Green Solvents Based on Ionic Liquids and Alcohols: Volumetric and Spectroscopic Studies

Submitted by:

Md. Ahad Ali

Research Fellow

Bose Center for Advanced Study and Research in Natural Sciences

Supervised by

Dr. Md. Abu Bin Hasan Susan

Professor

Department of Chemistry

University of Dhaka

Dhaka-1000, Bangladesh

March, 2023

Dr. Md. Abu Bin Hasan Susan
Professor
Department of Chemistry
University of Dhaka
Dhaka-1000, Bangladesh

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Md. Ahad Ali
Research fellow

Abstract

In this study, densities, dynamic viscosities, and refractive indices of 1-ethyl-3-methylimidazolium ethyl sulfate ($[C_2mim]C_2H_5SO_4$) with propane-1-ol at T = 293.15 to T = 333.15 K at atmospheric pressure have been measured over the entire composition range. Excess molar volumes, dynamic viscosity deviations, excess molar Gibbs free energy of activation, and refractive index deviations for the binary systems have been calculated and were satisfactorily fitted to a Redlich–Kister type polynomial equation. The outcomes were correlated with the molecular-level interactions. From the Eyring equation, the thermodynamic activation parameters were also calculated, and their variation with $[C_2mim]C_2H_5SO_4$ implied a shift in molecular-level interactions. The near-infrared (NIR) spectroscopic measurements were done at temperatures from 293.15 K to 333.15 K. Principal component analysis and two-dimensional correlation spectroscopy were used to further evaluate the unprocessed NIR data. The expected molecule-level interactions came from the combination of volumetric properties and NIR spectroscopy. The binary combination opened up a plethora of possible uses due to its novel, distinctive molecular-level interactions, and better thermodynamic properties.

Keywords

Ionic liquid, two-dimensional correlation spectroscopy, principal component analysis

Introduction

One of the most interesting developments in solvent chemistry is the use of ionic liquids (ILs). The term "ILs" refers to solvent materials that are liquids below 373.15 K and only consist of ions. They have been referred to as "designer solvents" due to their capacity to adjust the ions, hence modifying and optimizing the physical properties of ILs for a particular application. Scientists are interested in ILs because of their environmentally friendly features and superior physicochemical properties, which include relatively low melting point, imperceptible vapor pressure, wide electrochemical window, high electrical conductivity, non-flammability, tremendous thermal stability, good recyclability, a wide liquidus range, and a high capacity to dissolve a variety of inorganic and organic substances.[1-5] Numerous works on the characteristics of IL or their uses in catalytic reactions, separation techniques, membrane technology, chemical analysis, batteries, solar cells, or lubricants have recently been reported. Even still, little is known about the molecular-level interactions of ionic liquids because, in general, these novel solvents are highly hygroscopic[6], and even modest traces of water or other substances induce significant changes in molecular-level interactions in an IL.[7-9] The formation of binary IL mixtures using common molecular solvents is one method of adjusting physicochemical characteristics. In addition to enhancing the characteristics of a medium for task-specific applications, binary mixtures of ILs significantly reduce costs. One of the most used molecular solvents for the binary combination with ILs is alcohol. The main reason for using alcohol is the presence of both hydrogen bond (H-bond) donor and acceptor site in the structure of alcohols as well as prospects of using numbers of alcohols with a variable number of -OH groups and/or alkyl groups.[9,10] Finding the molecular interactions between ILs and molecular solvents is the most important step since it will allow for the prediction of physicochemical parameters and the creation of optimal binary combinations. A useful tool for predicting the information about the covalent bonds existing in a molecule or in a mixture of molecules is infrared spectroscopy. Because the NIR spectrum gives resolvable peaks for various types of hydrogen bonds in a system, rather than the MIR spectrum, which gives a single broad peak for all hydrogen bonds in the system, NIR spectroscopy may be used to predict intermolecular and intramolecular hydrogen bonds more accurately than MIR spectroscopy. The properties of the combination can be easily comprehended after molecular-level interactions are fully established

Experimental

Materials

Propane-1-ol (CAS No. 71-23-8) was obtained from Lab-Scan Analytical Sciences, Thailand, and 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2mim]C_2H_5SO_4$) (CAS Nos. 342573-75-5) was purchased from Merck. None of the compounds were further purified before being employed.

Preparation of binary mixtures

The following compositions were used to create binary mixtures using gravimetric methods: 0 (pure propane-1-ol), 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1. (pure $[C_2mim]C_2H_5SO_4$.

