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Interactions in Binary Mixed Solvents of Propylene carbonate +Diethyl carbonate and Propylenecarbonate+Dimethylformamide at 298.15K

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ABSTRACT: In thermodynamics, it is essential to be aware of the various forms of intermolecular interactions taking place in solvent mixtures. The study was carried out to evaluate the interactions in mixed binary organic solvents of propylene carbonate (PC) and Diethyl carbonate (DEC) and Propylene carbonate and Dimethylformamide (DMF) at 298.15K. The densities and viscosities of binary mixed organic solvents, propylene carbonate and Diethyl carbonate and Propylene carbonate and Dimethylformamide were measured at a varied percentage solvent constitution of 298.15K. The excess volumes V^E and excess viscosities ηE were calculated from the density and viscosity values obtained fromexperimentst. These were fitted into the Redlich-Kister polynomial equation to obtain the fitting coefficients and the corresponding standard deviations. Excess volume values for PC+DEC mixtures were positive at lower mole fractions of PC and negative at higher mole fractions, while the excess volume values obtained for the PC+DMF mixtures were all negative. The excess viscosities for both PC+DEC and PC+DMF were negative over the whole span of solvent compositions. These behaviors have been attributed to the dominance of weak dispersion forces and strong attractive interactions between the mixed solvent components. As a result, there are more intermolecular interactions than solvent-solvent interactions in solvent systems. The mixed systems could be employed as possible mixed organic electrolyte solvents and other solvent applications, as the data provided can act as a guide..

Keywords: Interactions, solvent, density, viscosity, propylene carbonate, diethyl carbonate, dimethylformamide, excess function, excess viscosity, excess volume, mixture.

INTRODUCTION

Mixed organic solvent data have become useful tools in many industrial applications. The foundation for developing optimal electrolytes for high-energy density batteries and other applications is a fundamental molecular understanding of the useful properties of liquid mixtures. Usually, it is required that a liquid electrolyte maintain a low viscosity to facilitate ionic movement and a high dielectric constant for better dissociation of ions in solution. However, this is practically unrealistic, as no single electrolyte possesses these two properties. Studies have shown that mixing organic solvents complements or enhances the properties of the individual solvents. It is pertinent that data be provided on mixed organic solvent systems. Derived thermodynamic functions such as excess volumes and viscosities are normally suitable and practical frameworks for interpreting and understanding the nature of intermolecular interactions in mixtures. Fundamental understanding of the useful properties of mixtures of liquid mixtures forms the basis for designing optimal electrolytes for various applications (Nain et al., 2007). For example, liquid electrolytes for high energy density batteries such as lithium ion batteries are mostly binary mixed aprotic organic

solvents (Nwokobia et al., 2015). Specific interactions such as hydrogen bonding, dipole-dipole interactions, and charge transfer reactions could be induced in mixed solvent systems. This usually leads to deviations from ideality. In binary liquid mixtures, deviations from ideality are associated with synergism. They are attributed to differences in the chemistry and molecular architecture of mixed solvents, the mixing ratios, as well as the experimental conditions such as temperature (Athuwaim The literature is replete with thermodynamic data on solvent mixtures, such as excess molar volumes and excess viscosity of non-aqueous, binary organic solvents. Ayasen et al. (2015) studied the volumetric behavior of binary mixtures of some alkoxyethanols and some selected amines at 298.15K. Densities of binary mixtures of 2-methoxyethanol and 2- ethoxyethanol with hexylamine, diethylamine, triethylamine, tert-butylamine, aniline, and benzylamine were measured by varying compositions of the alkoxyalkanols and 298.15 K. The molar volumes of the mixtures were calculated from the density data and fitted into the Redlich-Kister polynomial to obtain the fitting coefficients and standard deviations. Negative excess volumes were obtained over the entire range and were suggested to be due to stronger hydrogen bond formations between unlike molecules of the mixtures than those between like molecules of the pure components. A study on the interactions of the binary liquid mixtures of 2-chloroaniline with some carboxylic acids was done by Chandra et al. (2016). Densities, speed of sound, and dynamic viscosities of liquid mixtures of 2-chloroaniline with carboxylic acids (ethanoic acid, propanoic acid, and butanoic acid) have been measured at 303.15 and 318.15K. The excess molar volumes and Gibbs free energy of activation for viscous flow, ΔG^{*E} of the mixtures were calculated from density and viscosity data. These results were used to identify the evolution of strong and weak interactions between dimers in the binary mixtures. Regiane et al. (2018) investigated the density, viscosity, and excess properties of binary mixtures of protic ionic liquid (2-hDEAF, 2-hDEAA) + water at various temperatures. Excess molar volumes and viscosity deviations were computed from experimental density and viscosity values. These were fitted to the Redlich-Kister equation to determine the difference between experimental and theoretical values. They reported negative values for the excess functions for the ionic intermolecular liquids and their water mixtures, which they attributed to the shrinkage of the mixtures and stronger intermolecular interactions within the systems.

