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Density, Speed of Sound, Viscosity, Refractive Index, and Excess Volume of *N*-Methyl-2-pyrrolidone (NMP) + Water + Ethanol from *T* = (293.15 to 323.15) K

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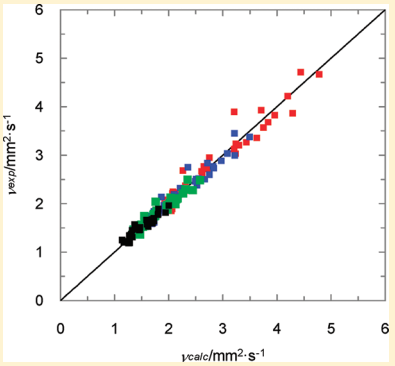
Supporting Information

ABSTRACT: The present work analyzes the composition and temperature influence upon different physical properties (density, speed of sound, viscosity, and refractive index) corresponding to the ternary mixture *N*-methyl-2-pyrrolidone (NMP) + water + ethanol. The influence of composition has been evaluated over the entire mole fraction range. In relation with the influence of temperature, the studied range was (293.15 to 323.15) K. Also, excess volume and isentropic compressibility deviations have been calculated on the basis of density and speed of sound values.



INTRODUCTION

Short chain *N*-alkyl-2-pyrrolidones are used as cosolvents in the petroleum industry to increase the selectivity and solvent efficiency for extracting aromatic hydrocarbons. These cyclic amides have excellent thermal and chemical stability, and they are used as absorbents of sour gases from crude natural gas or entrainers to alter the separation factor in distillation processes.[1]

These pyrrolidones are also used in pharmaceutical formulations and in the administration of therapeutic agents to the bloodstream painlessly in a controlled manner because they enhance the transdermal transport of drugs. The composition of a percutaneously administrable drug includes, between other components, a lower molecular weight alcohol (i.e., ethanol), a humectant substance, water, abirritant, and an absorption promoter, like *N*-methyl-2-pyrrolidone (NMP).[2]

The knowledge of physical properties of the system cyclic amides + water + ethanol over the entire composition range and at different temperatures is highly useful to understand some interfacial phenomena. For example, viscosity plays an important role regarding the behavior and hydrodynamics in mass transfer operations.[3,4] Previous studies have studied different physical properties and analyze the interaction between amides and water[5,6] concluded that strong *N*-methyl-2-pyrrolidone-water interactions are observed, with the formation of a variety of aggregates. Also the speed of sound data showed the formation of clathrate-like structures.[5] These experimental results are in agreement with previous studies developed by our research team about binary mixtures of *N*-methyl-2-pyrrolidone.[7]

The present work shows the behavior of different physicochemical properties (density, viscosity, speed of sound, and refractive index) and excess volume for *N*-methyl-2-pyrrolidone + ethanol + water at different temperatures and over the entire composition range to study the influence of composition and temperature and the role of the substituent.

EXPERIMENTAL SECTION

Materials. Reagents employed in present work are included in Table 1. Bidistilled water was used to prepare aqueous mixtures.

Table 1. Sample Description Table

chemical name	source	initial mole fraction purity
NMP[a]	Fluka	≥0.99
ethanol	Sigma-Aldrich	≥0.995

[a]*N*-methyl-2-pyrrolidone.

All solutions were prepared by mass using an analytical balance (Kern 770) with a precision of 10^{-4} g. The uncertainty in the mole fraction for prepared sample solutions was found to be ± 0.0007.

Methods. *Density and Speed of Sound.* The density of pure components and the mixtures of different compounds were measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer. The uncertainty in the density and speed of sound measurements was ± $2 \cdot 10^{-4}$ g·cm^{-3} and ± 0.7 m·s^{-1}, respectively.