Measurements and methods

An Anton Paar (DMA 4500 M) densimeter and an Anton Paar (Lovis 2000 ME) microviscometer, each automatically thermostated within 0.01 K by an integrated Peltier device, were used to measure densities and dynamic viscosities in the temperature range of 293.15 K to 333.15 K with a 5 K interval. The NIR spectra of the samples were recorded using a Fourier transform spectrophotometer (FTIR/NIR, PerkinElmer, USA) in absorbance mode with 64 scans for each sample in the range of 4000–10000 cm^{-1} at a resolution of 2 cm^{-1}. With two rectangular CaF_2 windows with curved edges, a susceptible liquid sampling cell was used to analyze the temperature-dependent NIR spectra of several materials (Specac model no. GS20522). A rectangular polytetrafluoroethylene (PTFE) spacer was used to maintain the route length at 0.02 mm.

Mathematical Calculations

OriginPro 2019b was used for statistical analysis and mathematical calculations. The unprocessed NIR data were baseline corrected and smoothed before processing. All mathematical and statistical operations were carried out for NIR data between 6000 and 7500 cm^{-1}.

Results and discussion

Densities, refractive indices, and viscosities of the binary mixtures

The densities, refractive indices, and viscosities of pure $[C_2mim]C_2H_5SO_4$ and propane-1-ol were measured along with their binary mixtures at a mole fraction of $[C_2mim]C_2H_5SO_4$] 0.1 to 0.9 keeping 0.1 mole fraction difference over the temperature range from 293.15 K to 333.15 K at 5 K interval.

For a binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol, density increases with increasing the mole fraction of $[C_2mim]C_2H_5SO_4$ At lower mole fraction of $[C_2mim]C_2H_5SO_4$, the system behaves like a very dilute ionic solution. As the mole fraction of $[C_2mim]C_2H_5SO_4$ increases the system gradually becomes concentrated ionic solution with more or less conspicuous ion pairing.[9,11] The changes in density with temperature for all three binary mixtures are depicted in Figure 1a. Density decreases with increasing temperature. The molecular movements (translational, rotational, and vibrational) of $[C_2mim]C_2H_5SO_4$ and alcohol molecules increase as the temperature rises. As a result, the volumes of binary mixtures and pure components increase, as a result, the densities decrease.

The refractive indices of the binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol increase with increasing mole fraction of $[C_2mim]C_2H_5SO_4$. The trend is similar to the density of the binary mixtures. The reason behind this is similar to that of density values. The change in refractive index with temperature is depicted in Figure 1b. The refractive indices decrease with increasing temperature for all the binary systems. With temperature, the molecular movements increase, thus the velocity of light increases hence refractive index decreases.

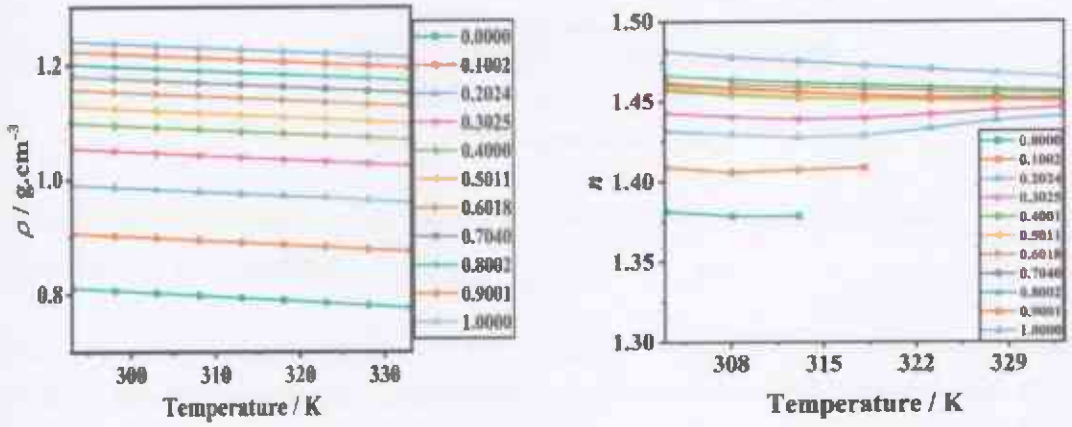


Figure 1. Variation of (a) density, (b) refractive index with the temperature at different mole fractions of $[C_2mim]C_2H_5SO_4$ (lines are predicted for visual aid only)

The viscosities of pure $[C_2mim]C_2H_5SO_4$ and propane-1-ol at 293.15 K are 96.0240 mPa.s and 2.2996 mPa.s respectively (Figure 2). $[C_2mim]C_2H_5SO_4$ has a greater viscosity, which indicates stronger intermolecular association forces. The primary pathways of intermolecular association for $[C_2mim]C_2H_5SO_4$ are coulombic interaction and intermolecular hydrogen bonding. Hydrogen bonds are the dominant contributor of intermolecular force for alcohols. As the mole fraction of propane-1-ol rises, a binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol becomes less viscous. The solvation of the ions by propane-1-ol, which is the cause of this behavior, lowers the strong coulombic attraction between the ions in $[C_2mim]C_2H_5SO_4$.