PC, DEC and DMF are often employed in industrial and laboratory practice. Their mixed solutions could be possible electrolyte solvent high-energy batteries and other applications. This study provides data regarding some excess functions of binary mixtures of PC+DEC and PC+DMF and uses such to interpret interactions in the systems. This could act as a guide to the application of solvent mixtures.

MATERIALS AND METHODS

Sigma Aldrich, United Kingdom, supplies propylene carbonate (PC), diethyl carbonate (DEC), and dimethylformamide (DMF).These were obtained commercially. The reagents were of analytical grade and were used without extra purification.

Statistical Tool: Redlich-Kister Correlation
Binary mixed solvents of (PC-DEC), and (PC-DMF) were prepared in the volume ratios of 0, 15, 35, 55, 65, 75, and 100% of PC. The densities of pure and mixed solvents (of varying volume ratios) were measured with a 10 mL density bottle at 298.15K. The viscosities of the pure and mixed solvents were determined at 298.15K with an Ubbelhode viscometer after calibration. The viscometer calibration was done with distilled water, and the viscometer constant was 0.0447. For each measurement, the viscometer was continuously cleansed with distilled water and rinsed with the appropriate solvent mixture at frequent intervals so as to enable an accurate flow of the sample mixtures. The kinematic viscosity of the mixtures was calculated using the relationship in the equation below.

$$\nu = kt \qquad (1)$$

where, t is the flow time through the viscometer capillary, ν is the kinematic viscosity and k is the viscometer constant. The dynamic viscosities were calculated from the kinematic viscosities using equation 2

$$\eta = \nu\rho \qquad (2)$$

where, η is dynamic viscosity (absolute viscosity), ν is the kinematic viscosity and ρ is the density of the mixture. The experimental density and viscosity data were used to calculate the solutions' excess molar volumes and viscosities using equations 3 and 4, respectively.
The excess volumes, V^E were calculated using the relationship

$$V^E = X_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + X_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \qquad (3)$$

where X_1 and X_2 are the mole fractions of components 1(PC) and 2(DEC or DMF), respectively, V^E is the excess molar volume, M_1 is the molar mass of PC while M_2 is that of DMF or DEC and ρ_1 and ρ_2 are their respective densities (gcm^{-3}). ρ is the density of the mixed solvent.

Excess viscosities of the solutions were calculated using;

$$\eta^E = \eta \left(X_1 \eta_1 + X_2 \eta_2 \right) \qquad (4)$$

Where, η^E is the excess viscosity in (cP), η is the viscosity of mixed electrolyte, $\eta1$ is the viscosity of component 1(PC), $\eta2$ is the viscosity of component 2(DEC or DMF), X_1 and X_2 are the mole fractions of component 1and 2 in that order. The calculated values of the excess functions were fitted at 298.15K for the mixed systems into Redlich-Kister polynomial (equation6) and the fitting coefficients a_n calculated by the method of least squares as shown in equation 5

$$y^E = X(1-X)^2 \Sigma a_n (2X-1)^n \qquad (5)$$

where y^E can be either V^E, η^E or ΔG^{*E} and X is the mole fraction of PC, n is the number of experimental data. The standard deviations of the excess functions were correlated using the equation below:

$$\sigma(y^E) = \sqrt{\frac{\varepsilon(y^E expt - y^E cal)^2}{m-n}} \qquad (6)$$

Here m is the total number of experimental data points.