Viscosity. The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary viscosimeter

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Table 2. Comparison between Density ρ, Speed of Sound c, Viscosity η, and Refractive Index n_D, Experimental and Literature Data for Pure Components at T = 298.15 K at p = 10^5 Pa[a]

	NMP		water		ethanol	
	lit.	exptl	lit.	exptl	lit.	exptl
ρ/g·cm^{-3}	1.02831[5]	1.0283	0.99705[8]	0.99706	0.78522[11]	0.78521
c/m·s^{-1}	1545.1[5]	1545.2	1497[9]	1496.7	1143.49[12]	1144.2
η/mPa·s	1.663[5]	1.681	0.890[8]	0.891	1.082[8]	1.091
n_D	1.4675[5]	1.4680	1.33248[10]	1.3324	1.35922[10]	1.3595

[a]Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 20 Pa, $u(x)$ = 0.0007, and the combined expanded uncertainties U_c (level of confidence = 0.95, k = 2) are $U_c(\rho)$ = 2·10^{-4} g·cm^{-3}, $U_c(c)$ = 0.7 m·s^{-1}, $U_c(\eta)$ = 0.0026 mPa·s, and $U_c(n_D)$ = 1.4·10^{-4}.

Table 3. Density ρ for the System *N*-Methyl-2-pyrrolidone (1) + Water (2) + Ethanol (3) from T = (293.15 to 323.15) K at p = 10^5 Pa[a]

x_1	x_2	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		ρ/g·cm^{-3}			
0.0999	0.8008	0.99884	0.99085	0.98261	0.97413
0.1008	0.6993	0.96942	0.96091	0.95218	0.94327
0.1005	0.6137	0.94124	0.93253	0.92353	0.91438
0.1003	0.4993	0.91666	0.90777	0.89869	0.88939
0.0996	0.4013	0.89591	0.88700	0.87791	0.86860
0.0995	0.3010	0.87262	0.86371	0.85463	0.84535
0.0994	0.2038	0.86013	0.85127	0.84224	0.83301
0.0996	0.1038	0.84483	0.83602	0.82707	0.81793
0.2004	0.6997	1.01446	1.00476	0.99606	0.98677
0.2004	0.5987	0.98480	0.97571	0.96646	0.95702
0.1993	0.5013	0.95879	0.94973	0.94047	0.93104
0.1995	0.4003	0.93561	0.92655	0.91733	0.90793
0.1993	0.3010	0.91504	0.90603	0.89687	0.88753
0.2001	0.1986	0.89651	0.88757	0.87848	0.86923
0.1997	0.1019	0.88034	0.87145	0.86243	0.85326
0.2994	0.6010	1.02134	1.01206	1.00263	0.99307
0.2997	0.5007	0.99398	0.98476	0.97540	0.96588
0.2999	0.4008	0.96984	0.96070	0.95141	0.94197
0.2978	0.3042	0.94830	0.93923	0.93002	0.92067
0.2997	0.2020	0.92891	0.91991	0.91079	0.90153
0.2981	0.1063	0.91157	0.90262	0.89356	0.88438
0.3992	0.5016	1.02360	1.01430	1.00489	0.99534
0.4010	0.3992	0.99856	0.98937	0.98005	0.97061
0.3997	0.3017	0.97691	0.96781	0.95859	0.94924
0.3963	0.2058	0.97656	0.96745	0.95823	0.94889
0.3989	0.1002	0.95667	0.94764	0.93851	0.92926
0.4997	0.4023	1.02378	1.01457	1.00525	0.99583
0.5004	0.2986	1.00065	0.99154	0.98233	0.97302
0.5011	0.1987	0.98047	0.97144	0.96231	0.95310
0.4998	0.1006	0.96207	0.95308	0.94402	0.93488
0.5991	0.3013	1.02228	1.01316	1.00397	0.99468
0.5971	0.2020	1.00162	0.99258	0.98347	0.97428
0.5995	0.0990	0.98332	0.97433	0.96528	0.95618
0.6959	0.2032	1.02097	1.01193	1.00284	0.99369
0.6940	0.1084	1.00295	0.99397	0.98493	0.97585
0.8043	0.0949	1.01941	1.01044	1.00144	0.99240

