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Densities and Dynamic Viscosities of Methyltriphenylphosphonium Bromide-based Deep Eutectic Solvents and Excess Properties of Their Pseudo-binary Mixtures with Ethanol

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Abstract – This study investigates the effects of ethanol mole fraction and temperature on the density and dynamic viscosity of pseudobinary mixtures containing ethanol and deep eutectic solvents (DESs) composed of methyltriphenylphosphonium bromide (MTPPB) and ethylene glycol (EG). DESs were prepared with fixed mole ratios of 1:6, 1:8, and 1:10 (MTPPB:EG). The mole fraction of ethanol varied from 0.1998 to 0.9000, and the temperature ranged from 293.15 K to 323.15 K. Experimental data were correlated using empirical equations to assess the effects of composition and temperature on the mixtures' properties. Density and dynamic viscosity measurements demonstrated that both properties decrease with increasing temperature and ethanol content. Excess molar volume and excess viscosity calculations revealed negative deviations from ideal solution behavior, indicating strong molecular interactions. These deviations were attributed to the interstitial effect and hydrogen bonding influenced by the mole fraction of the components. The study highlights significant differences in molecular packing among the DES1, DES2, and DES3 systems, which were evident in both density and viscosity trends. The findings provide valuable insights into the design and application of DES-ethanol mixtures in environmentally friendly processes, showcasing their potential in various industrial applications.

Key words: Deep eutectic solvent, Dynamic viscosity, Excess molar volume, Correlation

1. Introduction

Since the term deep eutectic solvents (DESs) was coined by Abbott et al. [1], research on DESs has expanded rapidly, particularly towards environmentally friendly process development [2-4]. DESs exhibit superior properties such as low vapor pressure, high thermal stability, excellent acid gas solubility, and customizable attributes. Moreover, DESs are abundant in nature, making them cost-effective and simple to prepare from a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at a fixed mole ratio. Among many HBDs, polyols like glycol and ethylene glycol are widely used, with ethylene glycol being especially common due to its simplicity as the smallest diol chemical [5]. Phosphonium salts, particularly methyltriphenylphosphonium bromide (MTPPB) are applied as HBAs in DES preparation because they provide high affinity with carbon dioxide [6] and hold significant potential for various other applications [7-8].

Recent research has shifted towards DES mixtures formed by adding cosolvents. The addition of cosolvents such as water and alcohols significantly influences key properties of DESs, including density and viscosity, and carbon dioxide solubility, thereby expanding their potential industrial applications [9-11]. The use of alcohols as cosolvents has been extensively investigated [12-15]. Alcohol presence notably affects the density and viscosity of the mixture, with both physical properties decreasing as the amount of cosolvent increases at constant temperature and pressure. For example, Brennecke and colleagues [14] observed a density decrease from 1.1195 g×cm^{-3} to 0.8095 g×cm^{-3} in a choline chloride and ethylene glycol-based DES upon adding 1-butanol at 293.15 K. Due to their typically high viscosity, DESs are often diluted with dispersing agents in extraction applications [4,16]. In addition, binary systems made of phosphonium–based compounds and short-chain alcohols have properties that make them promising candidates for use as working fluids in absorption refrigeration technology [17].

This study aimed to evaluate the effects of ethanol mole fraction and temperature on the density and dynamic viscosity of pseudobinary mixtures containing ethanol and DESs prepared using methyltriphenylphosphonium bromide (MTPPB) and ethylene glycol (EG) at mole ratios of 1:6, 1:8 and 1:10. The ethanol mole fraction in the pseudobinary mixtures ranged from 0.1998 to 0.9000, with temperatures varying from 293.15 K to 323.15 K at 5 K intervals under atmospheric pressure. The experimental data were analyzed using two different equations to correlate temperature and composition. Furthermore, the solution behavior of the pseudobinary mixtures was examined in terms of excess molar volume and excess viscosity with temperature, composition, and the properties of pure components.

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2. Experimental Section

2-1. Chemicals and preparation of the DESs

Ethanol, methyltriphenylphosphonium bromide (MTPPB), and ethylene glycol (EG) were purchased from Merck Inc. and utilized without further purification, as shown in Table 1. Chemical masses were measured using an analytic balance with an uncertainty of 0.2 mg. The DESs were prepared using EG as an HBD and MTPPB as HBA with a fixed mole ratio above 350 K for several hours. The standard uncertainty of the mole ratio between HBD and HBA is 0.001. DES1, DES2, and DES3 were formulated with EG and MTPPB at mole ratios of 6:1, 8:1, and 10:1, respectively. The water content in DESs was determined using a Karl-Fisher titrator (Model V20, Mettler Toledo Inc.), with results detailed in Table 2, showing a water content of less than 0.27 wt% water for all DESs.

