Influence of Temperature and Composition upon Density, Viscosity, Speed of Sound, and Refractive Index of Aqueous Solutions of 1-Ethyl-2-pyrrolidinone

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Experimental density, viscosity, speed of sound, and refractive index for aqueous solutions of 1-ethyl-2-pyrrolidinone were measured over the entire composition range and at different temperatures (293 to 323) K. Excess properties and deviations have been calculated, and their dependence on composition was mathematically represented by a Redlich−Kister-type equation. The hydration of pyrrolidinone molecules plays an important role in the thermophysical behavior of this mixture.

Introduction

Short chain *N*-alkyl-2-pyrrolidinones are completely miscible over the entire composition range with water. They have been used as cosolvents in the petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbons. These pyrrolidinones 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. These cyclic amides have excellent thermal and chemical stability, and they are used as absorbents of sour gases from crude natural gas or entrainer to alter the separation factor in distillation process.[1]

The knowledge of physical properties of the systems water + cyclic amides 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.[2,3]

Previous studies have analyzed other cyclic amides, such as 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, or 1-vinyl-2-pyrrolidinone,[4−7] with regard to different physicochemical properties, and the influence of the substituent upon the behavior obtained for different properties and excess parameters has been analyzed.

The present work shows the behavior of different physicochemical properties (density, viscosity, speed of sound, and refractive index) for 1-ethyl-2-pyrrolidinone + water at different temperatures and over the entire composition range to study the influence of composition and temperature and the role of substituent.

Experiments

Materials. 1-Ethyl-2-pyrrolidinone (CAS number: 2687-91-4) was supplied by Fluka with a mass fraction purity ≥ 0.98. All liquid mixtures were prepared by mass using an analytical balance (Kern 770). The uncertainty of the sample's preparation in mole fraction was ± 0.0006. Water contents were measured using a Karl Fischer titration method in a Metrohm 737 KF coulometer with a mass fraction of 0.001.

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Methods. Density and Speed of Sound. The densities of pure components and the mixture of different solutes 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 $\pm 1.6 \cdot 10^{-4}$ g·cm^{-3} and ± 0.29 m·s^{-1}, respectively.

Also, the adiabatic compressibility, κ_s, was calculated from speed of sound values and density values using the Laplace equation

$$\kappa_s = \frac{1}{u^2 \cdot \rho} \tag{1}$$

where u is the speed of sound and ρ is the density of the solution.

Viscosity. The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary viscosimeter supplied by Schott, capillary N° 0c, (0.46 ± 0.01) mm internal diameter, and $K = 0.003201$ mm^2·s^{-1}, using eq 2.

$$\nu = K \cdot (t - \theta) \tag{2}$$

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 5 times, and the uncertainty of this measurement is ± 0.0054 mm^2·s^{-1}. The dynamic viscosity (η) was obtained from the product of the kinematic viscosity (ν) and the corresponding density (ρ) of the mixture, in terms of eq 3 for each mixture composition.

$$\eta = \nu \cdot \rho \tag{3}$$

Refractive Index. Refractive index was determined using an Atago RX-5000 refractometer. Before measurements, the refractometer was calibrated using distilled−deionized 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

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Table 1. Density ρ for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from T = (293 to 323) K

	T/K				
x_2	293	298	303	313	323
			ρ/g·cm^{-3}		
0.000	0.99826	0.99710	0.99570	0.99226	0.98808
0.022	1.00349	1.00176	0.99983	0.99535	0.98991
0.050	1.01045	1.00734	1.00282	0.99746	0.99101
0.100	1.02031	1.01676	1.01312	1.00563	0.99784
0.200	1.02626	1.02182	1.01734	1.00828	0.99906
0.300	1.02390	1.01933	1.01471	1.00538	0.99592
0.400	1.02218	1.01658	1.01216	1.00182	0.99273
0.500	1.01916	1.01460	1.01000	1.00071	0.99130
0.600	1.01404	1.00945	1.00410	0.99500	0.98581
0.700	1.01043	1.00598	1.00150	0.99248	0.98337
0.800	1.00666	1.00226	0.99783	0.98894	0.97996
0.900	1.00319	0.99884	0.99448	0.98571	0.97689
1.000	1.00055	0.99624	0.99193	0.98326	0.97456

Table 2. Viscosity η for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from T = (293 to 323) K

	T/K				
x_2	293	298	303	313	323
			η/mPa·s		
0.000	1.0089	0.9029	0.8133	0.6693	0.5611
0.022	1.5929	1.4328	1.2544	0.9966	0.8044
0.050	2.3683	2.0469	1.7673	1.3272	1.0725
0.100	4.1492	3.4184	2.8424	2.0512	1.3582
0.200	6.1590	4.8491	4.0883	2.8787	2.1643
0.300	6.1891	5.0293	4.1638	2.9662	2.2344
0.400	5.3487	4.3860	3.6214	2.5998	2.0136
0.500	4.5060	3.8555	3.2798	2.5089	1.9864
0.600	3.6390	3.2444	2.8597	2.2618	1.8557
0.700	3.1303	2.8358	2.5274	2.0404	1.6701
0.800	2.6706	2.4297	2.2182	1.7765	1.5405
0.900	2.4578	2.2101	2.0113	1.7017	1.4348
1.000	2.1333	2.0220	1.8321	1.6213	1.3582