Table 4. Speed of Sound c for the System *N*-Methyl-2-pyrrolidone (1) + Water (2) + Ethanol (3) from T = (293.15 to 323.15) K at p = 10^5 Pa[a]

x_1	x_2	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		c/m·s^{-1}			
0.0999	0.8008	1680.4	1649.7	1618.7	1587.3
0.1008	0.6993	1593.1	1561.2	1529.0	1495.7
0.1005	0.6137	1515.7	1482.9	1450.0	1416.3
0.1003	0.4993	1448.2	1415.0	1381.0	1346.8
0.0996	0.4013	1394.2	1360.1	1326.0	1291.6
0.0995	0.3010	1333.7	1299.4	1264.8	1230.2
0.0994	0.2038	1303.5	1269.0	1234.4	1199.9
0.0996	0.1038	1263.9	1229.7	1195.2	1160.9
0.2004	0.6997	1683.4	1648.5	1611.5	1574.9
0.2004	0.5987	1595.0	1559.6	1523.1	1486.9
0.1993	0.5013	1523.0	1487.7	1451.9	1415.7
0.1995	0.4003	1461.0	1425.9	1390.1	1354.5
0.1993	0.3010	1407.7	1372.8	1337.2	1301.7
0.2001	0.1986	1360.8	1325.7	1290.3	1255.1
0.1997	0.1019	1320.9	1285.8	1250.4	1215.6
0.2994	0.6010	1663.9	1626.1	1587.5	1549.4
0.2997	0.5007	1585.9	1549.2	1511.4	1473.8
0.2999	0.4008	1519.8	1483.7	1447.1	1410.0
0.2978	0.3042	1464.1	1428.1	1392.0	1355.5
0.2997	0.2020	1414.6	1378.8	1342.8	1307.0
0.2981	0.1063	1372.4	1336.5	1300.5	1265.0
0.3992	0.5016	1640.5	1602.2	1563.3	1524.7
0.4010	0.3992	1570.0	1532.6	1494.4	1456.9
0.3997	0.3017	1512.6	1475.7	1439.7	1404.1
0.3963	0.2058	1511.8	1475.0	1437.6	1400.6
0.3989	0.1002	1461.6	1425.0	1388.4	1352.1
0.4997	0.4023	1615.4	1577.1	1538.7	1499.6
0.5004	0.2986	1553.0	1515.4	1477.5	1439.7
0.5011	0.1987	1500.8	1463.7	1426.5	1389.2
0.4998	0.1006	1455.5	1418.7	1381.8	1345.2
0.5991	0.3013	1591.3	1553.2	1514.9	1476.7
0.5971	0.2020	1537.9	1500.1	1462.5	1425.0
0.5995	0.0990	1491.8	1454.4	1417.1	1379.6
0.6959	0.2032	1491.8	1454.4	1417.1	1379.6
0.6940	0.1084	1571.6	1488.3	1450.9	1413.4
0.8043	0.0949	1552.9	1514.6	1477.3	1440.5

supplied by Schott, capillary no. I, (0.63 ± 0.01) mm internal diameter, and K = 0.01013 mm^2·s^{-1}, using eq 1.

$$\nu = K(t - \theta) \quad (1)$$

where t is the efflux time; K is the characteristic constant of the capillary viscometer; and θ is a correction value to correct end effects. Both parameters were obtained from the capillaries supplier (Schott). An electronic stopwatch with an accuracy of ± 0.01 s was used to measure efflux times. In the measurements, a Schott-Geräte AVS 350 Ubbelohde viscometer was used. Each measurement was repeated at least five times, and the uncertainty of this measurement is ± 0.0024 mm^2·s^{-1}. The dynamic viscosity (η) was obtained from the product of the kinematic viscosity (ν) and the corresponding density (ρ) of

