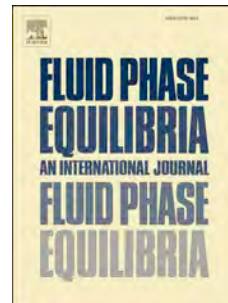


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Thermophysical characterization of the deep eutectic solvent choline chloride:ethylene glycol and one of its mixtures with water

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ABSTRACT

The deep eutectic solvent ethaline, containing choline chloride as H-bond acceptor and ethylene glycol as H-bond donor and one of its mixture with water are studied in this work. Ethaline is anhydrous, with a 1:2 mole ratio. Hydrated ethaline, choline chloride:ethylene glycol:water, was studied in a 1:1.98:0.95 mole ratio. Several volumetric, acoustic, optical, thermal, surface, and transport properties were measured and calculated. The working temperature ranges from 278.15 to 338.15 K at pressure = 0.1 MPa. The effects of temperature, water inclusion, and the nature of the donor compound are evaluated. With regard to temperature, the system's behaviour is as expected: a linear relation for the thermodynamic properties and agreement with the Vogel-Fulcher-Tammann equation for the transport properties. The water molecules hardly modify the ethaline structure. The choline chloride – ethylene glycol interactions are weaker than those for choline chloride - glycerol.

Keywords: Choline chloride; Ethylene glycol; Thermophysical properties; DES.

1. Introduction

Currently, deep eutectic solvents (DESs) are being promoted as alternatives to ionic liquids due to their special characteristics. They can be formed from raw materials of natural origin (carbohydrates, choline chloride, organic acids or amino acids, among others) with a preparation process that is very easy and cheap. Furthermore, they have equal or superior performance when compared with certain volatile organic compounds. All of these characteristics could facilitate a reduction in costs in a multitude of industrial applications; therefore, currently available DESs are very attractive as possible green solvents [1-3].

A DES contains at least one substance that is a hydrogen bond donor (HBD) and another that is an acceptor (HBA). During mixture, an H-bond network causes a deep decrease in the fusion temperature and other solvent properties. However, an undesirable consequence of these intermolecular interactions is high viscosity values, which can be a handicap in industry. To avoid this problem, the plasticizer effect of water can be used: the addition of small amounts of water greatly modifies the viscosity without impairing other properties.

Determining the physicochemical properties of the DESs in the widest range of experimental conditions (pressure, temperature) is of great importance for proposing new applications, defining limits, and deepening our knowledge of their molecular and macroscopic behaviour. In addition, it is necessary to understand how these solvents will interact with surrounding molecules. Research fields such as catalysis, biobased chemical extraction and purification, chemical synthesis, electrochemistry, transdermal protein delivery, drug solubility, and extraction of natural compounds for the pharmaceutical industry can benefit from the use of DESs [4-8]. Recently, the amount of experimental data available has grown but still remains scarce [9].

The DES composed of choline chloride as HBA and ethylene glycol as HBD, in mole ratio 1:2, is called ethaline (Etha). It has several advantages as a solvent: it is stable at room temperature and has high conductivity and low viscosity compared to other DESs such as reline or glyceline [10-13]. With respect to green properties, Etha exhibits high biodegradability and low toxicity [14], which is quite promising. Currently, it is being used in the extraction of natural and therapeutic compounds [15] or in low oxygen content detection [16]. Previous studies have examined ethaline's thermophysical properties [17-29]. In some cases, the information given in these previous works is disjointed and limited to certain experimental temperature conditions. On the other hand, the water content of ethaline varies appreciably from one study to another, and some studies do not provide the water content. With the aim of offering a comprehensive view of the DES ethaline, a broad study of the thermophysical properties is presented in this work in a temperature range of 278.15 - 338.15 K and at $p = 0.1$ MPa. Properties such as density, speed of sound, refractive index, isobaric molar heat capacity, surface tension, kinematic viscosity and electrical conductivity have been measured, while other properties such as isobaric expansibility, isentropic compressibility, intermolecular free length, molar refractivity, free volume, surface thermodynamic properties, dynamic viscosity, and transport activation energy have been calculated from the experimental data. Furthermore, in order to study the effect of water inclusion on the ethaline structure, an aqueous mixture has been prepared with a final composition of choline chloride:ethylene glycol:water (1:1.98:0.95 mole ratio); the abbreviation EthaW is used in this paper for this mixture. This water mole ratio was chosen, apart from the abovementioned reason, in order to compare the behaviour of this aqueous mixture with the one containing choline chloride, glycerol and water with the same mole ratio [30]. Moreover, a comparative evaluation with data previously

published by us for another similar deep eutectic solvent, glyceline (Gly), which has glycerol as HBD, has also been carried out.

2. Materials and methods

2.1. Materials

The characteristics of the chemicals used in this work are listed in Table 1. The EthaW was prepared from choline chloride, ethylene glycol and water in 1:1.98:0.95 mole ratio; its molar mass, $M = 70.44 \text{ g}\cdot\text{mol}^{-1}$, is calculated from the addition of molar contributions. EthaW was prepared taking into account the amount of water that was contained in the pure chemicals separately. Milli-Q water with resistivity less than $18.2 \text{ M}\Omega\cdot\text{cm}$ was utilized in the preparation of the aqueous mixture. For sample preparation, the components were weighed with a Sartorius balance BP210S ($\pm 0.1 \text{ mg}$), and the eutectic was obtained by heating under magnetic agitation. All the chemicals were dried under vacuum for 24 h before use. The water content was determined by the Karl Fisher Method with an Automatic Titrator Crison KF 1S-2B.

Table 1

Sample table.

Chemical name	CAS No	Source	Purification method	Mass fraction purity ^a	Water content / ppm	Molar mass / $\text{g}\cdot\text{mol}^{-1}$
Ethaline		Scionix	Vacuum	0.98	317	87.92
Choline chloride	67-48-1	Sigma-Aldrich	Vacuum	0.993	1050	139.62
Ethylene glycol	107-21-1	Sigma-Aldrich	Vacuum	0.995	550	62.07

^aAs stated by the supplier.