2-2. Measurements of the physical properties

The density (ρ) and dynamic viscosity (η) of the prepared pseudobinary mixtures were measured using an Anton Paar DMA 5000 M density meter and Lovis 2000 viscometer, with accuracies of 5×10^{-6} $g{\cdot}cm^{-3}$ and 0.5%, respectively. The density meter underwent periodic calibration using ultra-pure water and dry air. Viscometry was conducted using a steel ball with a diameter of 1.5 mm and a density of 7.689 $g{\cdot}cm^{-3}$, along with a capillary Lovis apparatus with a diameter of 1.8 mm, over a temperature range of 293.15 to 323.15 K with 5 K increments, at atmospheric pressure. Calibration of the viscometer was performed using a viscosity reference standard solution (N26, Product No. 100046) purchased from Anton Paar Inc. (Seoul, S. Korea), ensuring a % deviation of less than 4% in the calibration procedure. The relative standard uncertainty of the density and viscosity measurements were 0.005 and 0.02, respectively. The densities and viscosities of the three binary solutions comprising DES and ethanol were measured over a DES mole fraction range of 0.1998 to 0.9000 and a temperature range from 293.15 to 323.15 K. Special caution is required when preparing pseudobinary mixtures due to the high volatility of ethanol. The density and dynamic viscosity values for pure ethanol [18] and prepared DES [19] were reported and utilized for subsequent calculations.

3. Results and Discussion

3-1. Density

Tables 3-5 display the experimental density values of three pseudobinary mixtures of DES and ethanol. As anticipated, the densities of these mixtures decrease with rising temperature and increasing mole fraction of ethanol. The trend is consistent across all

Table 1. Chemicals used in this study

Compound	CAS-No	Supplier	Purity (%)
Ethanol	64-17-5	Merck Inc.	≥ 99.5
Methyltriphenylphosphonium Bromide (MTPPB)	1779-49-3	Merck Inc.	98
Ethylene glycol (EG)	107-21-1	Merck Inc.	≥ 99

Table 2. List of DESs prepared in this study

DESs	HBD	HBA	Mole ratio	Water Content (wt%)	MDES ($g{\cdot}mol^{-1}$)
DES1	Ethylene glycol	MTPPB	6:1	0.27	104.24
DES2	Ethylene glycol	MTPPB	8:1	0.26	94.87
DES3	Ethylene glycol	MTPPB	10:1	0.23	88.90

Table 3. Experimental density, ρ ($g{\cdot}cm^{-3}$), of the pseudobinary mixture DES1 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.1998	0.9203	0.9159	0.9114	0.9068	0.9021	0.8974	0.8926
0.3999	1.0164	1.0124	1.0085	1.0045	1.0006	0.9966	0.9926
0.5997	1.0909	1.0872	1.0833	1.0793	1.0750	1.0707	1.0666
0.7000	1.1298	1.1260	1.1223	1.1185	1.1148	1.1110	1.1072
0.7991	1.1630	1.1593	1.1556	1.1519	1.1482	1.1445	1.1407
0.9000	1.1935	1.1899	1.1863	1.1826	1.1790	1.1754	1.1717

The standard uncertainties are $u(T) = 0.01$ K and $u(x_1) = 0.0002$ and relative standard uncertainty of density is $u_r(\rho) = 0.005$.

Table 4. Experimental density, ρ ($g{\cdot}cm^{-3}$), of the pseudobinary mixture DES2 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.1999	0.9146	0.9105	0.9064	0.9022	0.8980	0.8938	0.8895
0.3999	1.0033	0.9993	0.9954	0.9914	0.9874	0.9834	0.9794
0.5000	1.0423	1.0384	1.0345	1.0306	1.0267	1.0228	1.0188
0.5999	1.0784	1.0746	1.0707	1.0669	1.0631	1.0592	1.0553
0.7999	1.1405	1.1370	1.1336	1.1302	1.1267	1.1231	1.1195

The standard uncertainties are $u(T) = 0.01$ K and $u(x_1) = 0.0002$ and relative standard uncertainty of density is $u_r(\rho) = 0.005$.

Table 5. Experimental density, ρ (g·cm^{-3}), of the pseudobinary mixture DES3 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.2001	0.9066	0.9025	0.8984	0.8942	0.8900	0.8858	0.8815
0.4002	0.9922	0.9883	0.9843	0.9804	0.9764	0.9723	0.9683
0.5002	1.0301	1.0263	1.0224	1.0185	1.0146	1.1061	1.0066
0.6002	1.0656	1.0618	1.0579	1.0541	1.0503	1.0464	1.0425
0.7001	1.0987	1.0950	1.0912	1.0875	1.0837	1.0799	1.0760
0.8001	1.1289	1.1252	1.1215	1.1178	1.1141	1.1103	1.1066