RESULTS AND DISCUSSION

Table 1: Mole Fractions (X), of the mixed solvents.

	PC/DEC		PC/DMF	
Vol% PC	X_{PC}	X_{DEC}	X_{PC}	X_{DMF}
100	1	0	1	0
75	0.786	0.214	0.791	0.209
65	0.690	0.310	0.701	0.299
55	0.599	0.401	0.607	0.393
35	0.397	0.603	0.405	0.595
15	0.177	0.823	0.223	0.777
0	0	1	0	1

Table 2: Densities (g/cm^3) and Dynamic Viscosities(cP) of the Pure and Mixed Solvents at 298.15K

	Density			Dynamic viscosity	
Vol %PC	PC/DEC	PC/DMF		PC/DEC	PC/DMF
100	1.205	1.205		2.451	2.451
75	1.131	1.109		1.909	1.923
65	1.092	1.060		1.636	1.647
55	1.044	1.023		1.386	1.433
35	1.019	0.998		1.149	1.213
15	0.999	0.968		0.947	0.991
0	0.977	0.946		0.749	0.778

Table 3: Excess Volumes V^E (cm^{3}mol^{-1}) of Mixed Solvents at 298.15K

	PC/DEC		PC/DMF	
Vol% PC	Xpc(mole fractionPC)	V^E	Xpc(mole fractionPC)	V^E
100	1	0	1	0
75	0.786	-0.1953	0.791	-1.3875
65	0.690	-0.2348	0.701	-1.8646
55	0.599	-0.1889	0.607	-2.5610
35	0.397	0.3191	0.405	-4.02327
15	0.177	0.1173	0.223	-3.59403
0	0	0	0	0

Table 4.: Excess viscosities η^E(Kg/ms) of Mixed Solvents at 298.15K

Vol% PC	Xpc	η^E (PC/DEC)	Xpc	η^E (PC/DMF)
100	1	0	1	0
75	0.786	-0.5066	0.791	-0.4898
65	0.690	-0.8169	0.701	-0.7835
55	0.599	-1.05841	0.607	-1.03997
35	0.397	-1.05811	0.405	-1.31656
15	0.177	-0.34878	0.223	-1.17733
0	0	0	0	0

Table 5: Redlick-Kister Fitting Coefficients(A_0-A_3) and Standard Deviation for Excess Functions of Mixed Solvents at 298.15K