2.2. Methods

Several pieces of equipment were used to perform the thermophysical characterization of the studied liquids at $p = 0.1$ MPa.

The density, ρ , and speed of sound, u , were measured using a thermostated device (Anton Paar DSA 5000) including a vibrating tube densimeter and sound analyser; the frequency of the analyser is approximately 3 MHz. The estimated uncertainties of density and speed of sound are, respectively, $0.1 \text{ kg}\cdot\text{m}^{-3}$ and $0.5 \text{ m}\cdot\text{s}^{-1}$, while the uncertainty in temperature is 0.005 K. Due to the high viscosities of the liquids it must be mentioned that the densimeter takes into account the viscosity to calculate the density.

The refractive index at the sodium D line (wavelength $\lambda=589.3$), n_D , was determined using an Abbemat-HP Dr Kernchen refractometer with an uncertainty of $5\cdot 10^{-5}$ in which the temperature was internally controlled; the temperature uncertainty was 0.01 K. The measurement of the isobaric molar heat capacity, $C_{p,m}$, was performed with a DSC Q2000 calorimeter from TA Instruments. The corresponding uncertainties are 1% for capacity and 0.005 K for temperature; this calorimeter uses a synthetic sapphire sample as reference standard. The surface tension data, σ , were obtained with a Lauda TVT-2 tensiometer with an uncertainty in the measurements of $0.2 \text{ mN}\cdot\text{m}^{-1}$; the temperature is kept constant with a Lauda E-200 thermostat, and the uncertainty in temperature was 0.01 K.

With regard to transport properties, the kinematic viscosity, ν , was determined using Ubbelohde capillaries and a measurement unit Schoot-Geräte AVS-440; the uncertainty of the viscosity determination is 1%. The electrical conductivity, κ , was obtained with a conductimeter Crison LPG31 operating at alternating frequency (2 kHz) with an estimated uncertainty of 1%. An aqueous solution of KCl was used as a

calibration standard. The temperature was stabilized in both cases with a thermostat Schoot-Geräte CT (1150/2); the temperature uncertainty is 0.01 K.

3. Results and discussion

The thermophysical properties reported in this paper, except refractive index, were measured at $p = 0.1$ MPa in the temperature range (278.15-338.15) K with the temperature interval being 2.5 K; for n_D measurements the starting temperature is 283.15 K. Measurements at all temperature steps within these ranges were performed. All the experimental values along with some derived properties are listed in Table 2 and plotted in Fig. 1-7. In supplementary material, figures S1-S7 show a comparison between the experimental data obtained for the studied properties for Etha/EthaW and Gly/GlyW.

Now, we evaluate several properties related to the volumetric, thermal and surface behaviour of Etha and EthaW, the composition of which has been indicated above; namely, density, ρ , speed of sound, u , refractive index, n_D , isobaric molar heat capacity, $C_{p,m}$, and surface tension, σ .

A linear dependence with the temperature was found for these properties:

$$Y = A \cdot T + B \quad (1)$$

where Y is the corresponding property. The coefficients A and B are the fit parameters that are presented in Table 3. The adjustment quality has been evaluated with the relative root-mean square deviation, $RMSD_r$, defined as:

$$RMSD_r / \% = 100 \left(\frac{1}{n} \sum_{i=1}^n \left(\frac{Y_{i,\text{exp}} - Y_{i,\text{cal}}}{Y_{i,\text{exp}}} \right)^2 \right)^{1/2} \quad (2)$$

The obtained values for these deviations are also included in Table 3.

Table 2

Experimental thermophysical properties,^a at $p = 0.1$ MPa, of the studied liquids as a function of the temperature, T . Density, ρ ; speed of sound, u ; isentropic compressibility, κ_S ; refractive index, n_D ; isobaric heat capacity, $C_{p,m}$; surface tension, σ ; kinematic and dynamic viscosities, ν and η ; and electrical conductivity, κ :

T / K	$\rho /$ ($\text{kg}\cdot\text{m}^{-3}$)	$u /$ ($\text{m}\cdot\text{s}^{-1}$)	$\kappa_S /$ TPa^{-1}	n_D	$C_{p,m} /$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	$\sigma /$ ($\text{mN}\cdot\text{m}^{-1}$)	$\nu /$ ($\text{mm}^2\cdot\text{s}^{-1}$)	$\eta /$ ($\text{mPa}\cdot\text{s}$)	$\kappa /$ ($\text{mS}\cdot\text{cm}^{-1}$)
Etha (choline chloride:ethylene glycol; 1:2)									
278.15	1127.50	1950.2	233.21		164.2	56.30	89.50	100.9	3.53
280.65	1126.06	1944.5	234.86		164.8	56.20	78.65	88.55	4.00
283.15	1124.61	1938.9	236.54	1.47232	165.2	56.10	69.30	77.95	4.52
285.65	1123.17	1933.2	238.24	1.47174	165.8	55.95	61.35	68.95	5.06
288.15	1121.72	1927.5	239.95	1.47118	166.4	55.85	54.60	61.25	5.66
290.65	1120.28	1921.9	241.66	1.47063	167.2	55.75	48.75	54.60	6.33
293.15	1118.84	1916.3	243.38	1.47005	167.4	55.65	43.75	48.95	7.01
295.65	1117.40	1910.7	245.13	1.46948	168.2	55.55	39.30	43.95	7.76
298.15	1115.97	1905.1	246.89	1.46889	168.8	55.45	35.50	39.60	8.47
300.65	1114.54	1899.5	248.66	1.46832	169.4	55.30	32.05	35.70	9.32
303.15	1113.11	1894.0	250.45	1.46774	169.8	55.20	29.15	32.40	10.2
305.65	1111.68	1888.4	252.25	1.46701	170.4	55.10	26.55	29.50	11.1
308.15	1110.26	1882.8	254.07	1.46641	171.1	54.95	24.25	26.95	12.1
310.65	1108.83	1877.3	255.90	1.46567	171.8	54.85	22.25	24.65	13.1
313.15	1107.41	1871.8	257.74	1.46505	172.2	54.75	20.45	22.65	14.2
315.65	1105.99	1866.3	259.60	1.46443	172.8	54.65	18.85	20.85	15.3
318.15	1104.58	1860.7	261.48	1.46379	173.2	54.50	17.40	19.25	16.7
320.65	1103.17	1855.2	263.39	1.46317	174.0	54.35	16.15	17.80	17.7
323.15	1101.75	1849.6	265.32	1.46264	174.6	54.25	14.95	16.50	18.9
325.65	1100.34	1844.0	267.28	1.46192	175.2	54.15	13.90	15.30	20.2
328.15	1098.93	1838.4	269.26	1.46130	175.8	54.00	12.95	14.25	21.6