The standard uncertainties are $u(T)$ = 0.01 K and $u(x_1)$ = 0.0002 and relative standard uncertainty of density is $u_r(\rho)$ = 0.005

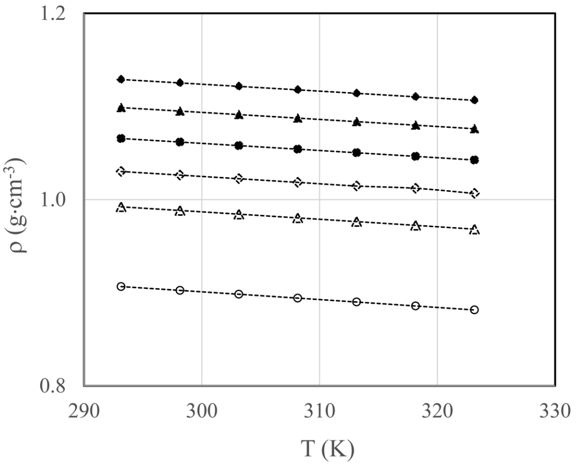

Fig. 1. The density of pseudobinary solution DES3 (1) and ethanol (2) at different mole fraction of the DES3 (○: 0.2001, △: 0.4002: ◇: 0.5002: ●: 0.6002: ▲: 0.7001: ◆: 0.8001). The solid line represents a fit to the Eq. (1).

pseudobinary systems studied. For illustration, Fig. 1 presents the experimental density data for the pseudobinary mixture of DES3 and ethanol within the temperature range of 293.15 K to 323.15 K. Considering the linear relationship with temperature observed in pseudobinary mixture, the experimental results were fitted using the following equations [13,18,20].

$$\rho = \alpha + \beta T \tag{1}$$

$$\alpha = \sum_{i=1}^{5} a_i (x_1)^{i-1} \tag{2}$$

$$\beta = \sum_{i=1}^{5} b_i (x_1)^{i-1} \tag{3}$$

where r represents density in g·cm^{-3}, T is the absolute temperature in K, a_i and b$_i$ are the regression parameters, and x_1 is the mole fraction of DES. The regression parameters for each binary system were determined using the multiple linear regression method and are listed in Table 6, along with the average absolute relative deviations (AARDs) defined in Eq. (4).

$$AARD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\rho_i^{cal} - \rho_i^{exp}}{\rho_i^{exp}}\right| \tag{4}$$

where n is the number of data points, and ρ_i^{cal} and ρ_i^{exp} represent the calculated density and experimental density, respectively. It is evident that the experimental density data for all three pseudobinary mixture systems, studied across the entire concentration range and within the temperature range of 293.15 to 323.15 K, can be satisfactorily correlated.

Table 6. Parameters for the correlation of Eqs. (2) and (3)

	DES1+ethanol	DES2+ethanol	DES3+ethanol
a_1	1.6244E-01	1.8788E-01	2.4404E-01
a_2	1.0838E+00	9.7827E-01	8.6628E-01
a_3	-1.2400E+00	-1.3423E+00	-1.2106E+00
a_4	9.7753E-01	1.1983E+00	1.0125E+00
a_5	-1.3418E+00	-1.2255E+00	-1.3215E+00
b_1	9.5922E-04	1.0375E-03	9.0720E-04
b_2	1.0107E-03	9.7190E-04	1.1746E-03
b_3	1.1661E-03	9.7501E-04	1.0491E-03
b_4	1.0274E-03	1.1150E-03	1.1123E-03
b_5	9.2015E-04	1.2600E-03	9.1247E-04
AARD*	0.1249	0.2207	0.1380

*AARD: average absolute relative deviation

3-2. Excess molar volume for the pseudobinary mixture

To investigate the interaction between DES and ethanol, the excess molar volume, V^E, was determined from experimental density using Eq. (5):

$$V^E = V_m - (x_1V_1 + x_2V_2) = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \tag{5}$$

where V_m is the molar volume of the pseudobinary mixture, x_1 and x_2 are the mole fractions of DES and ethanol, respectively, V_1 and V_2 are the molar volume of DES and ethanol, respectively, and r_1, r_2, and r_m are the densities of DES, ethanol, and the pseudobinary mixture, respectively. M_1 and M_2 are the molecular weight of DES and ethanol, respectively. The molecular weight of the DES prepared in this study was calculated from its individual components of MTPPB and ethylene glycol using Eq. (6):

$$M_1 = x_{MTPPB}M_{MTPPB} + x_{EG}M_{EG} \tag{6}$$

Fig. 2 depicts the excess molar volumes of the pseudobinary mixture as a function of the mole fraction of DES1 at different temperatures. Similar behavior has been observed by Mjalli and Ahmad [21] for the glucose and choline chloride based DES and water pseudobinary mixture. However, as evident in Figs. 3 and 4, the excess molar volumes of DES2 and DES3, respectively, exhibit different observations, resembling other pseudobinary systems [18, 22-23]. Across all temperature studies, while the DES1 pseudobinary