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Table 5. Viscosity η for the System *N*-Methyl-2-pyrrolidone (1) + Water (2) + Ethanol (3) from T = (293.15 to 323.15) K at $p = 10^5$ Pa[a]

x_1	x_2	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		η/mPa·s			
0.0999	0.8008	3.888	2.726	2.005	1.527
0.1008	0.6993	3.807	2.726	2.023	1.569
0.1005	0.6137	3.463	2.546	1.933	1.534
0.1003	0.4993	3.076	2.357	1.788	1.416
0.0996	0.4013	2.715	2.109	1.644	1.326
0.0995	0.3010	2.572	2.005	1.586	1.280
0.0994	0.2038	2.038	1.676	1.351	1.138
0.0996	0.1038	1.756	1.457	1.209	1.022
0.2004	0.6997	4.781	3.465	2.484	1.865
0.2004	0.5987	4.155	2.959	2.216	1.706
0.1993	0.5013	3.422	2.629	1.984	1.579
0.1995	0.4003	2.925	2.278	1.768	1.424
0.1993	0.3010	2.484	1.964	1.567	1.289
0.2001	0.1986	2.057	1.676	1.376	1.143
0.1997	0.1019	1.735	1.442	1.203	1.033
0.2994	0.6010	4.765	3.416	2.489	1.945
0.2997	0.5007	3.801	2.841	2.158	1.708
0.2999	0.4008	3.136	2.405	1.876	1.528
0.2978	0.3042	2.584	2.028	1.625	1.342
0.2997	0.2020	2.094	1.707	1.402	1.181
0.2981	0.1063	1.723	1.460	1.218	1.050
0.3992	0.5016	3.955	3.036	2.287	1.808
0.4010	0.3992	3.198	2.490	1.965	1.574
0.3997	0.3017	2.704	2.089	1.716	1.431
0.3963	0.2058	2.619	2.066	1.670	1.375
0.3989	0.1002	2.115	1.743	1.447	1.225
0.4997	0.4023	3.343	2.538	2.012	1.634
0.5004	0.2986	2.668	2.169	1.732	1.433
0.5011	0.1987	2.144	1.756	1.467	1.260
0.4998	0.1006	1.781	1.539	1.286	1.114
0.5991	0.3013	2.686	2.147	1.743	1.452
0.5971	0.2020	2.231	1.836	1.541	1.312
0.5995	0.0990	1.837	1.541	1.329	1.153
0.6959	0.2032	2.292	1.866	1.561	1.331
0.6940	0.1084	1.939	1.611	1.384	1.192
0.8043	0.0949	1.903	1.604	1.373	1.194

Table 6. Refractive Index n_D for the System *N*-Methyl-2-pyrrolidone (1) + Water (2) + Ethanol (3) from T = (293.15 to 323.15) K at $p = 10^5$ Pa[a]

x_1	x_2	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		n_D			
0.0999	0.8008	1.3940	1.3915	1.3887	1.3878
0.1008	0.6993	1.3944	1.3912	1.3888	1.3867
0.1005	0.6137	1.3928	1.3895	1.3869	1.3857
0.1003	0.4993	1.3913	1.3877	1.3846	1.3819
0.0996	0.4013	1.3891	1.3855	1.3822	1.3799
0.0995	0.3010	1.3870	1.3833	1.3800	1.3772
0.0994	0.2038	1.3848	1.3810	1.3773	1.3747
0.0996	0.1038	1.3824	1.3785	1.3747	1.3719
0.2004	0.6997	1.4198	1.4164	1.4135	1.4097
0.2004	0.5987	1.4164	1.4130	1.4096	1.4070
0.1993	0.5013	1.4126	1.4089	1.4059	1.4038
0.1995	0.4003	1.4095	1.4054	1.4020	1.3999
0.1993	0.3010	1.4055	1.4018	1.3985	1.3957
0.2001	0.1986	1.4021	1.3984	1.3948	1.3923
0.1997	0.1019	1.3989	1.3951	1.3919	1.3890
0.2994	0.6010	1.4352	1.4316	1.4283	1.4247
0.2997	0.5007	1.4305	1.4267	1.4233	1.4199
0.2999	0.4008	1.4258	1.4220	1.4187	1.4155
0.2978	0.3042	1.4215	1.4174	1.4137	1.4094
0.2997	0.2020	1.4177	1.4136	1.4099	1.4057
0.2981	0.1063	1.4135	1.4092	1.4056	1.4026
0.3992	0.5016	1.4449	1.4411	1.4375	1.4335
0.4010	0.3992	1.4397	1.4358	1.4321	1.4281
0.3997	0.3017	1.4347	1.4307	1.4266	1.4227
0.3963	0.2058	1.4298	1.4259	1.4221	1.4194
0.3989	0.1002	1.4255	1.4214	1.4182	1.4159
0.4997	0.4023	1.4516	1.4478	1.4438	1.4398
0.5004	0.2986	1.4460	1.4426	1.4385	1.4341
0.5011	0.1987	1.4411	1.4370	1.4330	1.4292
0.4998	0.1006	1.4364	1.4322	1.4285	1.4242
0.5991	0.3013	1.4561	1.4522	1.4480	1.4438
0.5971	0.2020	1.4507	1.4466	1.4425	1.4388
0.5995	0.0990	1.4459	1.4418	1.4377	1.4338
0.6959	0.2032	1.4592	1.4552	1.4513	1.4471
0.6940	0.1084	1.4543	1.4502	1.4463	1.4422
0.8043	0.0949	1.4621	1.4580	1.4539	1.4497