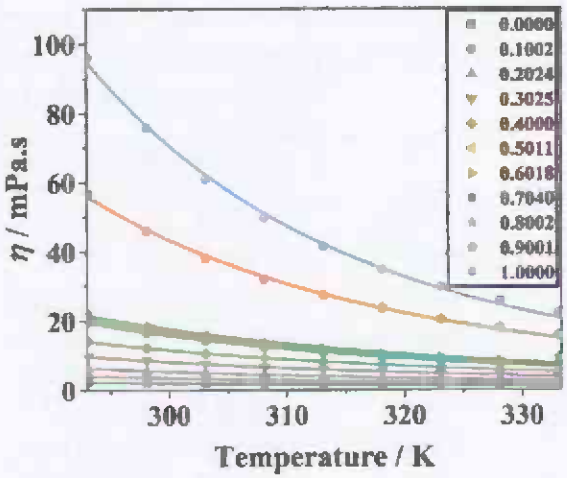


Figure 2. Variation of viscosity with temperature at different mole fraction of $[C_2mim]C_2H_5SO_4$ (lines are predicted by VFT equation).

As the temperature increases, the dynamic viscosity decreases, indicating a gradual drop of structural relaxation. At lower temperatures, the temperature dependence of viscosity is more prominent. Standard models can describe the temperature dependencies of binary mixtures. The most popular model is the two-parameter Arrhenius one. Among the three-parameter models, the Vogel–Fulcher–Tammann (VFT) and modified VFT (mVFT) equations (eqns 1-3) are also employed to fit the temperature dependence of viscosity of the three binary mixtures as well as their pure components.

$$\eta = A.e^{\frac{-B}{RT}} \quad \text{.....(1)}$$

$$\eta = A.e^{\frac{-B}{T-T_0}} \quad \text{.....(2)}$$

$$\log \eta\,(T) = \log \eta_0 + \frac{(12-\log \eta_0)^2}{m\left(\frac{T}{T_g}-1\right)+(12-\log \eta_0)} \quad \text{..... (3)}$$

The fitting parameters for binary mixtures and their pure components are estimated from each equation and listed in Table 1 along with their correlation coefficient values (R^2).

Table 1. Fitted parameters *(A, B, T_0)* and corresponding fitting coefficient *(R^2)* of the various equations for the viscosities of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propanol-1 as well as of their pure components at different temperatures.

Equation	Mole fraction of $[C_2mim]C_2H_5SO_4$	*A*	*B*	T_0	R^2
Arrhenius	0.0000	1.19E-06	-18437.3	-	1.00000
	0.1002	2.78E-06	-17733.7	-	1.00000
	0.2024	2.95E-06	-18689.9	-	1.00000
	0.3025	3.12E-06	-19596.2	-	1.00000
	0.4000	2.89E-06	-20671.7	-	1.00000
	0.5011	1.09E-06	-24097	-	1.00000
	0.6018	3.08E-06	-21456.4	-	1.00000
	0.704	2.18E-06	-22159	-	1.00000
	0.8002	3.07E-06	-21570.6	-	1.00000
	0.9001	8.94E-07	-26906.2	-	1.00000
	1.0000	2.86E-07	-30975.1	-	1.00000
VFT	0.0000	-2.92348	963.07045	12.58222	0.99998
	0.1002	-1.80858	521.50991	77.17513	0.99996
	0.2024	-1.55576	466.42281	95.38703	1.00000
	0.3025	-2.06326	768.20013	41.29891	0.99999
	0.4000	-1.02986	347.93836	133.3624	0.99999
	0.5011	-0.74568	262.04063	167.3227	0.99805
	0.6018	-0.78961	308.89519	146.4351	0.99991
	0.704	-0.53245	215.31811	175.1653	0.99993
	0.8002	0.30284	58.2058	237.3679	0.98292
	0.9001	-0.4347	255.7822	176.202	0.99993
	1.0000	-0.38121	256.99713	184.4203	0.99999
mVFT	0.0000	-7.08431	112.73167	16.82047	1.00000
	0.1002	-4.37364	147.11866	30.32588	1.00000
	0.2024	-3.55947	164.76345	37.48333	1.00000
	0.3025	-4.7502	146.90533	23.30608	1.00000
	0.4000	-2.42859	188.07111	47.65671	1.00000
	0.5011	-1.16494	220.39732	83.71358	1.00000
	0.6018	-1.66307	200.6623	56.64393	1.00000
	0.704	-1.35406	210.26868	70.62928	1.00000
	0.8002	1.05227	258.72461	354.34723	0.99998
	0.9001	-1.26819	218.10942	57.95974	1.00000
	1.0000	11.87183	14823.7908	0.13302	0.99997