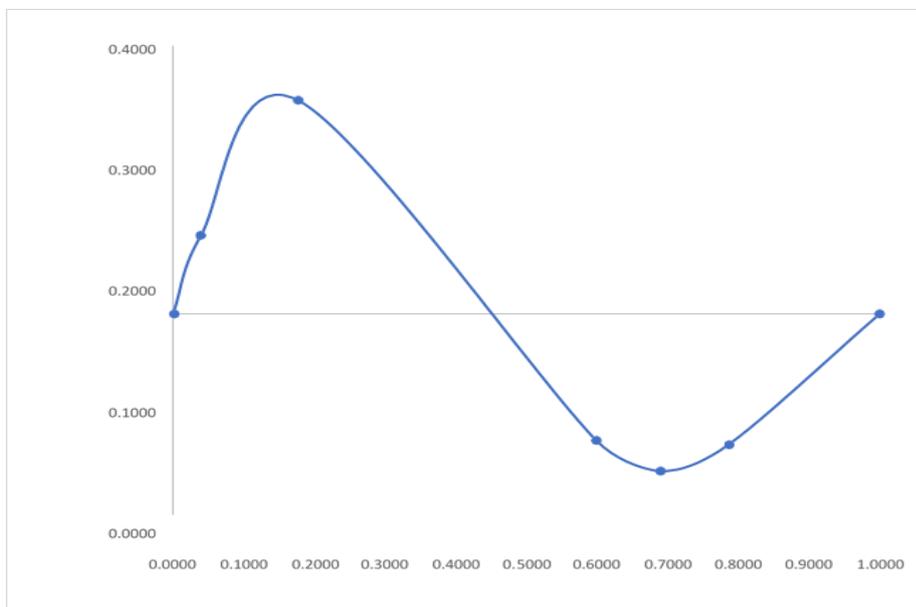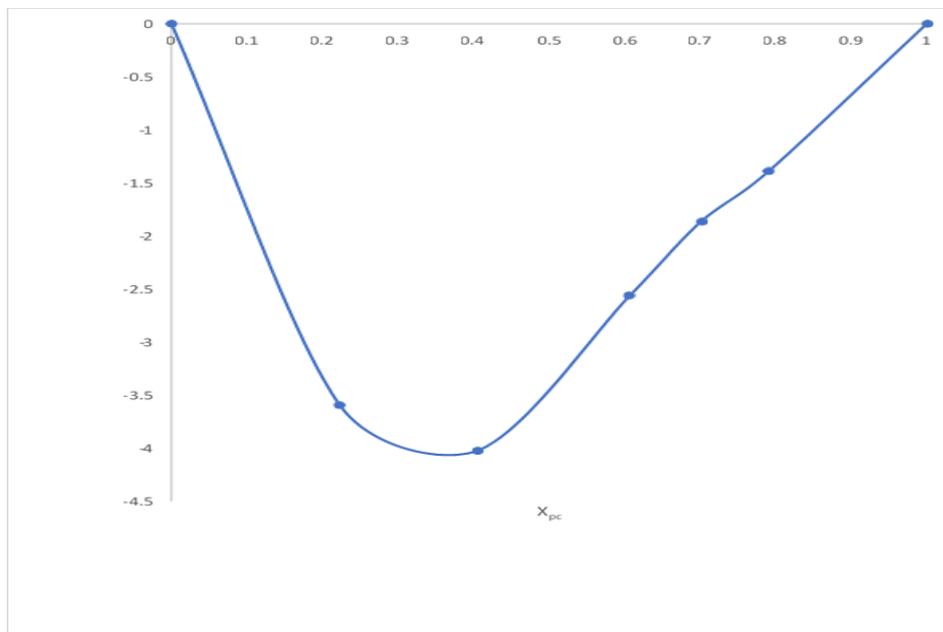| Excess Parameters	AO	A1	A2	A3	σ
V^E	-0.192	-0.307	0.354	-0.038	97.934
η^E	-0.0177	0.253	-3.969	-0.054	2.599