the mixture, in terms of eq 2 for each mixture composition and with a uncertainty of ± 0.0026 mPa·s.

$$\eta = \nu \cdot \rho \tag{2}$$

Refractive Index. The refractive index was determined using an Atago RX-5000 refractometer. Before measurements, the refractometer was calibrated using distilled water in accordance with the instrument instructions. The mixtures were directly injected from the stock solution stored at work temperature to avoid evaporation. The refractive index measurements were done after the liquid mixtures attained the constant temperature of the refractometer. This procedure was repeated at least three times, and the uncertainty of the measurement was ± $1.3 \cdot 10^{-4}$. The average of these readings was taken for the refractive index values.

RESULTS AND DISCUSSION

Table 2 shows a comparison between experimental data for density, speed of sound, viscosity, and refractive index obtained in present work and literature data for pure components, to confirm the purity of components and procedures to physical properties determination.

The present work analyzes the influence of mixture composition and temperature upon the density, speed of sound, viscosity, and refractive index of ternary systems formed by NMP (1) + ethanol (2) + water (3), at temperatures from (293.15 to 323.15) K, and the experimental results are listed in Tables 3 to 6.

In Table 3, density data of the NMP + ethanol + water mixture are shown for the entire range of composition and different temperatures analyzed in present study. With regard to ternary mixture density data, the value of this physical property increases when the *N*-methyl-2-pyrrolidone and water concentration increases in the system. A maximum inside the triangular diagram does not exist, and it is located in the axis corresponding to the *N*-methyl-2-pyrrolidone + water binary mixture.[7,13]

The speed of sound determined experimentally in the present study is shown in Table 4. Figure 1 shows the influence of mixture composition upon the value of the speed of sound,

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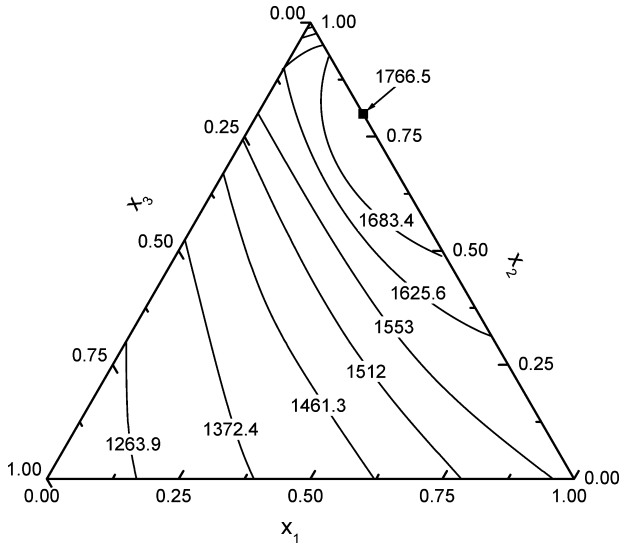

Figure 1. Speed of sound c for the system *N*-methyl-2-pyrrolidone (1) + water (2) + ethanol (3) at T = 293.15 K. Solid lines are speed of sound isolines.

by means of constant speed of sound isolines. As in the case of density, the maximum in the value of speed of sound is reached in the axis corresponding to NMP + water mixture, as can be observed in this figure.[7] The isolines indicate that the speed of sound increases when the presence of water or NMP increases in the mixture.