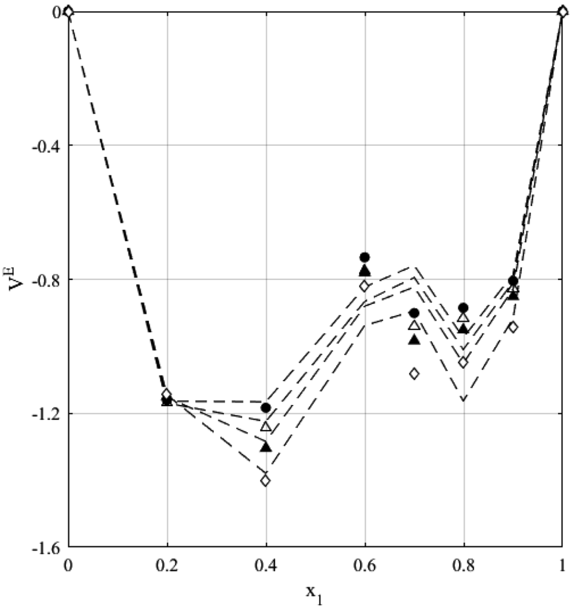

Fig. 2. V^E versus mole fraction of DES1 (x_1) for the pseudobinary mixture of DES1 and ethanol at different temperatures (●: 293.15 K; △: 303.15 K; ▲: 313.15 K; ◇: 323.15 K). The solid lines represent a fit to the Eq. (7).

system reached maximum molar excess volume deviation at a DES1 mole fraction of about 0.4, DES2 and DES3 systems showed a maximum value at DES mole fraction of about 0.2. Similar trend in V^E distribution were found by other systems [5,14,23]. The results indicate that the excess molar volumes are negative for each system studied at any temperature and mole fraction of DES, indicating a negative deviation from the ideal solution behavior and a strong interaction between DES and ethanol.

As reported by Kim and Park [24], the hydrogen bonding formed by the interaction of the hydroxyl group in ethanol with MTPPB is associated with an increase in V^E in the system. The effect of DES, the molar ratio of HBA and HBD, on the excess molar volume is significant. The absolute values of V^E for DES2 and ethanol pseudobinary mixture were slightly lower than those for DES1 and DES3 counterparts, as shown in Figs. 2-4. In addition, the absolute value of V^E with x_1 value of 0.4 was lowest for the DES1 and ethanol system. These finding could be ascribed to both the interstitial effect in molecular packing resulting from the variances in size and shape of the component comprising the DES and ethanol pseudobinary system, as well as to the mole ratio between HBA, HAD, and ethanol, which significantly influence the extent of hydrogen bonding.

In general, the hydrogen bond weakens with increasing temperature. However, in all three DES and ethanol pseudobinary mixtures, as the temperature increased, the absolute value of the excess molar volumes also increased accordingly, illustrating the degree of hydrogen bond contributing to the interaction between MTPPB and ethanol, while solvation of DES in ethanol becomes a much more predominant effect, as observed in the case of choline chloride based DES and water [21,23,25].

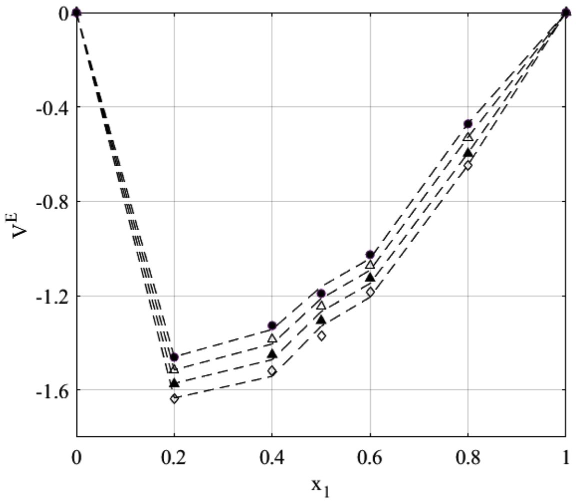

Fig. 3. V^E versus mole fraction of DES2 (x_1) for the pseudobinary mixture of DES2 and ethanol at different temperatures (●: 293.15 K; △: 303.15 K; ▲: 313.15 K; ◇: 323.15 K). The solid lines represent a fit to the Eq. (7).