Figure 1: Plot of Excess Volumes V^E of Mixed Solvents of PC/DEC at 298.15K

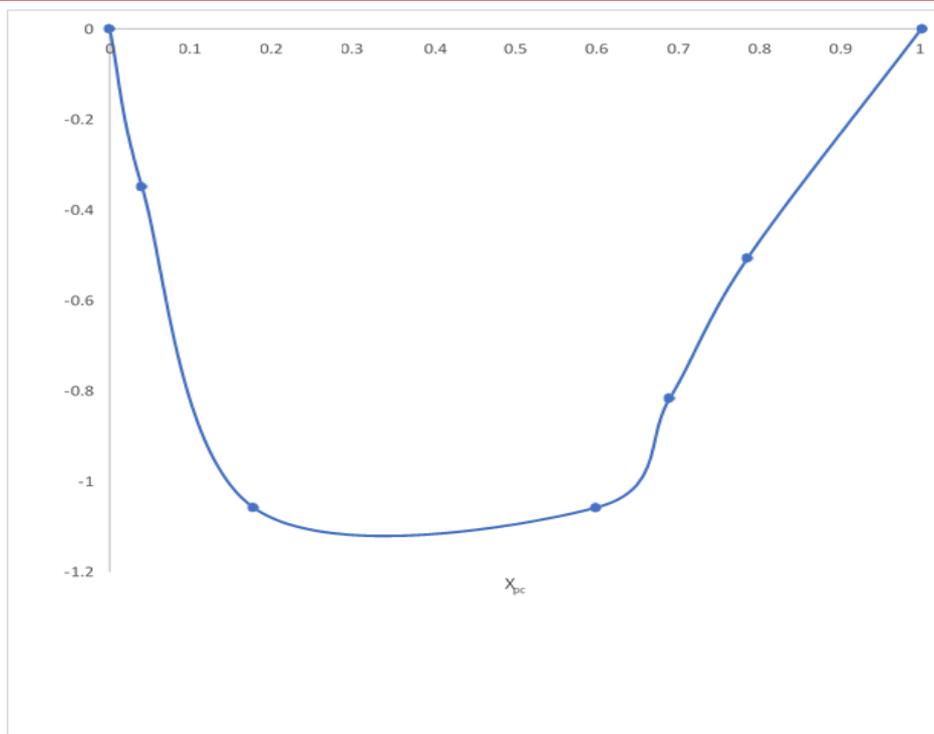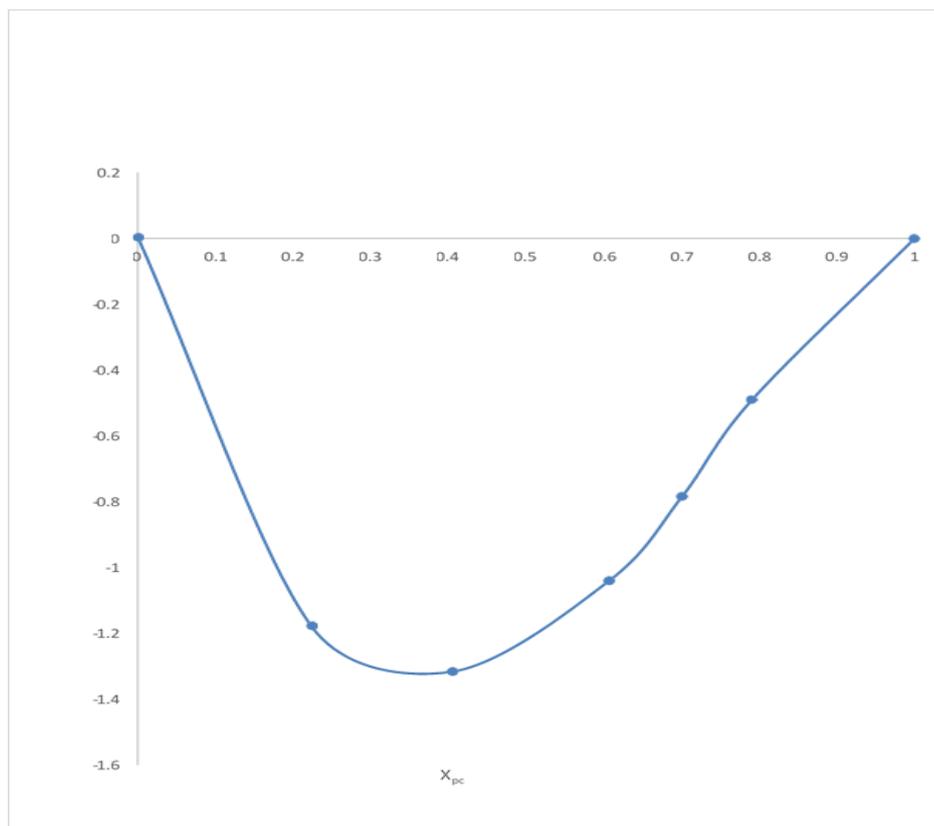Figure 2: Plot of Excess Volume VE of Mixed Solvents of PC/DMF at 298.15K