Excess thermodynamic properties

The values of excess molar volumes, refractive index deviations, dynamic viscosity deviations and excess molar Gibbs free energy of activation for viscous flow are calculated by eqns 4-7.

$$V_m^E = \frac{\sum x_i M_i}{\rho_{mix}} - \sum_{i=2}^{n} \frac{x_i M_i}{\rho_i} \quad \text{.....(4)}$$

$$\Delta\eta = \eta_{experimental} - \sum x_i \eta_i \quad \text{.....(5)}$$

$$\Delta n = n_{experimental} - \sum x_i n_i \quad \text{.....(6)}$$

$$\Delta G^{*E} = RT[\ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1 \ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right) \quad \text{.....(7)}$$

The variation in excess molar volume of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol with mole fraction of $[C_2mim]C_2H_5SO_4$ at different temperatures are shown in Figure 3.

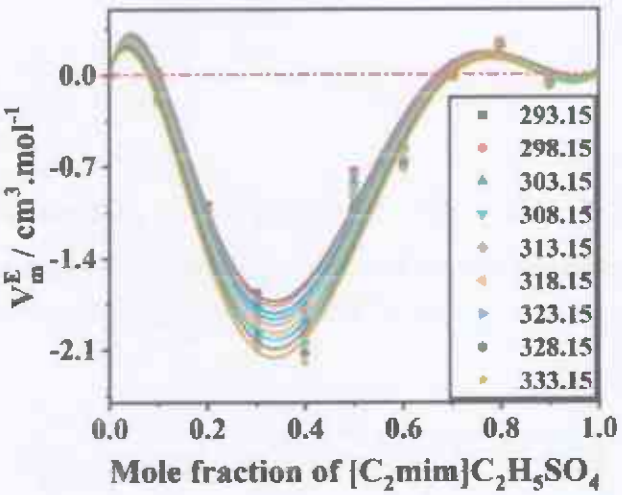


Figure 3. Excess molar volumes of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of mole fraction of $[C_2mim]C_2H_5SO_4$ at various temperatures (Lines are predicted by Redlich-Kister type polynomial equation).

With the exception of 0.7 and 0.8 $[C_2mim]C_2H_5SO_4$ mole fraction, the values of excess molar volume are negative across the whole composition range. In contrast to the individual homo-molecular associations between the molecules, this suggests contraction of volume, which denotes a strong hetero-molecular association between $[C_2mim]C_2H_5SO_4$ and propane-1-ol. In other words, solvation of each ion by polar propane-1-ol solvent by ion-dipole interaction between them causes the ion-ion interactions between positive 1-ethyl-3- methylimidazolium ions and negative ethylsulfate ions to weaken. The large value of excess molar volume is due to contraction owing to free volume differences between unlike molecules and also owing to the hydrogen bond formation between $[C_2mim]C_2H_5SO_4$ and propane-1-ol molecules. The significant negative value at or near 0.4 IL mole fraction suggests that hydrogen bonds, particularly at this composition, predominate between $[C_2mim]C_2H_5SO_4$ and propane-1-ol molecules. However, for $[C_2mim]C_2H_5SO_4$ mole fractions of 0.7 and 0.8, the system has a greater intermolecular void because there are fewer propane-1-ol molecules present. As a result, excess molar volume values at these mole fractions are positive. The values of excess molar volume are progressively

negative as the temperature rises. The competition for packing efficiency and the hydrogen bonding interaction in the binary mixtures are to account for the variation in excess molar volume with temperature. As temperature increases, the stronger intermolecular hydrogen bonding interactions typically deteriorate. This trend is consistent with increasing excess molar volume values. However, as the temperature rises, the packing efficiency between the asymmetric positive and negative ions improves in comparison to similar molecules, which causes the excess molar volume to decrease. Heteromolecular hydrogen bonding interactions and overall packing efficiency are in competition with one another. The data points of excess molar volumes for binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are fitted with the Redlich-Kister type polynomial expression,

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where, Y^E is the excess properties, n is the polynomial order, x_1 and x_2 are the mole fractions of $[C_2mim]C_2H_5SO_4$ and propane-1-ol respectively. A_0 –A_n are Redlich-Kister parameters calculated by the least-squares type algorithm. The coefficients of the Redlich-Kister type expression are tabulated in Table 2.