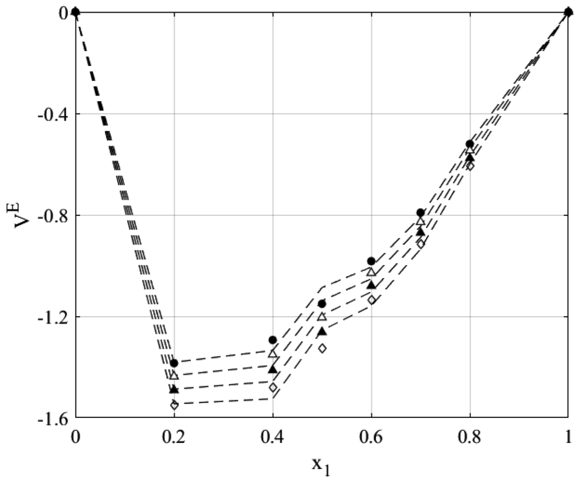

Fig. 4. V^E versus mole fraction of DES3 (x_1) for the pseudobinary mixture of DES3 and ethanol at different temperatures (●: 293.15 K; △: 303.15 K; ▲: 313.15 K; ◇: 323.15 K). The solid lines represent a fit to the Eq. (7).

The calculated excess molar volumes were correlated using a Redlich-Kister expression [26], a method commonly employed by various research groups to determine the excess molar volumes of mixtures [12,14,22].

$$V^E = x_1 x_2 \sum_{j=0}^{p} s_j (x_1 - x_2)^j \qquad (7)$$

where x_1 and x_2 are the mole fractions of DES and ethanol, respectively, s_j are the adjustable parameters, and p is the degree of polynomial extension, set to be 5. Table 7 shows the regressed parameters, and the values of R^2 for DES2 and DES3, as expected, are higher than those for DES1.

3-3. Dynamic viscosity

The dynamic viscosity, η, of the pseudobinary mixtures was

Table 7. Parameters for the correlation of Eq. (7) along with the R^2 for the three binary systems studied

Temp (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15
DES1							
s_0	-4.24	-4.38	-4.465	-4.548	-4.589	-4.619	-4.921
s_1	4	4.023	4.218	4.435	4.837	5.324	5.419
s_2	4.297	4.793	4.636	4.542	3.731	2.609	4.148
s_3	-10.85	-11.23	-12.34	-13.83	-16.01	-18.43	-20.9
s_4	-48.11	-49.15	-48.37	-47.36	-44.42	-40.71	-46.18
s_5	6.832	7.186	8.106	9.377	11.15	13.09	15.45
s_6	48.03	48.72	48.18	47.35	45.26	42.7	46.93
R^2	0.9864	0.9866	0.9861	0.9854	0.9841	0.9826	0.9816
DES2							
s_0	-4.648	-4.751	-4.85	-4.962	-5.073	-5.197	-5.319
s_1	2.665	2.737	2.812	2.872	2.953	3.039	3.09
s_2	-8.619	-8.984	-9.391	-9.829	-10.24	-10.59	-10.84
s_3	12.31	12.07	11.7	11.26	10.94	10.79	10.67
s_4	13.27	13.73	14.24	14.79	15.31	15.79	16.16
s_5	-14.98	-14.81	-14.51	-14.13	-13.9	-13.83	-13.76
R^2	0.9996	0.9996	0.9995	0.9995	0.9995	0.9994	0.9994
DES3							
s_0	-4.349	-4.453	-4.555	-4.668	-4.78	-5.062	-5.022
s_1	2.473	2.531	2.583	2.624	2.685	2.862	2.802
s_2	-14.34	-14.53	-14.71	-14.91	-15.11	-14.59	-15.52
s_3	26.28	26.54	26.82	27.02	27.31	27.3	27.86
s_4	27.73	28.12	28.5	28.91	29.31	29.19	30.18
s_5	-57.26	-57.87	-58.5	-59.03	-59.71	-60.21	-61.04
R^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9998	0.9999

Table 8. Experimental viscosity, h (mPa×s), of the pseudobinary mixture DES1 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.1998	3.19	2.83	2.51	2.25	2.03	1.84	1.69
0.3999	6.95	5.94	5.11	4.44	3.88	3.41	3.05
0.5997	15.28	12.60	10.51	8.87	7.54	6.45	5.57
0.7000	24.21	20.09	16.76	13.85	11.66	9.85	8.48
0.7991	36.39	28.67	22.99	18.65	15.39	12.81	10.80
0.9000	49.60	38.23	30.12	24.14	19.65	16.23	13.62

The standard uncertainties are $u(T) = 0.01$ K and $u(x_1) = 0.0002$ and relative standard uncertainty of density is $u_r(\eta) = 0.02$.

Table 9. Experimental viscosity, h (mPa·s), of the pseudobinary mixture DES2 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.1999	3.37	2.99	2.64	2.39	2.16	1.98	1.82
0.3999	6.30	5.37	4.65	4.04	3.53	3.11	2.74
0.5000	8.84	7.42	6.30	5.40	4.67	4.06	3.52
0.5999	12.70	10.53	8.82	7.45	6.37	5.50	4.71
0.7999	26.28	20.99	17.02	13.99	11.64	9.78	8.30

The standard uncertainties are $u(T) = 0.01$ K and $u(x_1) = 0.0002$ and relative standard uncertainty of density is $u_r(\eta) = 0.02$.

