules (DME-PC and DGM-PC); while positive
 159 excess volume results from strong interactions between like molecules (DME-DME, DGM-DGM and
 160 PC-PC), indicating breakup interactions between unlike molecules of the mixtures. Positive values of
 161 excess volume are the result of rupture of hydrogen bonds and loosening of dipole interactions [12].
 162 The non-zero results for values of the excess parameters in this study point towards the existence of
 163 interactions between the components of the binary mixtures (Figures 5 to 8). Various workers have
 164 explained the nature and strength of these interactions on the grounds of the sign and magnitude of
 165 excess parameters [13]. In both binary solvent systems studied, one factor which may contribute to
 166 excess molar volume is the disruption of the intermolecular dipolar forces in component 2 (PC) by the
 167 addition of component 1 (DME or DGM). The values of V_m^E for the mixtures (Figure 5) are negative
 168 over the entire constitution range and it appears that intermolecular interactions between unlike
 169 molecules predominate over intermolecular interactions between like molecules. The molar volumes
 170 of PC and DME molecules are 85.22 and $104.74 \text{ cm}^3 \text{ mol}^{-1}$ while that for PC and DGM are 85.22 and
 171 $142.44 \text{ cm}^3 \text{ mol}^{-1}$ respectively. It is apparent that the accommodation of one component into the
 172 structure of the other interstitially is not favorable enough. Therefore, it may not significantly contribute
 173 towards the V_m^E values. Thus, dipolar and dispersion forces between DME-PC and DGM-PC
 174 molecules are primarily responsible for negative values of V_m^E [14].

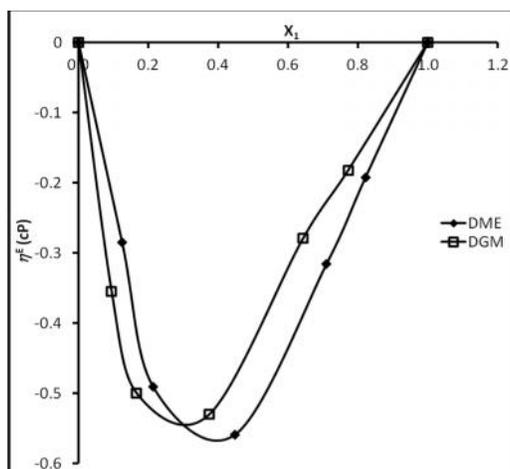
175 According to Fort and Moore [15], the negative values of η^E suggest the existence of dispersion
 176 forces; thus, negative deviation of η^E suggests that dipole interactions are more probable in DME-PC
 177 and DGM-PC (Figure 6) systems.

178 To understand the forces acting between the unlike molecules of DME-PC and DGM-PC, the support
 179 of excess Gibbs free energy of activation of flow (G^{*E}) and Grunberg-Nissan interaction parameter (d)
 180 is needed. The negative values of excess Gibbs free energy of activation for viscous flow (Figure 7)
 181 indicate the dominance of dispersion forces characterized by decrease in the internal energy of
 182 viscous flow; revealing the incidence of weak interaction in the systems. Positive deviations in values
 183 of excess activation energy of flow indicate specific interactions between the components of the
 184 mixture [16]. The Gibbs free energy of activation for viscous flow is negative over the constitution
 185 range (0.125 to 0.710 mole fraction of DME and 0.095 to 0.772 mole fraction of DGM), indicating the
 186 dominance of dispersion forces.

187 The sign and magnitude of Grunberg-Nissan interaction d-parameter is considered the measure of
 188 strength of interactions. The negative values of the d-parameter (Figure 8) show the existence of
 189 weak interactions between the unlike molecules DME-PC and DGM-PC. Furthermore, positive values
 190 of the d-parameter indicate that interactions between unlike molecules are strong [16]. The resolved
 191 negative trend of d-parameter values in most of the experimental cases is suggestive of dipole-dipole
 192 and dipole-induced dipole interaction of little magnitude between species of dissimilar molecules
 193 (DME-PC and DGM-PC) [9].
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 196 **Fig. 5. Plot of Molar Excess Volume versus Mole Fraction**



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 198 **Fig. 6: Plot of Excess Viscosity versus Mole Fraction**
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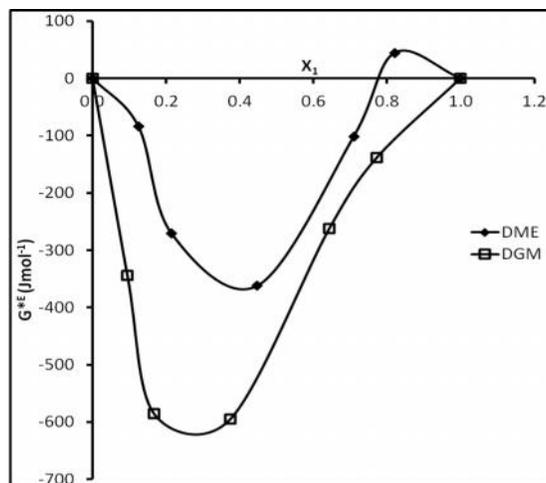


Fig. 7. Plot of Excess Gibbs Free Energy versus Mole Fraction

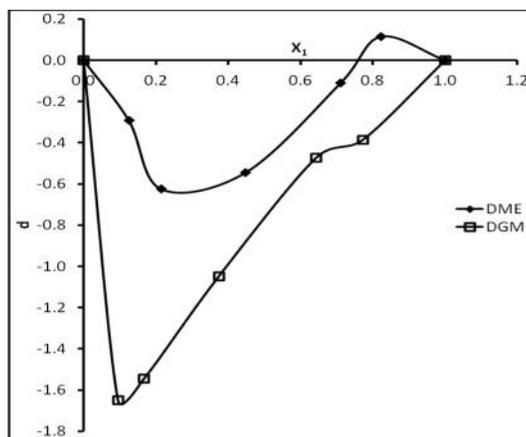


Fig. 8. Plot of Grunberg-Nissan Parameter versus Mole Fraction

4. CONCLUSION

The study on excess parameters of binary mixtures (DME-PC and DGM-PC) has revealed its usefulness in understanding the nature of intermolecular interactions between two liquids. Parameters such as density and viscosity of pure solvents and binary liquid mixtures measured at different temperatures over 0 to 100 % composition range provide statistics on thermodynamic properties associated with heat and fluid flow. Dipolar and dispersion forces in DME-PC and DGM-PC molecules are principally responsible for negative values of V_m^E and η^E ; and it appears that intermolecular interactions between unlike molecules predominate over that of like molecules. The perusal of the sign and magnitude of G^{*E} and d , indicated that interactions between dissimilar molecules in both binary systems studied follow the order: DME-PC > DGM-PC. This means that solvent-solvent interactions between unlike molecules are stronger in the DME-PC system than in DGM-PC system. Thus, DGM molecules are relatively free from hindrances credited to strong dispersion and dipolar forces between unlike molecules. DGM molecules will therefore exhibit great affinity for electrolyte, and easily stabilize cations in solution, which in turn affords better conducting electrolytes.

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