Table 3. Speed of Sound u for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from T = (293 to 323) K

	T/K				
x_2	293	298	303	313	323
			u/m·s^{-1}		
0.000	1482.72	1496.94	1509.36	1529.06	1542.73
0.022	1574.75	1579.97	1583.92	1588.33	1588.35
0.050	1651.86	1648.90	1645.06	1634.83	1622.28
0.100	1711.89	1699.44	1686.65	1660.41	1633.15
0.200	1712.15	1694.15	1675.85	1639.14	1602.06
0.300	1677.60	1658.56	1639.26	1600.65	1561.88
0.400	1640.39	1621.15	1601.66	1562.77	1523.70
0.500	1610.72	1591.48	1572.12	1533.29	1494.43
0.600	1583.14	1563.96	1544.64	1505.96	1467.52
0.700	1562.07	1542.94	1523.64	1485.26	1447.09
0.800	1541.71	1522.58	1503.38	1465.20	1427.34
0.900	1526.12	1507.05	1487.86	1449.87	1412.23
1.000	1511.62	1492.47	1473.32	1435.35	1397.96

was $\pm$ 1.3·10^{-4}. The average of these readings was taken for the refractive index values.

Results and Discussion

The present work analyzes the influence of mixture composition and temperature upon density, viscosity, speed of sound, and refractive index of systems formed by water and 1-methyl-2-pyrrolidinone at temperatures from (293 to 323) K. Tables 1, 2, 3, and 4 show the value of these properties determined for all the compositions and temperatures employed in the present work.

The values obtained for the density of this system show that a maximum in the value of the density (see Figure 1) exists,

Table 4. Refractive Index n_D for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from T = (293 to 323) K

	T/K				
x_2	293	298	303	313	323
			n_D		
0.000	1.33298	1.33251	1.33191	1.33061	1.32902
0.022	1.35197	1.35144	1.34954	1.34880	1.34707
0.050	1.37085	1.37012	1.36940	1.36692	1.36431
0.100	1.39584	1.39478	1.39291	1.39022	1.38757
0.200	1.42603	1.42432	1.42304	1.41887	1.41711
0.300	1.44127	1.43983	1.43715	1.43310	1.42913
0.400	1.44975	1.44776	1.44605	1.44180	1.43762
0.500	1.45510	1.45307	1.45147	1.44694	1.44273
0.600	1.45859	1.45647	1.45435	1.45035	1.44622
0.700	1.46118	1.45900	1.45680	1.45270	1.44864
0.800	1.46326	1.46096	1.45860	1.45496	1.45075
0.900	1.46478	1.46230	1.46016	1.45641	1.45217
1.000	1.46461	1.46192	1.45791	1.45415	1.45147

which has not been observed in the water + 2-pyrrolidinone system,[4,5] but it has for the aqueous solutions of 1-methyl-2-pyrrolidinone.[5] Extending the alkyl chain, the maximum for the value of the density is located nearer to the water-rich region.

A similar behavior, in connection with the location of a maximum when the influence of the composition has been analyzed, was observed for other physical properties analyzed in the present study. About the value of the viscosity (see also Figure 1), a maximum is observed again at low composition of 1-ethyl-2-pyrrolidinone.[5] Moreover, similar behaviors have been observed for other aqueous systems in which molecules with amino groups[8,9] have been used.

In the same way, another physical property like the speed of sound shows a similar behavior for the two physical properties mentioned above (density and viscosity). For these physical properties, the maximum is located in values of similar mole fraction. Also, as it has been mentioned above, these behaviors are similar to results obtained by other authors for the system made up of water and 1-methyl-2-pyrrolidinone;[7] however, the maxima have greater magnitude and they are located in regions richer in water. This implies that the number of needed molecules of 1-ethyl-2-pyrrolidinone is lower than in the case of other pyrrolidinones, to generate the interactions which produce the presence of these maxima.