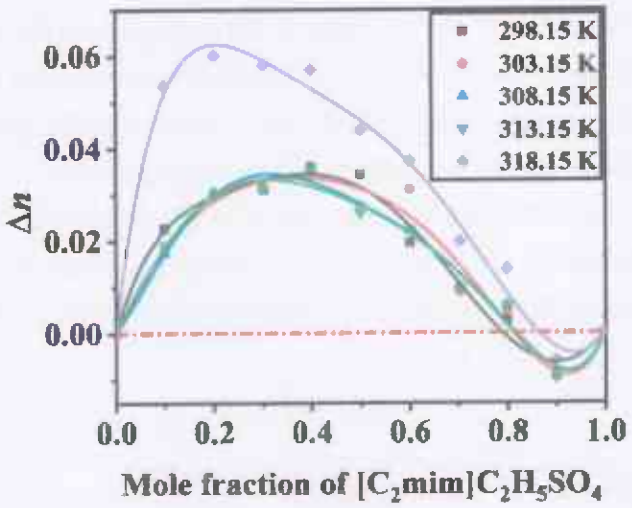


Figure 4. Refractive index deviations of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of mole fraction of $[C_2mim]C_2H_5SO_4$ at various temperatures (Lines are predicted by Redlich-Kister type polynomial equation).

As shown in Figure 4, with the exception of 0.9 $[C_2mim]C_2H_5SO_4$ mole fraction, the refractive index deviations of the binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are all positive over the whole composition range, and the deviations rise to a more positive value with rising temperature. The data

points of refractive index deviation for binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are fitted in equation (1). The coefficients of the Redlich-Kister type expression are tabulated in Table 2.

Figure 5 reveals that the values of were asymmetrical and all negative across the entire concentration range at each temperature for the binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol. The viscosity deviation values decrease till the mole fraction of $[C_2mim]C_2H_5SO_4$ approaches 0.80 as the composition of $[C_2mim]C_2H_5SO_4$ increases. The value eventually becomes zero. The dynamic viscosity deviation values decrease as the binary mixture's temperature increases. The viscosity of a binary liquid mixture is significantly influenced by the molecular composition of both liquids. As a result, in addition to molecular interactions, the size and shape of both types of species also influence viscosity. Intermolecular interactions and molecular sizes and shapes are two factors that are in competition with one another. Viscosity deviation values that are negative imply that intermolecular interactions predominate in this scenario. The negative values of additionally show that the interaction between positive 1-ethyl-3-methylimidazolium cations and ethylsulfate anions decreases when propane-1-ol is introduced. Because propane-1-ol molecules may dissolve both cations and anions, this is the case. Meanwhile, the negative values for binary mixtures reveal that the associations formed between pure components have substantially higher viscosities than molecules that are dissimilar to them. Positive viscosity deviation may also point to the dominance of dispersion forces, particularly in mixtures with various molecular sizes. On the other hand, the values of viscosity deviation increase as more propane-1-ol is introduced. This is because $[C_2mim]C_2H_5SO_4$ and propane-1-ol interact via a hydrogen bonding interaction that is stronger in the combination with a high propane-1-ol content than in the mixture with a low propane-1-ol level. Strong self-association and dispersion forces, as well as a relatively weak hydrogen bonding contact between the molecules of $[C_2mim]C_2H_5SO_4$ and propane-1-ol, may be responsible for the negative viscosity deviations exhibited in Figure 5. The data points of viscosity deviation for binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are fitted in eqn (1).

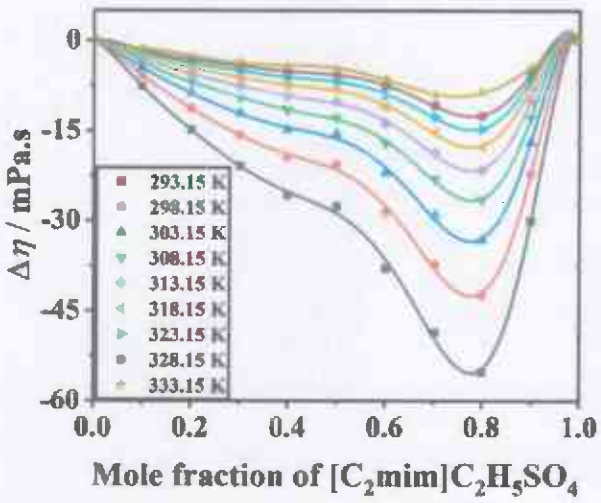


Figure 5. Dynamic viscosity deviations of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of mole fraction of $[C_2mim]C_2H_5SO_4$ at various temperatures (Lines are predicted by Redlich-Kister type polynomial equation).