Table 2 Continuation

T / K	$\rho /$ ($\text{kg}\cdot\text{m}^{-3}$)	$u /$ ($\text{m}\cdot\text{s}^{-1}$)	$\kappa_S /$ TPa^{-1}	n_D	$C_{p,m} /$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	$\sigma /$ ($\text{mN}\cdot\text{m}^{-1}$)	$\nu /$ ($\text{mm}^2\cdot\text{s}^{-1}$)	$\eta /$ ($\text{mPa}\cdot\text{s}$)	$\kappa /$ ($\text{mS}\cdot\text{cm}^{-1}$)
330.65	1097.53	1832.7	271.26	1.46069	176.2	53.90	12.10	13.30	23.2
333.15	1096.12	1827.0	273.31	1.46010	176.8	53.80	11.30	12.40	24.5
335.65	1094.72	1821.3	275.38	1.45951	177.4	53.70	10.60	11.65	26.0
338.15	1093.32	1815.5	277.50	1.45889	178.2	53.60	9.970	10.90	27.6
EthaW (choline chloride:ethylene glycol:water; 1:1.98:0.95)									
278.15	1123.47	1963.8	230.81		157.2	56.90	59.30	66.65	5.22
280.65	1122.05	1958.4	232.37		158.0	56.80	52.25	58.60	5.93
283.15	1120.62	1953.1	233.93	1.46632	158.8	56.70	46.35	51.95	6.69
285.65	1119.18	1947.8	235.52	1.46572	159.2	56.60	41.20	46.15	7.52
288.15	1117.56	1942.5	237.15	1.46512	159.8	56.50	36.90	41.20	8.41
290.65	1116.33	1937.1	238.73	1.46450	160.4	56.35	33.15	37.00	9.40
293.15	1114.93	1931.8	240.35	1.46390	161.0	56.25	29.90	33.30	10.5
295.65	1113.49	1926.4	242.01	1.46328	161.6	56.10	27.05	30.10	11.5
298.15	1112.08	1921.0	243.67	1.46268	162.4	56.00	24.80	27.55	12.7
300.65	1110.66	1915.7	245.35	1.46206	162.8	55.90	22.25	24.70	13.7
303.15	1109.25	1910.3	247.03	1.46147	163.6	55.80	20.30	22.55	14.9
305.65	1107.83	1905.0	248.74	1.46079	164.2	55.65	18.65	20.65	16.2
308.15	1106.42	1899.7	250.45	1.46015	164.8	55.50	17.05	18.90	17.5
310.65	1105.01	1894.3	252.18	1.45954	165.4	55.45	15.70	17.35	18.9
313.15	1103.60	1889.0	253.94	1.45892	165.8	55.30	14.50	16.00	20.4
315.65	1102.19	1883.6	255.71	1.45831	166.6	55.20	13.45	14.80	22.0
318.15	1100.78	1878.3	257.50	1.45751	167.2	55.10	12.50	13.75	23.7
320.65	1099.38	1873.0	259.29	1.45697	167.8	55.00	11.55	12.70	25.5
323.15	1097.97	1867.7	261.09	1.45639	168.4	54.85	10.75	11.85	27.3
325.65	1096.57	1862.4	262.92	1.45578	169.2	54.75	10.05	11.00	29.1
328.15	1095.16	1857.1	264.77	1.45517	169.6	54.60	9.405	10.30	30.7
330.65	1093.76	1851.6	266.66	1.45457	170.4	54.50	8.802	9.627	32.5

Table 2 Continuation

T / K	$\rho /$ ($\text{kg}\cdot\text{m}^{-3}$)	$u /$ ($\text{m}\cdot\text{s}^{-1}$)	$\kappa_S /$ TPa^{-1}	n_D	$C_{p,m} /$ ($\text{J}\cdot\text{mol}\cdot\text{K}^{-1}$)	$\sigma /$ ($\text{mN}\cdot\text{m}^{-1}$)	$\nu /$ ($\text{mm}^2\cdot\text{s}^{-1}$)	$\eta /$ ($\text{mPa}\cdot\text{s}$)	$\kappa /$ ($\text{mS}\cdot\text{cm}^{-1}$)
333.15	1092.35	1846.3	268.55	1.45393	170.8	54.40	8.266	9.029	34.5
335.65	1090.95	1840.9	270.47	1.45335	171.4	54.30	7.775	8.482	36.6
338.15	1089.54	1835.6	272.40	1.45276	172.2	54.15	7.311	7.966	38.8

^a Standard uncertainties u are $u(T) = 0.005$ K for density and speed of sound and $u(T) = 0.01$ K for the rest of the properties; $u(p) = 1$ kPa, and the combined expanded uncertainties U_c are $U_c(\rho) = 0.1$ $\text{kg}\cdot\text{m}^{-3}$, $U_c(u) = 0.5$ $\text{m}\cdot\text{s}^{-1}$, $U_c(n_D) = 5\cdot 10^{-5}$, $U_c(C_{p,m}) = 1\%$, $U_c(\sigma) = 0.2$ $\text{mN}\cdot\text{m}^{-1}$, $U_c(\nu) = 1\%$, $U_c(\eta) = 1\%$, $U_c(\kappa) = 1\%$, with 0.95 level of confidence ($k = 2$).

Table 3

Fitting parameters, A , B , and C , for the correlation equations and their corresponding root-mean square relative deviations, $RMSD_r$.