With regard to the influence of concentration and temperature upon the value of viscosity, Table 5 shows the experimental data. In Figure 2 the behavior obtained for the

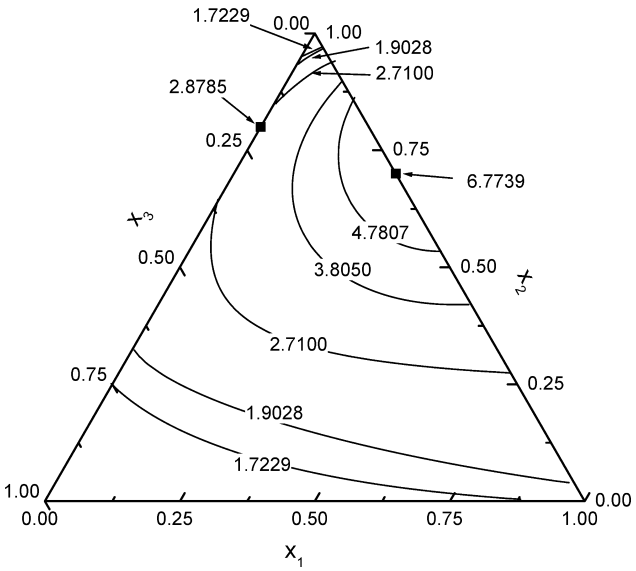

Figure 2. Viscosity η for the system *N*-methyl-2-pyrrolidone (1) + water (2) + ethanol (3) at T = 293.15 K. Solid lines are viscosity isolines.

influence of composition over the value of viscosity is shown. This behavior is similar to the corresponding one commented previously for the speed of sound, thus observing a maximum for the value of speed of sound in the NMP + water binary mixture. A continued increase toward that maximum, from any part of the triangular diagram, is observed. The minimum value of viscosity corresponds for pure ethanol.

The last analyzed property in the present study for this ternary system has been the refractive index. The same treatment and determination of experimental data has been made, and in Table 6 the experimental results are shown. Figure 3 shows, in the same way that for the physical properties

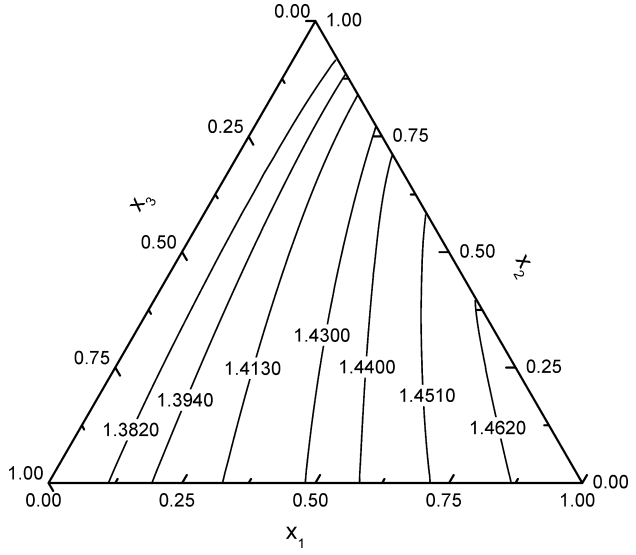

Figure 3. Refractive index n_D for the system *N*-methyl-2-pyrrolidone (1) + water (2) + ethanol (3) at T = 293.15 K. Solid lines are refractive index isolines.

analyzed previously, the influence of ternary mixture composition. The behavior is simpler than the previously analyzed ones for the speed of sound and viscosity and is relatively similar to the observed for the density, although in this case the maximum value for refractive index is for the pure NMP.

Regarding the influence of temperature over the analyzed physical properties in present study, the experimental values included in Tables 3 to 6 allow us to observe that, as the temperature increases, a decrease in all physical properties is produced.