Table 10. Experimental viscosity, h (mPa×s), of the pseudobinary mixture DES3 (1) + ethanol (2) at various temperatures (K)

x_1	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.2001	2.94	2.59	2.29	2.04	1.83	1.66	1.48
0.4002	5.75	4.92	4.25	3.70	3.24	2.86	2.54
0.5002	8.04	6.80	5.79	4.97	4.30	3.87	3.45
0.6002	10.89	9.08	7.66	6.53	5.60	4.84	4.21
0.7001	15.84	12.97	10.74	9.02	7.61	6.53	5.64
0.8001	22.25	17.90	14.60	12.05	10.09	8.49	7.26

The standard uncertainties are $u(T) = 0.01$ K and $u(x_1) = 0.0002$ and relative standard uncertainty of density is $u_r(\eta) = 0.02$.

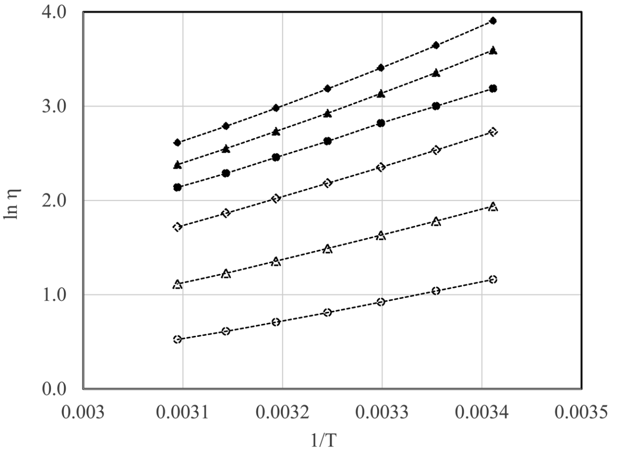

Fig. 5. The viscosity of the pseudobinary solution consisting of DES1 (1) and ethanol (2) at different mole fraction of the DES1 (○: 0.1998, △: 0.3999: ◇: 0.5997: ●: 0.7000: ▲: 0.7991: ◆: 0.9000). The solid line represents a fit to the Eq. (8).

examined across a wide range of compositions at temperatures ranging from 293.15 K to 323.15 K. The experimentally determined results are presented in Tables 8–10. Across the three pseudobinary systems investigated, viscosity decreased with increasing temperature and ethanol mole fraction. Given the similar trend of viscosity changes with temperature for all three systems across various mole fractions, the results for DES1 are depicted in Fig. 5 as an illustrative example.

Fig. 5 illustrates the natural logarithm of viscosity, ln η, values decrease linearly with increasing temperature at fixed compositions of the pseudobinary mixture [18]. In general, the Arrhenius equation is considered the simplest equation for describing the temperature dependence of dynamic viscosity. The experimental results were fitted using Eq. (8), as explored by many other researchers [13,18,20].

$$\ln\eta = \ln\eta_\infty + \frac{E_a}{RT} \tag{8}$$

$$E_a = \sum_{i=1}^{5} p_i x_1^{i-1} \tag{9}$$

$$\eta_\infty = \sum_{i=1}^{5} q_i x_1^{i-1} \tag{10}$$

where η_∞ represents the viscosity at infinite temperature, E_a is the activation energy in J·mol^{-1}, of the mixture, x_1 is the mole fraction of DES, p_i and q_i are the regression parameters. These parameters were determined using multiple linear regression and are listed in Table 11. The AARD values for all cases are below 0.18. Similar to the density, it is evident that the dynamic viscosity data studied can be satisfactorily correlated within the temperature range of 293.15 K to 323.15 K.

Table 11. Parameters for the correlation of Eqs. (9) and (10)

	DES1 + ethanol	DES2 + ethanol	DES3 + ethanol
p_1	4.133	1.897	-1.396
p_2	99.01	115.1	179
p_3	-230.4	-290.4	-550.4
p_4	280.9	395.9	757.6
p_5	-117.9	-196.7	-361.5
ARD	0.0119	0.0006	0.0054
q_1	0.009786	0.01828	0.008181
q_2	-0.04895	-0.1126	-0.05704
q_3	0.09742	0.27	0.1688
q_4	-0.0882	-0.2903	-0.2213
q_5	0.03001	0.1167	0.1047
AARD*	0.1773	0.1533	0.1341

*AARD: average absolute relative deviation

3-4. Excess dynamic viscosity for the pseudobinary mixture

The excess viscosity, η^E, was calculated using Eq. (11) to investigate the interaction within the mixture.