	Property	Equation	A	B	C	$RMSD_r / \%$
Etha	$\rho / (\text{kg}\cdot\text{m}^{-3})$	1	-0.5697	1285.87		0.005
	$u / (\text{m}\cdot\text{s}^{-1})$	1	-2.235	2571.6		0.008
	n_D	1	$-2.474\cdot 10^{-4}$	1.54257		0.006
	$C_{p,m} / (\text{J}\cdot\text{mol}\cdot\text{K}^{-1})$	1	0.232	99.6		0.049
	$\sigma / (\text{mN}\cdot\text{m}^{-1})$	1	-0.0456	69.00		0.041
	$\eta / (\text{mPa}\cdot\text{s})$	5	0.074	970.3	143.85	0.22
	$\kappa / (\text{mS}\cdot\text{cm}^{-1})$	5	1721.7	-746.4	157.58	0.36
EthaW	$\rho / (\text{kg}\cdot\text{m}^{-3})$	1	-0.5647	1280.46		0.004
	$u / (\text{m}\cdot\text{s}^{-1})$	1	-2.136	2557.8		0.004
	n_D	1	$-2.485\cdot 10^{-4}$	1.53674		0.003
	$C_{p,m} / (\text{J}\cdot\text{mol}\cdot\text{K}^{-1})$	1	0.246	89.1		0.049
	$\sigma / (\text{mN}\cdot\text{m}^{-1})$	1	-0.0461	69.74		0.029
	$\eta / (\text{mPa}\cdot\text{s})$	5	0.073	903.4	145.57	0.27
	$\kappa / (\text{mS}\cdot\text{cm}^{-1})$	5	1656.2	-650.4	165.00	0.67

The observed density difference between the two studied mixtures is due to changes in the molecular organization and the extent of intermolecular interactions of the components [5] that are affected by the presence of water within the internal structure. Etha is denser than EthaW, in a manner similar to the behaviour reported for glyceline and hydrated glyceline in a previous work [30]. However, for the mixtures containing ethylene glycol, the effect is less pronounced than for that containing glycerol (same water mole ratio): Etha is about 0.2% denser than EthaW, whereas Gly was 1% denser than GlyW. The water inclusion in Etha hardly disturbs the anhydrous compound structure. Furthermore, Etha density is about a 7% lower than Gly. These results may be due to the ChCl-ethylene glycol interactions being less significant than the ChCl-glycerol ones.

For both solvents, Etha and EthaW, the density decreases when the temperature increases, as expected. To take into account the extent of the effect of temperature, the isobaric expansibility, $\alpha_p = -1/\rho(\partial\rho/\partial T)_p$, has been calculated. The obtained values at three representative temperatures are listed in Table 4. It is observed that the volume variation with temperature is quite similar in both mixtures; thus, the effect of water inclusion does not significantly modify the increase of ion and molecule mobility due to the increase of temperature.

With regard to the speed of sound, u , the pure Etha shows higher values than EthaW; specifically, the difference is up to 1.4% at higher temperatures. An increase in the system temperature should cause greater intermolecular disorder, which is the reason why the fluid capacity to transmit the sound also decreases. The effect is more marked for the hydrated mixture. From ρ and u experimental values, we have calculated the isentropic compressibility using the Newton-Laplace equation assuming that

ultrasonic is negligible, $\kappa_s = 1/(\rho u^2)$. This property provides information about the internal organization of the

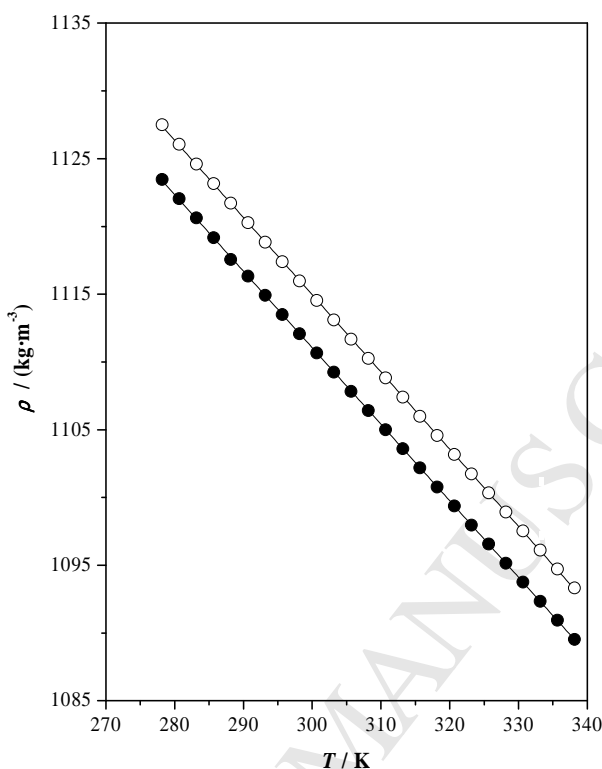


Fig. 1. Density, ρ , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

molecules, so lower values for this property indicate a more packed structure. According to the empirical relation proposed by Jacobson [31], the intermolecular free length, L_f , can be estimated:

$$L_f = K \sqrt{\kappa_s} \quad (3)$$

where K is the temperature-dependent Jacobson's constant. The calculated values for the two properties, κ_s and L_f , at three temperatures are found in Table 4. The slightly higher values for Etha (< 1%) indicate that both solvents have a similar structure but the anhydrous is marginally more poorly packaged. The thermal agitation causes the lability of the interactions within the liquid and, consequently, L_f values increase significantly (about 20%) in our working temperature range.

The n_D values for Etha are higher than EthaW, in good accord with the density relationship. In the same way as the above properties, n_D decreases when temperature increases, with the slope being quite similar for the two solvents. The electronic polarizability, α_e , is a measure of the dispersion forces of the fluid and is related to the molar refraction, R_m . From density and refractive index data, we have calculated the molar refraction through the Lorentz-Lorenz relation:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \quad (4)$$

where V_m and n_D are the molar volume and refractive index, respectively. The higher the electronic polarizability, the higher the solvent capacity for species with high polarizability. In our study, Etha exhibits stronger dispersion forces. The difference between the molar volume and the molar refraction is defined as the free volume, f_m . Both R_m and f_m at three temperatures are also shown in Table 4. Etha has the higher free volume, but the f_m/V_m ratio is similar, confirming that the effect of water inclusion does not significantly modify the internal structure of the Etha DES.