As shown in Figure 6, at all temperatures between 293.15 K and 333.15 K, the excess molar Gibbs free energy of the binary mixture is positive over the composition range of 0.1 to 0.6 mole fraction of $[C_2mim]C_2H_5SO_4$ and negative at higher $[C_2mim]C_2H_5SO_4$ content. The value of ΔG^{*E} offers a reliable criterion for determining whether or not new interactions between distinct molecules are present in a binary mixing system.[12] The $[C_2mim]C_2H_5SO_4$ and propane-1-ol exhibit more heteromolecular hydrogen bonds than related molecules, according to the significantly positive value of ΔG^{*E}, which results in atypical interactions in the binary system. The decrease in heteromolecular interaction in the system is shown by the negative value of ΔG^{*E}. Because homo molecular association between $[C_2mim]C_2H_5SO_4$ predominates when the amount of propane-1-ol in the system falls, this is due to a shortage of propane-1-ol in the system. The data points of excess molar Gibbs free energy for binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are fitted in eqn 1. The coefficients of the Redlich-Kister type expression are tabulated in Table 2.

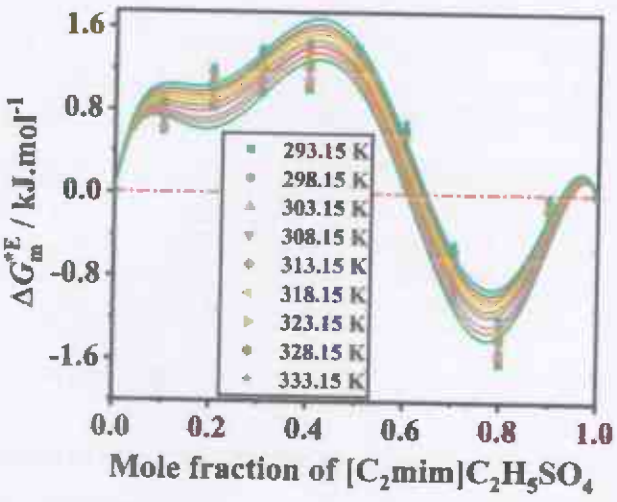


Figure 6. Excess molar Gibbs free energy of activation for viscous flow of binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of mole fraction of $[C_2mim]C_2H_5SO_4$ at various temperatures (Lines are predicted by Redlich-Kister type polynomial equation).

Table 2. Coefficients of Redlich-Kister equation (A_i) for binary mixtures of $[C_2mim]C_2H_5SO_4$ and propanol-1 at different temperatures.

T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	R^2
				V_m^E(cm^3.mol^{-1})				
293.15	-3.67573	-13.6617	-13.6349	19.16188	76.37914	3.95875	-72.0475	0.95723
298.15	-3.77803	-13.8429	-13.8195	19.34015	77.49962	3.91038	-73.6198	0.95774
303.15	-3.98791	-14.0411	-13.5719	19.50488	76.65212	3.7937	-72.9794	0.96021
308.15	-4.11895	-14.2359	-13.8163	19.45133	77.89731	4.3225	-74.3117	0.96048
313.15	-4.2744	-14.4921	-13.4587	19.52909	77.20956	4.29145	-74.0846	0.96259
318.15	-4.44862	-14.7423	-13.8493	19.49089	79.29652	4.49284	-76.8571	0.96337
323.15	-4.63912	-14.8028	-13.4781	18.47698	77.61987	5.9422	-75.3449	0.96758
328.15	-4.81532	-15.2928	-13.8451	19.34212	80.34693	5.49324	-78.9986	0.96605
333.15	-4.98257	-15.6614	-14.6643	19.51266	83.89891	5.31138	-82.9918	0.96511
				$\Delta\eta$ (mPa.s)				
293.15	-115.214	93.47562	-321.084	597.3032	-111.291	-777.56	595.5749	0.99582
298.15	-86.4142	70.35996	-254.507	480.4729	-91.7784	-640.34	495.7045	0.99614
303.15	-65.6201	53.10361	-213.189	397.7839	-51.1696	-539.13	393.6518	0.99596
308.15	-52.9512	40.49787	-140.12	332.7821	-171.359	-458.24	460.4401	0.99819
313.15	-42.2807	32.77192	-116.871	278.8701	-145.926	-392.37	399.1508	0.99779
318.15	-33.7643	25.73149	-98.5557	240.6557	-126.198	-344.65	350.5818	0.99787
323.15	-27.6972	20.92421	-84.7396	205.3579	-103.143	-292.65	293.0598	0.99824
328.15	-23.0709	17.15643	-74.4042	179.1118	-84.3606	-256.38	251.3379	0.9984
333.15	-18.5117	22.21166	-98.9173	66.02486	177.4032	-105.11	-89.5089	0.99577
				ΔG^{*E}(kJ.mol^{-1})				
293.15	4.10088	7.44364	-33.6435	34.94663	39.74128	-57.498	10.17727	0.98302
298.15	4.31123	7.42433	-32.0787	35.02599	34.89336	-57.760	14.76694	0.98651
303.15	4.60148	7.20485	-32.0523	35.84447	35.14508	-58.668	14.69977	0.98706
308.15	4.42414	7.00472	-24.2129	36.10544	7.05686	-58.510	42.26003	0.99632
313.15	4.63074	7.12997	-23.6629	35.27703	5.67051	-57.602	44.25278	0.99613
318.15	4.89082	6.98976	-23.3151	35.92159	4.71139	-58.473	45.93556	0.99697