$$\eta^E = \eta_m - (x_1\eta_1 + x_2\eta) \tag{11}$$

where η_m is the dynamic viscosity of the pseudobinary mixture, x_1 and x_2 are the mole fractions of DES and ethanol, respectively, η_1 and η_2 are the dynamic viscosity of DES and ethanol, respectively. The experimental excess viscosity at different temperatures and compositions were plotted for all three pseudobinary systems in Figs. 6-8. It is found that all of the pseudobinary mixtures studied here show a negative deviation from the ideal solution behavior, as indicated by the negative excess viscosities over the whole temperature and ethanol mole fraction. For all the systems in this study, the absolute value of η^E for the mixture at a certain ethanol content increased with decreasing temperature, implying that the interaction between the molecules became stronger. The maximum absolute value of η^E was in the DES-rich region about 0.6 value of DES mole fraction. Unlike with excess molar volume, the pseudobinary mixture with DES1exhibits a higher absolute value of η^E compared to systems with DES2 and DES3. However, the absolute values of η^E for DES2-ethanol pseudobinary system are greater than those for the DES3-ethanol system. Therefore, it remains

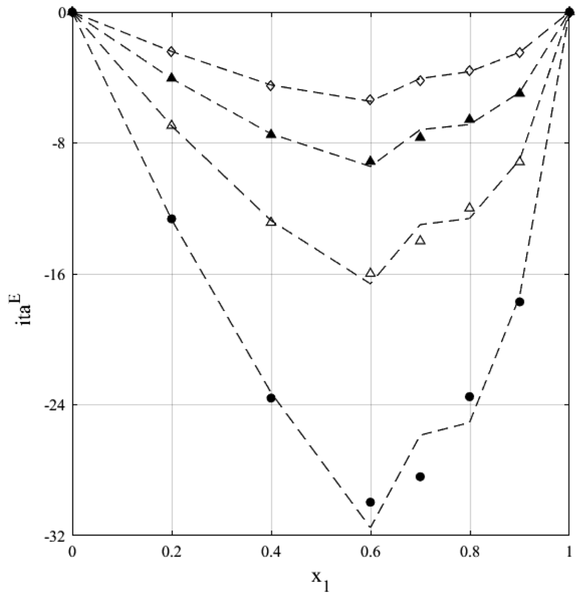

Fig. 6. The excess viscosity (η^E) versus mole fraction of DES1 (x_1) for the pseudobinary mixture of DES1 and ethanol at different temperatures (●: 293.15 K: △: 303.15 K:▲: 313.15 K: ◇: 323.15 K). The solid lines represent a fit to the Eq. (12).

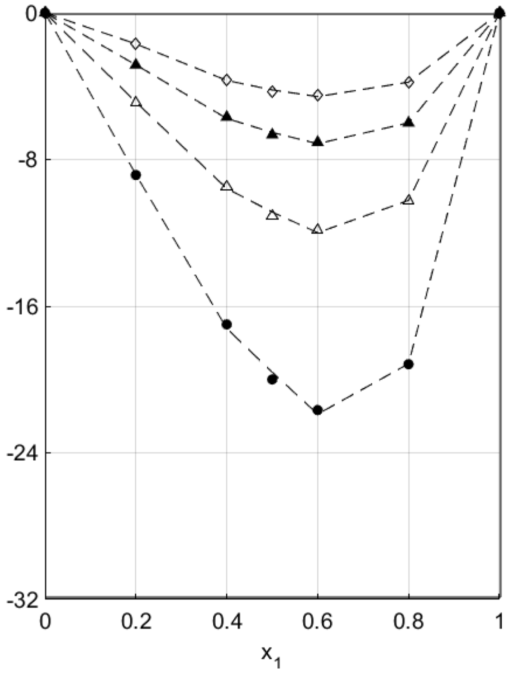

Fig. 7. The excess viscosity (η^E) versus mole fraction of DES2 (x_1) for the pseudobinary mixture of DES2 and ethanol at different temperatures (●: 293.15 K: △: 303.15 K: ▲: 313.15 K: ◇: 323.15 K). The solid lines represent a fit to the Eq. (12).