The lower κ_s and f_m/V_m values obtained in this study with respect to the previously published values for Gly and GlyW [30] prove that Etha and EthaW solvents are more poorly packaged than Gly and GlyW. For the acoustic and optical properties, the strongest interactions in the DES are shown to involve glycerol as donor.

Table 4

Derived thermophysical properties from density, speed of sound and refractive index of the studied mixtures at several temperatures, T . Isobaric expansibility, α_p , intermolecular free length, L_f , molar refractivity, R_m , and free volume, f_m .

Property	Etha			EthaW		
	T / K			T / K		
	283.15	298.15	338.15	283.15	298.15	338.15
$\alpha_p / \text{kK}^{-1}$	0.507	0.510	0.521	0.504	0.507	0.518
$L_f / \text{\AA}$	0.296	0.311	0.353	0.294	0.308	0.350
$R_m / \text{cm}^3 \cdot \text{mol}^{-1}$	21.904	21.936	21.979	17.420	17.435	17.466
$f_m / \text{cm}^3 \cdot \text{mol}^{-1}$	56.274	56.847	58.436	45.440	45.907	47.186

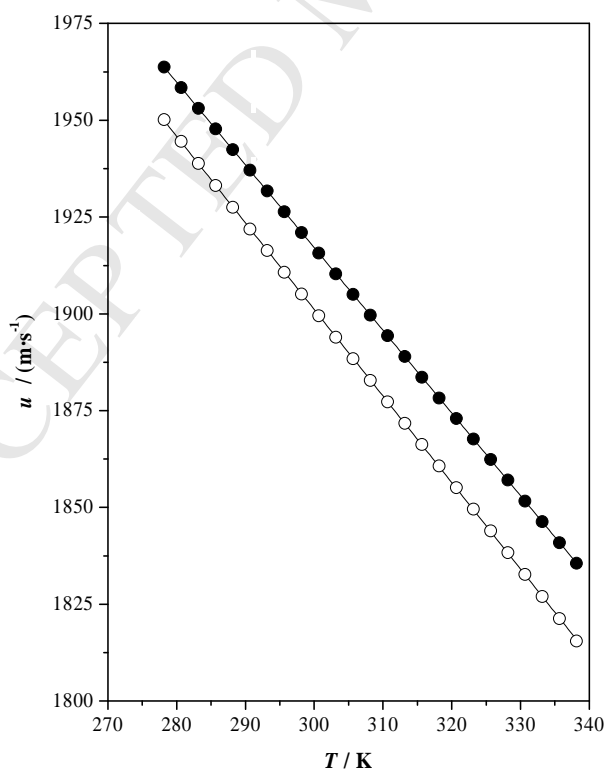


Fig. 2. Speed of sound, u , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

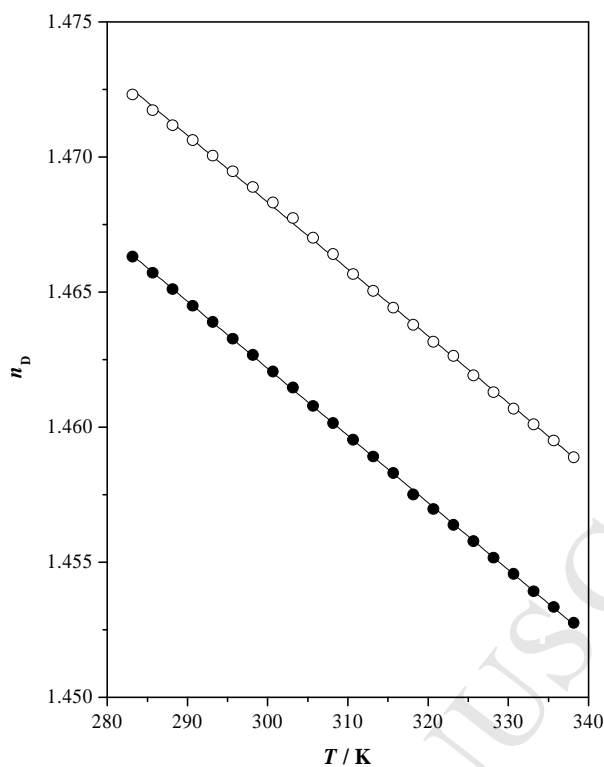


Fig. 3. Refractive index, n_D , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

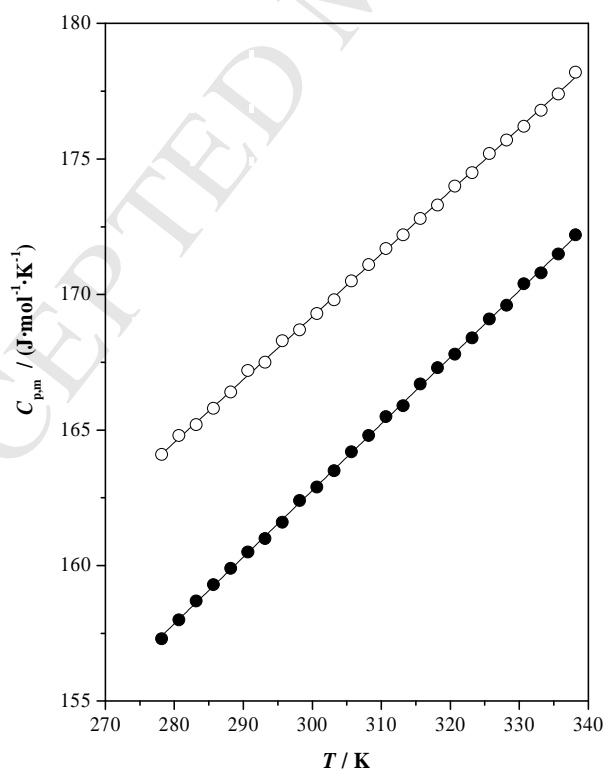


Fig. 4. Isobaric molar heat capacity, $C_{p,m}$, as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