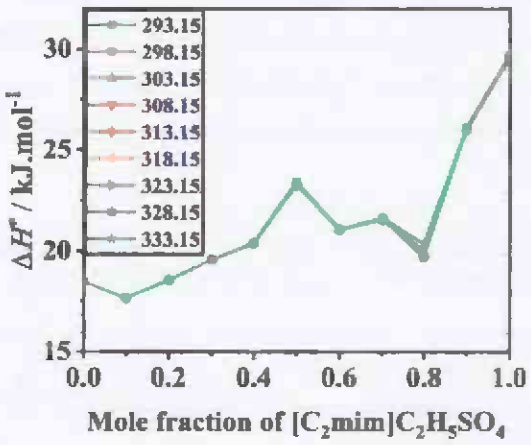
T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	R^2
323.15	5.1018	6.86678	-22.8972	35.97292	4.12817	-57.625	45.95874	0.99769
328.15	5.31037	6.71775	-23.3144	36.33257	6.61615	-57.561	43.67872	0.9984
333.15	5.74108	9.34624	-34.5694	6.37686	90.27779	-17.452	-59.719	0.98552
				Δn				
298.15	0.12629	0.10997	-0.15593	0.13631	0.15072	-	-	0.96741
303.15	0.12484	0.07917	-0.05244	0.16499	-0.09235	-	-	0.93122
308.15	0.11222	0.11128	0.03831	0.09077	-0.20508	-	-	0.96708
313.15	0.11026	0.10113	0.02382	0.12174	-0.15816	-	-	0.96108
318.15	0.18452	0.15272	0.06511	0.35445	0.10618	-	-	0.98044

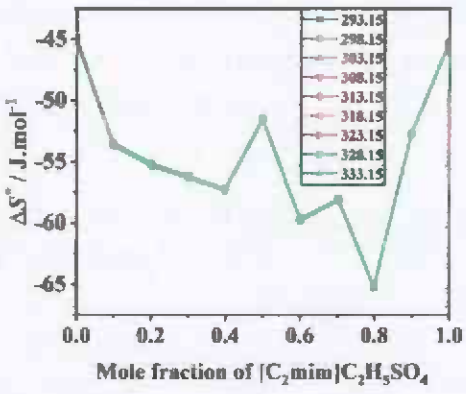
Thermodynamic activation parameters

The molar Gibbs free energy of activation of the viscous flow is calculated from the Eyring equation. The enthalpy and entropy of viscous flow are calculated using the least square fit method and enthalpy of activation for viscous flow is calculated from the values of ΔG^* and ΔS^* from the following equation,

$$\Delta G^* = \Delta H^* + T\Delta S^* \quad \text{.....(9)}$$

All the values of the activation parameters for the binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol are summarized in Table 3 respectively along with R^2 values. The variation in thermodynamic parameters for the viscous flow of the binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of temperature and mole fraction of $[C_2mim]C_2H_5SO_4$ are depicted in Figure 7.





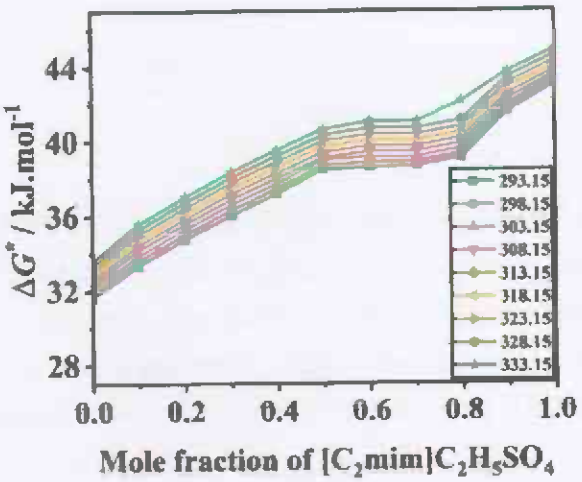


Figure 7. Variation of (a) enthalpy, (b) entropy, and (c) Gibbs free energy of activation for the viscous flow of the binary mixtures of $[C_2mim]C_2H_5SO_4$ and propane-1-ol as a function of mole fraction of $[C_2mim]C_2H_5SO_4$ (lines are for visual aid only).