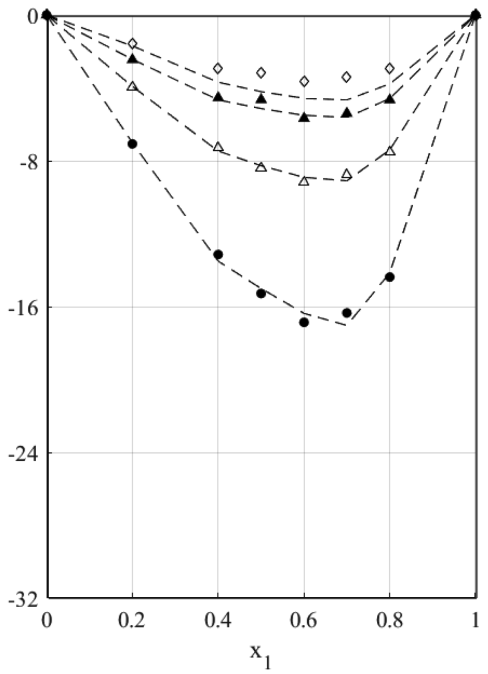

Fig. 8. The excess viscosity (η^E) versus mole fraction of DES3 (x_1) for the pseudobinary mixture of DES3 and ethanol at different temperatures (●: 293.15 K: △: 303.15 K: ▲: 313.15 K: ◇: 323.15 K). The solid lines represent a fit to the Eq. (12).

unclear whether the molar ratio between DES and ethanol is more critical than the ratios of HBA, HBD, and ethanol or if both factors play an equally significant role.

The η^E were fitted to the Redlich-Kister type polynomial expression [26].

$$\eta^E = x_1 x_2 \sum_{j=0}^{p} t_j (x_1 - x_2)^j \tag{12}$$

Table 12. Parameters for the correlation of Eq. (12)

	293.15	298.15	303.15	308.15	313.15	318.15	323.15
DES1							
t_0	-132.1	-94.17	-71.78	-54.9	-41.42	-28.79	-24.13
t_1	-86.03	-56.01	-40.2	-29.5	-20.72	-12.15	-10.4
t_2	522	380	307.7	238.6	180.2	110.9	99.36
t_3	3.081	4.029	-0.1674	-2.601	-0.1205	5.297	1.715
t_4	-1876	-1337	-1075	-831.3	-616.9	-358.3	-326
t_5	156.3	106.5	82.91	65.68	47.36	27.14	25.83
t_6	1486	1052	839.3	647.8	478.2	276.2	250.8
R^2	0.9932	0.9951	0.9962	0.9964	0.9973	0.9992	0.9994
DES2							
t_0	-78.41	-57.89	-43.47	-33.55	-26.1	-20.86	-16.82
t_1	-45.23	-31.76	-23.18	-17.51	-13.1	-10.1	-8.319
t_2	-83	-57.35	-40.56	-29.56	-21.23	-16.1	-10.75
t_3	-93.35	-70.36	-52.12	-41.52	-33.72	-30.05	-23.65
t_4	161.4	115.3	84.07	63.14	47.35	36.97	27.58
t_5	194	144.5	108.3	85.28	67.94	57.51	46.26
R^2	0.9998	0.9998	0.9998	0.9998	0.9998	0.9998	0.9998
DES3	0.0798	0.0777	0.0789	0.0781	0.0772	0.0803	0.0772
t_0	-60.03	-44.21	-33.07	-26.13	-20.53	-16.16	-12.88
t_1	-26.62	-18.71	-13.37	-9.877	-7.723	-5.692	-4.626
t_2	-60.21	-41.42	-28.57	23.54	-17.57	-15.09	-12.01
t_3	-85.97	-60.79	-43.23	-38.6	-29.39	-26.11	-19.56
t_4	120.2	85.62	61.63	49.67	38.1	31.25	24.9
t_5	157	113.5	83.11	70.02	54.59	46.19	36.13
R^2	0.9982	0.9983	0.9985	0.9983	0.9985	0.9982	0.9980

where x_1 and x_2 are the mole fractions of DES and ethanol, respectively, t_j are the adjustable parameters, and p is the degree of polynomial extension. Table 12 shows the regressed parameters, and the R^2 values for DES being close to 1.

4. Conclusions

Both the density and dynamic viscosity of three pseudobinary mixtures of ethanol and DES based on methyltriphenylphosphonium bromide and ethylene glycol were measured as a function of temperature and DES mole fraction in the mixture. The density and dynamic viscosity data were correlated by virtue of an empirical polynomial equation with good accuracy. Excess molar volume, an indicator of interaction between DES and ethanol, is analyzed, showing negative deviations from ideal solution behavior across all studied temperatures and compositions. The interaction is explained by the interstitial effect and hydrogen bonding affected by the mole ratio of HBA, HBD, and ethanol. Dynamic viscosity also decreases with increasing temperature and ethanol content, with a notable correlation between viscosity and temperature. Excess dynamic viscosity further illustrates the negative deviation from ideal solution behavior, emphasizing strong molecular interaction across varying DES mole fractions. The study sheds light on how DESs and ethanol interact, influencing their physical properties. The empirical polynomial equations accurately correlate density and dynamic viscosity data, revealing distinct packing characteristics among DES1, DES2, and DES3. As ethanol disrupts DES structures, densities decrease, providing insights into molecular interactions critical for designing efficient processes.

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