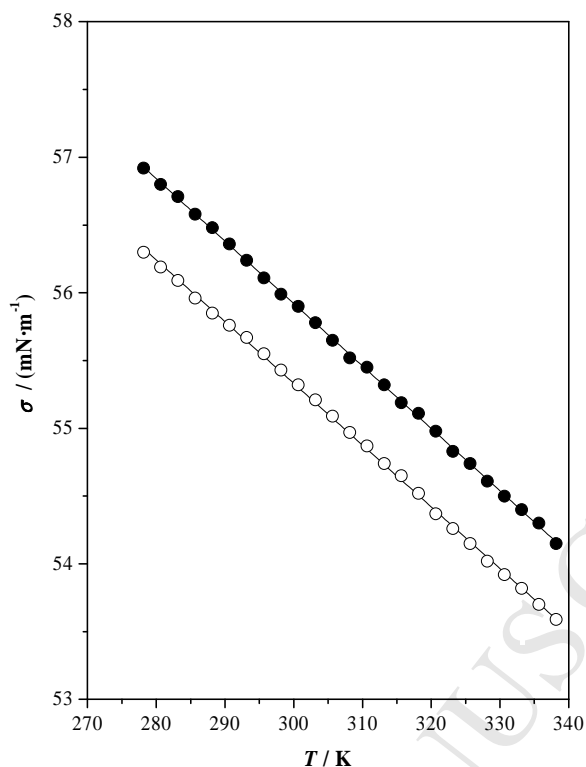


Fig. 5. Surface tension, σ , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

The isobaric molar heat capacity, $C_{p,m}$, is a thermal property that delineates the amount of heat energy necessary to increase the temperature of one mole of the substance under study. Therefore, it is needed in many industrial processes that involve heat transfer applications [19]. The determined values for Etha are higher than EthaW (nearly 3.7% at the lowest studied temperature), and for both, $C_{p,m}$ increases with temperature, showing behaviour similar to other solvents such as ILs [32].

The surface tension, σ , is caused by the action of the intermolecular forces that exist in the system interface compared to those of the bulk. This property depends on both the temperature and the nature of the molecules under study. In the bulk, each molecule is subjected to forces that on average are cancelled. However, on the surface, there is a net force towards the phase interior. The higher the difference between the total force in the bulk and the surface, the higher the surface tension. The surface

tension of EthaW is higher than that of Etha, which means that there is a higher extent of intermolecular interactions (hydrogen bonds, mainly). Again, the linear decrease with the temperature is similar for both solvents. From the σ data and its temperature dependence, the entropy of surface per unit surface area ($\Delta S_\sigma = -(\partial\sigma/\partial T)_p$) and the enthalpy of surface per unit surface area ($\Delta H_\sigma = \sigma - T(\partial\sigma/\partial T)_p$) have been calculated.

These thermodynamic properties allow us to evaluate the distribution of the molecules of our liquids. The linear relationship between the surface tension and temperature makes ΔS_σ constant. For Etha and EthaW, the estimated values were 0.0455 and 0.0461 $\text{mN}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. Taking into account the uncertainty in the ΔH_σ calculation, this property was found to be constant with temperature in our temperature range: 69.0 and 69.6 $\text{mN}\cdot\text{m}^{-1}$ for anhydrous and hydrated compound, respectively. For DESs with glycerol, these values are larger, especially those of the enthalpy (14 $\text{mN}\cdot\text{m}^{-1}$ higher). So, for the solvents (Etha, EthaW, Gly, and GlyW), Etha is the most structured liquid at the surface and it has the lowest intermolecular interaction energy.

Next, we evaluate the fluidity and ionicity of the solvents. For this purpose, we have measured the kinematic viscosity, ν , and the electric conductivity, κ : Using density values, we have obtained the dynamic viscosity, η , by means of the relationship: $\eta = \rho \cdot \nu$.

Both transport properties exhibit a temperature dependence that can be correlated with the Vogel-Fulcher-Tammann equation [33-35]:

$$Y = Y_0 \cdot \exp[B / (T - T_0)] \quad (5)$$

where Y is η or κ , and Y_0 , B , and T_0 are adjustable parameters. These adjustable parameters along with the $RMSD_r$ values are also listed in Table 3. The Y_0 coefficient

represents the corresponding property value at $T \rightarrow \infty$; i.e., the property contribution due

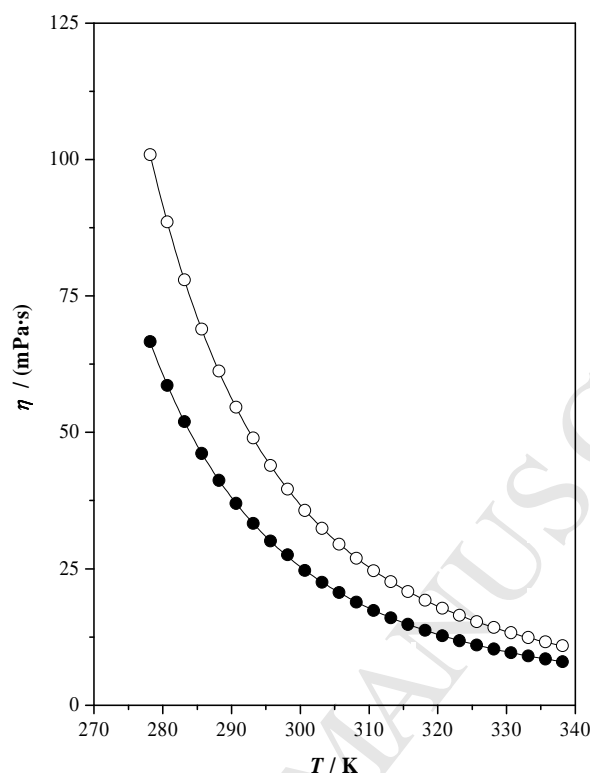


Fig. 6. Dynamic viscosity, η , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

to the molecular geometry. From B and T_0 values, the energy barriers corresponding to the two transport processes, $E_{a,Y}$, can be estimated [36]:

$$E_{a,Y} = R \left(\frac{\partial \ln Y}{\partial (1/T)} \right)_p \quad (6)$$

where Y is η or κ , T is the temperature and R is the ideal gas constant.