According to Figure 7, all of the values of ΔG^* are positive across the whole composition range. The system is not spontaneous if ΔG^* has a positive value. Energy is absorbed by molecules to carry out useful work. The value of G*increases with increasing mole fraction of $[C_2mim]C_2H_5SO_4$, and the rate of change of ΔG^* is larger at lower mole fraction of $[C_2mim]C_2H_5SO_4$ up to 0.5 mole fraction before decreasing up to 0.8 mole fraction, and again the rate increases as mole fraction of $[C_2mim]C_2H_5SO_4$ increases. The ability of molecules and/or ions to go into a structural hole and the capacity to form another are determined by the ΔG^*, which controls the fluid flow. Increased intermolecular attraction forces between dissimilar molecules are indicated by an increase in the ΔG^*value.

Table 3. Activation enthalpy and activation entropy of viscous flow of the binary system of $[C_2mim]C_2H_5SO_4$ and propanol-1 in the temperature range from 293.15 K to 333.15 K.

Mole fraction of $[C_2mim]C_2H_5SO_4$	ΔH^* (kJ.mol^{-1})	ΔS^* (J.mol^{-1})	R^2
0.0000	18.45567	-44.8492	0.9999
0.1002	17.63868	-53.4826	0.9998
0.2024	18.53404	-55.1631	0.9997
0.3025	19.53695	-56.204	0.9999
0.4000	20.35728	-57.2107	0.9992
0.5011	23.31531	-51.4726	0.9953
0.6018	21.03239	-59.6675	0.9985
0.7040	21.55786	-58.0527	0.9978
0.8002	19.83379	-65.1519	0.9364

0.9001	26.02827	-52.6925	0.9979
1.0000	29.60797	-45.3232	0.9968

For a binary mixture of $[C_2mim]C_2H_5SO_4$ and propane-1-ol, the entropy of activation of viscous flow is negative across the composition range. Negative value of entropy indicated that species in the activated state for viscous flow are more ordered than they were in the initial state.[13] The maximum entropy value observed for pure components suggests that they are more organized than binary mixtures. Entropy is measured at its lowest point at 0.8 $[C_2mim]C_2H_5SO_4$ mole fraction.

The fact that $[C_2mim]C_2H_5SO_4$ is mixed with propane-1-ol by an endothermic process is supported by the positive values of ΔH^* across the entire composition range at each temperature. The values of ΔH^* increase up to the mole fraction of $[C_2mim]C_2H_5SO_4$ and subsequently decrease with subsequent mole fraction increases up to 0.8 before increasing once again with $[C_2mim]C_2H_5SO_4$ content increases. The inclusion of a larger molecule inside the smaller propane-1-ol molecules is what causes the value of ΔH^* to increase. The mobility of the molecule is sterically hindered by these larger molecules. Therefore, making the holes for viscous flow requires more energy. However, the system starts to exhibit some disorder when the mole fraction exceeds 0.5, as evidenced by the entropy, and some holes begin to appear without using any more energy from the system, which lowers the ΔH^* values up to 0.8 mole fraction. By considering the aforementioned thermodynamic activation parameter, it follows that for smaller mole fractions of $[C_2mim]C_2H_5SO_4$ up to 0.5, the intermolecular interaction between similar propane-1-ol molecules reduces and the solvation of the ions in $[C_2mim]C_2H_5SO_4$ by propane-1-ol takes place. However, as additional $[C_2mim]C_2H_5SO_4$ is added, the system produces more ions and cannot be solvated by propane-1-ol because there aren't enough molecules of the solvent in the mixture to do so.

Conclusions

Physicochemical properties of the binary mixtures of [EMIM][ES] and alcohols change markedly from the pure components. The densities and viscosities of the binary mixtures of [EMIM][ES] and propane-1-ol increase with increasing mole fraction of [EMIM][ES]. With temperature, both the densities and viscosities of the binary system decrease. The temperature dependence of the viscosities of the binary mixtures of [EMIM][ES] and propane-1-ol gives good fit at Arrhenius equation. The excess molar volume of the binary mixtures of [EMIM][ES] and propane-1-ol are all negative except higher mole fraction of [EMIM][ES] indicates the more compactness of the binary system compared to the pure components. The viscosity deviation of the binary mixture of [EMIM][ES] and propane-1-ol are all negative and becomes more negative at higher mole fraction of [EMIM][ES] and also with increasing

temperature. The excess molar Gibbs free energy of activation of the viscous flow are positive at lower [EMIM][ES] content up to 0.6 [EMIM][ES] mole fraction and negative for the rest. The values of Gibbs free energy of activation for viscous flow are all positive over the whole composition range indicating the non-spontaneity of the viscous flow and are increasing as mole fraction of [EMIM][ES] increases.

Ongoing work

The near infrared (NIR) spectra will be measured for all the binary mixtures prepared along with their pure components. From the raw NIR 2D correlation spectra and principal component analyses will be done. Each of the data will be used to predict molecular level interactions.

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Dr. Md. Abu Bin Hasan Susan
Professor
Department of Chemistry
University of Dhaka
Dhaka-1000, Bangladesh