In the case of the viscosity, and according to the literature, the kinematic viscosity/composition values were fitted using the extended McAllister three-body model that is given by the following equation (eq 3).[13]

$$\begin{aligned}\ln \nu = {} & x_1^3\cdot\ln \nu_1 + x_2^3\cdot\ln \nu_2 + x_3^3\cdot\ln \nu_3 + 3x_1^2\cdot x_2\cdot\ln \nu_{12} \\ & + 3x_1^2\cdot x_3\cdot\ln \nu_{13} + 3x_2^2\cdot x_1\cdot\ln \nu_{21} + 3x_2^2\cdot x_3\cdot\ln \nu_{23} \\ & + 3x_3^2\cdot x_1\cdot\ln \nu_{31} + 3x_3^2\cdot x_2\cdot\ln \nu_{32} + 6x_1\cdot x_2\cdot x_3\cdot \\ & \ln \nu_{123} - \ln(x_1\cdot M_1 + x_2\cdot M_2 + x_3\cdot M_3) + x_1^3\cdot\ln M_1 \\ & + x_2^3\cdot\ln M_2 + x_3^3\cdot\ln M_3 + 3x_1^2\cdot x_2\cdot\ln\left[\frac{2\cdot M_1 + M_2}{3}\right] \\ & + 3\cdot x_1^2\cdot x_3\cdot\ln\left[\frac{2\cdot M_1 + M_3}{3}\right] + 3\cdot x_2^2\cdot x_1\cdot \\ & \ln\left[\frac{2\cdot M_2 + M_1}{3}\right] + 3x_2^2\cdot x_3\cdot\ln\left[\frac{2\cdot M_2 + M_3}{3}\right] \\ & + 3\cdot x_3^2\cdot x_1\cdot\ln\left[\frac{2M_3 + M_1}{3}\right] + 3\cdot x_3^2\cdot x_2\cdot \\ & \ln\left[\frac{2\cdot M_3 + M_2}{3}\right] + 6x_1\cdot x_2\cdot x_3\cdot\ln\left[\frac{M_1 + M_2 + M_3}{3}\right] \end{aligned} \quad (3)$$

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where x_1, x_2, and x_3 are the mole fractions of components 1, 2, and 3 in a ternary mixture, respectively, M_1, M_2, and M_3 are their molecular weights, and ν_1 , ν_2, ν_3, and ν are the kinematic viscosities of the pure components and the liquid mixture, respectively. There are six binary parameters ν_{12}, ν_{21}, ν_{13}, ν_{31}, ν_{23}, and ν_{32} and one ternary parameter, ν_{123}.

The adjustable parameters for this model were determined by fitting experimental viscosity−composition data ,and Table 7

Table 7. Fit Parameters of the McAllister Three-Body Equation

parameters	T/K			
$10^6/m^2 \cdot s^{-1}$	293.15	303.15	313.15	323.15
	McAllister Parameters			
ν_{12}	1.066	0.954	0.911	0.882
ν_{21}	2.422	2.101	1.789	1.494
ν_{13}	64.14	38.17	21.24	13.55
ν_{31}	9.602	6.253	4.459	3.308
ν_{23}	2.573	2.137	1.808	1.709
ν_{32}	3.137	2.677	2.151	1.874
ν_{123}	1.141	0.945	0.829	0.689
σ	0.18	0.16	0.15	0.14

shows the fitting parameters corresponding to the McAllister model. The standard deviations σ had been calculated (using eq 4), and they are presented in the tables.

$$\sigma = \left(\frac{\sum_i (z_{exp} - z_{calc})^2}{n_{data} - 1} \right)^{1/2} \quad (4)$$

where z_{exp} and z_{calc} are the experimental and calculated values and n_{data} is the number of experimental points.

The excess molar volumes of mixtures V^E were calculated from density measurements by applying eq 5.

$$V^E = \sum_{i=1}^{3} x_i \cdot M_i \cdot (\rho^{-1} - \rho_i^{-1}) \quad (5)$$

where x_i, M_i, and ρ_i are the mole fractions, molecular weights, and densities of pure components, respectively.