It is known that the high viscosity values of some DESs is a large drawback for their use as an industrial solvent [37]. One way to soften the H-bond network formed between the components and therefore decrease the viscosity is to incorporate water molecules, which can act as plasticizer agents [38, 39]. Accordingly, the adaptation of

these green solvents into chemical industry could be increased [5]. Furthermore, η gives us information about the changes produced in the structure when water is included. From reported values we can see that Etha has a moderate viscosity. On the other hand, the inclusion of water in the solvent causes a sharp drop in viscosity; in our study, more than 30% at the lowest studied temperature. This result may be related to a strong interaction between the donor component, ethylene glycol, and the water molecules. Regarding the variation with temperature, a normal behaviour for both solvents is observed: an exponential decrease as the temperature increases. The activation energy to overcome the molecules' movement has been calculated from equation (6). The higher values are associated with larger molecule size and stronger interactions. The obtained geometrical contribution to the viscosity, $A = \eta_0$, is very similar for the two solvents. Moreover, the lower value found for EthaW, 28.7 versus 30.1 $\text{kJ}\cdot\text{mol}^{-1}$ at $T = 298.15$ K, is in accord with the network debilitation provoked by the water.

Finally, the electrical conductivity values for EthaW are higher than for Etha: the water inclusion produces an increase of approximately 40% in conductivity. The temperature also has a great influence on κ values, although unlike the viscosity behaviour, the electrical conductivity increases with temperature. The relationship is well described by the VFT equation, and the calculated values for the activation energy for the conductivity at $T = 298.15$ K for Etha and EthaW were 27.9 and 27.1 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. For our systems, the $E_{a,\kappa}$ difference is much smaller than $E_{a,\eta}$.

There is a great difference between η and κ data for Etha and Gly. The latter is, at $T = 283.15$ K, 15 times more viscous with 4 times less electrical conductance.

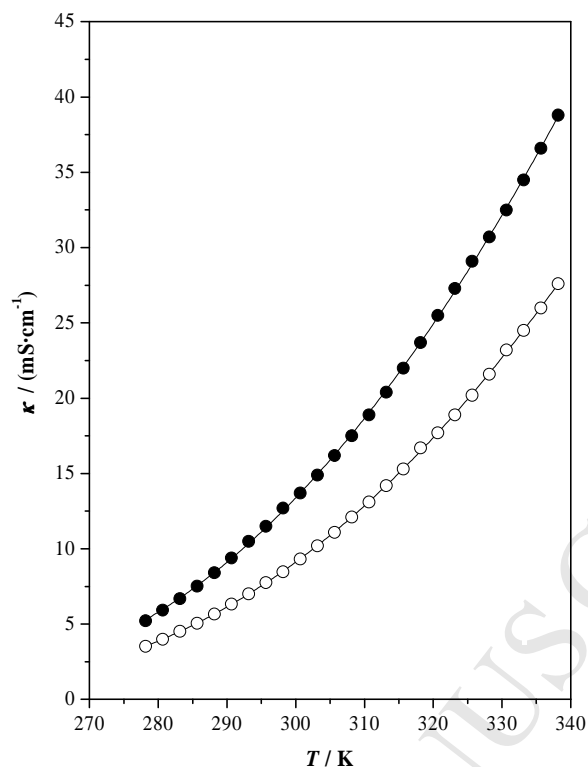


Fig. 7. Electrical conductivity, κ , as a function of temperature, T , at $p = 0.1$ MPa for the studied liquids: Etha (○) experimental; EthaW (●) experimental; (—) correlated values.

Taking into account these transport properties, we can say that ethaline is a solvent more suitable than glyceline in many industrial applications.

Several papers have been published that include experimental data of the thermophysical properties of Etha; the comparison with our data is summarized in Table 5. The comparison has been made through absolute deviations and $RMSD_r$ values. First, we must mention the disparity of values for the thermophysical properties of Etha provided by the different researchers, even for the values reported in different papers from a single laboratory. The studies that present a great variety of thermophysical properties are those of Mjalli et al. [22, 24, 25] and Troter et al. [28]; our results agree reasonably well with the results of Mjalli et al. [24], but deviations are noticeable with the others [22, 25, 28].

With respect to the ternary mixture (choline chloride:ethylene glycol:water), there are no data in the literature that specify the exact water content. Despite this, in Fig. 8 we show a graphical comparison with related works reporting ethaline-water data [19, 21, 40]. Density and viscosity results are in good agreement with the literature [21, 40] although our viscosity at $T = 313.15$ is slightly higher. Regarding the refractive indices and isobaric molar heat capacities, both sets of experimental data are slightly higher than previously reported ones [19, 21].

Table 5

Absolute deviations, Δy , and relative root-mean-square deviations, $RMSD_r$, between our experimental and literature data for ethaline, at $p = 0.1$ MPa.

Reference	Temperature (K)	Water content / ppm	$\rho / \text{kg} \cdot \text{m}^{-3}$		$u / \text{m} \cdot \text{s}^{-1}$		n_D		$C_{p,m} / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$		$\sigma / \text{mN} \cdot \text{m}^{-1}$		$\eta / \text{mPa} \cdot \text{s}$		$\kappa / \text{mS} \cdot \text{cm}^{-1}$	
			$\Delta\rho$	$RMSD_r / \%$	Δu	$RMSD_r / \%$	Δn_D	$RMSD_r / \%$	$\Delta C_{p,m}$	$RMSD_r / \%$	$\Delta\sigma$	$RMSD_r / \%$	$\Delta\eta$	$RMSD_r / \%$	$\Delta\kappa$	$RMSD_r / \%$
Bagh [17]	298.15-338.15	1000	1.38	0.13											1.25	8.89
Harifi-Mood [18]	308.15-338.15	600	0.72	0.07								2.49	12.42	1.43	8.86	
Leron [19]	303.15-338.15	1500							21.76	11.12						
Leron [20]	298.15-323.15	5000	1.34	0.12												
Leron [21]	298.15-333.15	2000	0.99	0.09			0.0006	0.04								
Mjalli [22]	293.15-333.15	2000	23.15	2.05	20.7	1.40					7.06	14.94	1.41	3.44		
Mjalli [23]	298.15-338.15	100	2.14	0.20							7.20	15.27				
Mjalli [24]	293.15-338.15	200	0.59	0.05			0.0006	0.04					0.32	1.00	0.84	13.61
Mjalli [25]	293.15-298.15	100	23.15	2.05			0.0006	0.04					1.08	4.16	4.42	40.68
Shahbaz [26]	298.15-338.15	1000	1.40	0.13												
Shazbaz [27]	298.15		1.73	0.15			0.0039	0.27								
Troter [28]	293.15-338.15	350	11.27	1.03			0.0168	1.14					9.20	30.37	3.78	32.55
Yadav [29]	283.15-333.15		1.70	0.15												