Figure 3: Plot of Excess Viscosities η^E of Mixed Solvents of PC/DEC 298.15K

Figure 4: Plot of Excess Viscosities η^E of Mixed Solvents of PC/DMF 298.15K

DISCUSSIONS

There was a consistent decrease in the density of the mixed solvents, as shown in Table 2. The in density with decreasing volume composition and mole fraction of PC in the mixture reflects the lower densities of DEC and DMF over that of PC. Introduction and gradual increase in volume compositions of the cosolvents (DEC, DMF) lowers the densities of the mixtures. The higher density values observed in the PC-DEC mixed solvents could be due to the higher density value of pure solvent of DEC ($0.975g/cm^3$) over that of DMF ($0.948g/cm^3$). The dynamic viscosities of the PC/DEC, PC/DMF mixtures in Table 2 also showed a decreasing range mainly due to the increasing volume percentage of the lower viscous co-solvents. This may be because of

weaker solvent-solvent interactions in contrast to the interactions between molecules of individual solvents, which improved the flow of solvent mixtures (Dikio, 2014).

The excess volumes for PC/DEC were positive at lower mole fractions of PC and negative at higher mole fractions (table3), giving rise to a sigmoid curve in figure 1 while the excess volumes for PC/DMF were negative over the span of mole fractions as seen in figure 2. The sign of the extra molar volume is a reflection of the contraction and expansion of the volume of the solvents as a result of mixing. The positive values at the lower mole fraction of PC(PC/DEC) could be due to dominance of dispersion forces and breaking of bonds and increase in chain length between the different components of the molecules of the solvents. Similar observations were made by Saleh et al. (2006) who they attributed the positive values of the excess volumes of the cumene-butanol mixtures to the dissociation of butanol in cumene and Kurnia et al. (2011), who stated that the positive excess molar volumes obtained in the protic ionic liquid bis-2-hydroxyethyl ammonium – alcohols mixture was due to the disruption of ordered molecular structure within the mixtures. But at higher mole fractions, specific interactions became more prominent, giving rise to negative values. The negative values observed all through the mole fraction of PC in the PC/DMF mixed solvents can be attributed to the interstitial fitting of smaller molecules of DMF into the larger molecules of PC. Fitting in of solvent molecules into one another and the formation of hydrogen bonding, will lead to negative excess volume (Dikio et al., 2013). Negative excess volumes were also obtained over an entire range of mole fractions by Ayasen et al (2015) and were suggested to be due to stronger interaction and bond formations between unlike molecules of the mixtures than those between like molecules of the pure components.

The excess viscosities for both PC/DEC and PC/DMF were negative over the whole span, as shown in figures 3 and 4. This signifies that the viscosity of the solutions is smaller than that of the ideal, indicating that there are more inter-molecular interactions between the solvents. The negative values for viscosities could reflect dominance of weaker interactions like dispersion forces due to differences in molecular sizes (Hina et al.,2015). Mixing different organic solvents disrupts interactions in the individual solvents. The difference in shape and size of component molecules, structural changes like the breaking up of hydrogen bonds and loss of dipolar association, gives rise to decrease in viscosity. This effect produces negative values in excess viscosity. Positive values of η^E indicate strong interactions like dipole-dipole interactions, whereas the negative values point to weaker interactions in the system, as reported in similar studies (Regiane et al. ,2018). Positive values invariably imply more viscous mixtures giving rise to more of solvent-solvent interactions. Negative excess viscosities obtained for the solvent systems used in this work point to less viscous mixtures, which may increase ions' mobility, inducing more ion- solvent and ion -ion interactions.

CONCLUSION

Interactions in the mixed systems of PC/DEC and PC/DMF were interpreted from the values of the excess volumes and viscosities. The values obtained indicated the existence of both dispersion forces (implying fewer solvent-solvent interactions) and strong interactive forces between molecules of the individual solvents. So, the interactions between molecules of the solvents prevailed over solvent-solvent interactions. For prospective electrolyte solvents, this holds sway. The mixed solvents could be employed as potential electrolyte solvents, and the data obtained in this work can be held as reliable baseline data.

Authors Contributions
All the authors contributed equally to this work.

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