The calculated data for the excess volume for the ternary system analyzed in this study are shown in the Supporting Information (Table S1). In all cases, the excess volume takes negative values, which is in agreement with previous studies,[8,14,15] which have analyzed individually the binary mixtures formed by the components used in this work. In all cases, an increase in temperature value produces a decrease in the value of excess volume. The values for this parameter observed in this system suggest that the structures of this system are more compact than in the pure state. The negative partial excess molar volumes may be taken either as a sign of strong solvation by H-bonding, mainly between NMP and water molecules.

The molar excess volume data for the ternary system were correlated with the composition data using the Redlich−Kister equation for ternary systems (eq 6).

$$\Delta V^E_{123} = \Delta V^E_{12} + \Delta V^E_{13} + \Delta V^E_{23} + x_1 \cdot x_2 \cdot x_3 \cdot (C_1 + C_2 \cdot x_1 + C_3 \cdot x_2) \quad (6)$$

where ΔV^E_{123} is the deviation considered, x_i is the mole fraction of component i, and ΔV^E_{ij} is the value of the Redlich−Kister polynomial for the same property fitted to the data for the corresponding binary system. Fitting parameters are included in Table 8. ΔV^E_{ij} of these properties was calculated using experimental data for molar excess volume from literature[7,8] using eq 7.

$$\Delta Y = x_1 x_2 \sum_{j=1}^{4} q_j x_2^{(j-1)/2} \quad (7)$$

where q_j are fitting parameters.

The experimental data of speed of sound and density were used to calculate isentropic compressibility (κ_s) using the Laplace equation (eq 8). The excess isentropic compressibility was calculated using eq 9.[16]

$$\kappa_s = \frac{1}{\rho \cdot c^2} \quad (8)$$

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (9)$$

where κ_s^E is the excess isentropic compressibility and κ_s and κ^{id} are the isentropic compressibility of the ternary mixture and the ideal contribution, respectively. The last parameter has been calculated by eq 10.

$$\kappa_s^{id} = \sum_{i=1}^{3} \varphi_i \cdot \left[\kappa_{si} + T \cdot V_i \cdot \frac{\alpha_i^2}{C_{pi}} \right] - \left[\frac{T \cdot (\sum_{i=1}^{3} x_i \cdot V_i)(\sum_{i=1}^{3} \varphi_i \cdot \alpha_i)^2}{(\sum_{i=1}^{3} x_i \cdot C_{pi})} \right] \quad (10)$$

where ϕ_i is the ideal state volume fraction, α_i is the isobaric thermal expansion coefficient, C_{pi} is the molar heat capacity, T is the temperature, x_i is the mole fraction, and V_i is the molar volume. The molar heat capacity for substances used in this work was obtained from literature.[17,18] The ideal state volume fraction was calculated using eq 11.

$$\varphi_i = \frac{x_i \cdot V_i}{(\sum_{i=1}^{3} x_i \cdot V_i)} \quad (11)$$

Calculated data for isentropic compressibility and its excess are included in the Supporting Information section (Tables 2 and 3). The negative values for excess isentropic compressibility are in agreement with the previously commented behavior of excess molar volume (the existence of specific interactions between mixture molecules).

Table 8. Fit Coefficients C_j of Equation 4 for the Molar Excess Volume

parameter	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
$C_1/mol \cdot cm^{-3}$	−10.4	−11.59	−12.23	−12.73
$C_2/mol \cdot cm^{-3}$	0.44	0.46	0.37	0.19
$C_3/mol \cdot cm^{-3}$	18.24	20.64	21.93	22.73

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CONCLUSIONS

Different physical properties (density, speed of sound, viscosity, and refractive index) were measured for the system NMP + water + ethanol over the entire composition range. Density increases with NMP concentration, and a maximum value is reached for a binary mixture of NMP and water. A similar behavior was observed for speed of sound and viscosity data, caused by the high interactions between NMP and water molecules. The refractive index shows a different behavior with a maximum value corresponding to pure NMP. Excess molar volumes shows negative values with large deviations that indicate the important interaction by means of hydrogen bonds.

ASSOCIATED CONTENT

Supporting Information

Calculated data for the excess volume, isentropic compressibility, and excess isentropic compressibility for the ternary system (Tables S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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