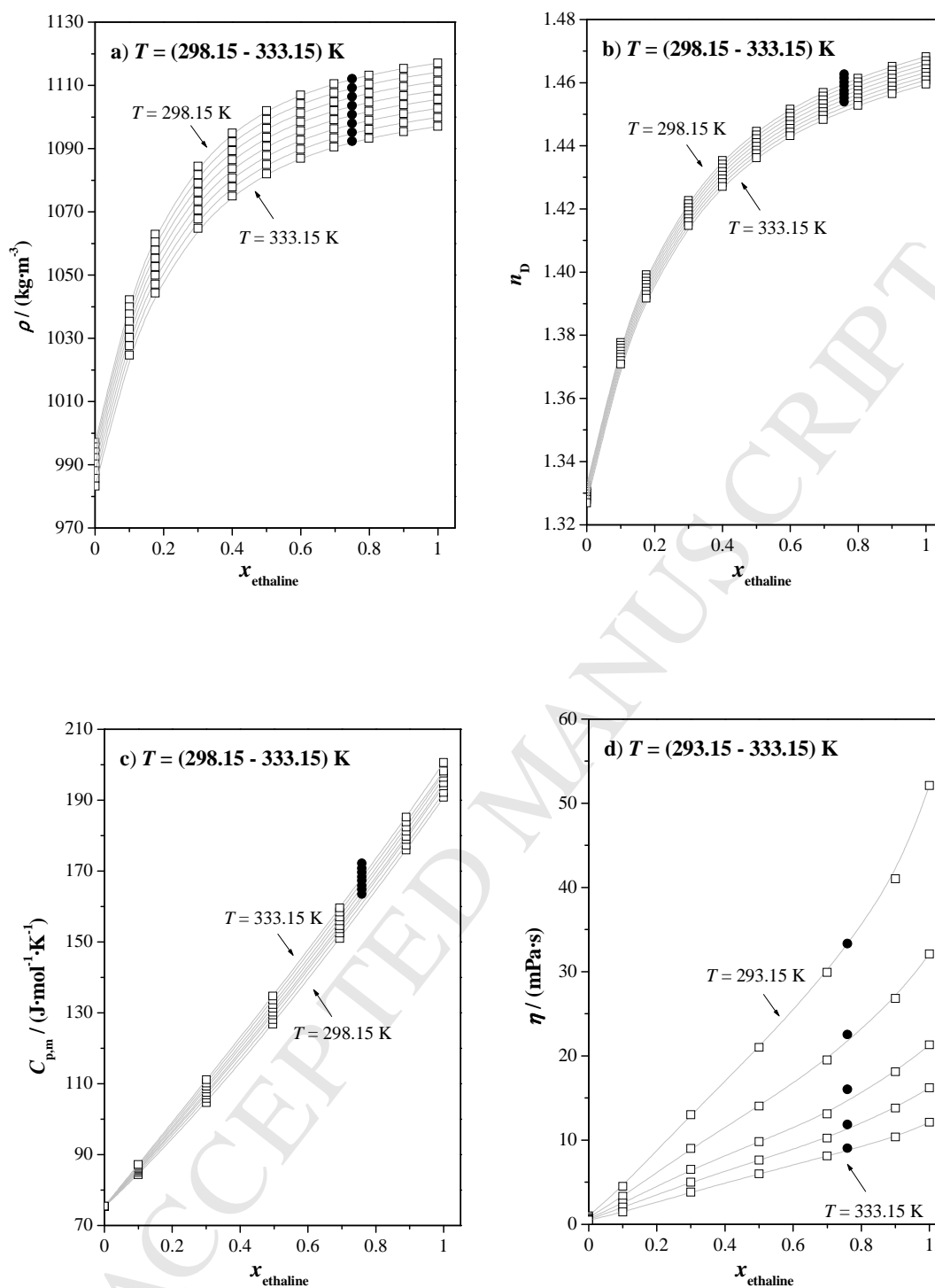


Fig. 8. Comparison of thermophysical properties between this work (●) and literature data (□) for EthaW: (a) Density, ρ , ref. [21]; (b) refractive index, n_D , ref. [21]; (c) isobaric molar heat capacity, $C_{p,m}$, ref. [19]; and (d), dynamic viscosity, η , ref. [40].

4. Conclusions

We have performed a comprehensive study of the thermophysical behaviour of (choline chloride + ethylene glycol) and (choline chloride + ethylene glycol + water). The composition, in molar ratio, was 1:2 and 1:2:1, respectively. The studied properties (density, speed of sound, refractive index, surface tension, isobaric molar heat capacity, viscosity and electrical conductivity) were measured in a wide range of temperatures (278.15-338.15) K at a pressure of 0.1 MPa. Several volumetric, surface and transport properties related to experimental properties were calculated. Taking into account all of the results, we can conclude that water inclusion does not significantly modify the internal structure of the anhydrous solvent, although it has an important effect on the transport properties. Additionally, we see that the intermolecular interactions are stronger when glycerol is the donor group.

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Highlights

Ethaline is a deep eutectic solvent made of choline chloride and ethylene glycol.

The mole ratio of ethaline is choline chloride:ethylene glycol; 1:2.

An analysis of the thermophysical properties of ethaline has been performed.

A mixture of ethaline and water was also prepared and characterized.

The results are discussed in terms of the water inclusion effect.