For the refractive index, a maximum is not observed, although a sudden increase in the value of this physical property is observed when small quantities of 1-ethyl-2-pyrrolidinone are added to the water up to values of composition similar to that before the presence of maxima

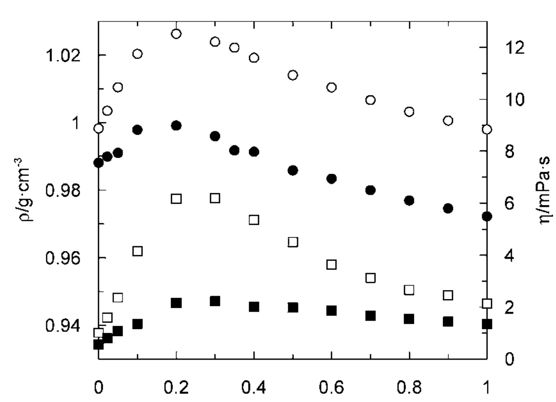

Figure 1. Influence of mixture composition and temperature upon density and viscosity for the water (1) + 1-ethyl-2-pyrrolidinone (2) system. Density: ○, T = 293 K; ●, T = 323 K. Viscosity: □, T = 293 K; ■, T = 323 K.

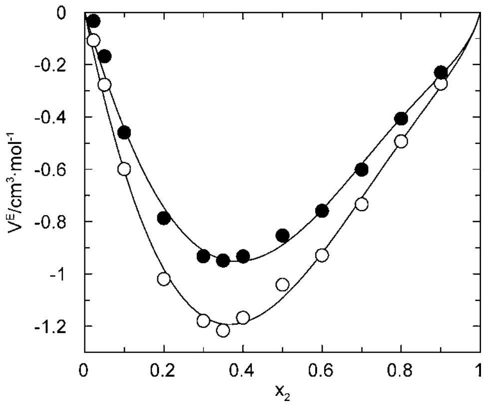

Figure 2. Excess molar volumes for the water (1) + 1-ethyl-2-pyrrolidinone (2) system. ○, $T = 293$ K; ●, $T = 323$ K. Solid lines correspond to the Redlich−Kister equation.

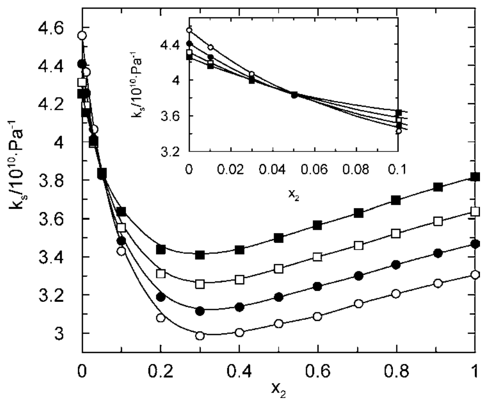

Figure 3. Influence of mixture composition and temperature upon isentropic compressibility for the water (1) + 1-ethyl-2-pyrrolidinone (2) system. ○, $T = 293$ K; ●, $T = 303$ K; □, $T = 313$ K; ■, $T = 323$ K.

in the different physical properties. Later, a slight influence of the pyrrolidinone concentration on the value of the refractive index was observed.

Another interesting aspect is the influence of temperature over the behavior of this system and over the different physical properties. For the density, viscosity, and refractive index, a constant decrease in the value of these physical properties is observed when temperature increases. In the case of speed of sound, a different and very characteristic behavior is observed. Depending on the mixture composition, a different type of influence of the temperature can be observed. So, for water-rich composition, an increase in the temperature produces an increase in the value of speed of sound too, whereas for values greater than 0.1 in molar fraction of 1-ethyl-2-pyrrolidinone, the behavior is the opposite. This kind of behavior has been observed before in other kinds of systems.[10]

To estimate the nonideality of these systems, the derived magnitudes and deviations were calculated for the physical properties analyzed in the present work, using eq 4.

$$\Delta Y = Y_\mathrm{m} - (x_1 \cdot Y_1 + x_2 \cdot Y_2) \qquad (4)$$

where Y_m is the value of the physical property considered for the mixture, and Y_1, Y_2, x_1, and x_2 are the values of the physical properties and mole fraction for pure components, respectively.

However, to calculate Δk_s, the following equations were used[11]

$$\Delta k_s = k_s - \sum_i \phi_i \cdot k_{si} \qquad (5)$$

$$\phi_i = \frac{x_i \cdot V_i}{\sum_i x_i \cdot V_i} \qquad (6)$$

where ϕ_i is the volume fraction for each component and V_i is the volume for pure components.

The behaviors of the excess volume (Figure 2), as well as regarding the obtained deviations, are in agreement with previous studies for other alkyl-pyrrolidinones.[6,7] The magnitude order for the excess volume agrees with these previous studies because the presence of the ethyl group (1-ethyl-2-pyrrolidinone) has a smaller effect on the decrease of the excess volume than the presence of a methyl group (1-methyl-2-pirrolidone).[7]

The negative deviations indicate that there are interactions among unlike molecules. On the basis of the deviation's sign and magnitude (large deviations), we consider that there are strong hydrogen bonding interactions in the mixtures studied in the present paper. Negative values for excess volume could be due to (i) the reaction between the water and pyrrolidinone compound where it is protoned and (ii) the reaction between two molecules of 1-ethyl-2-pyrrolidinone forming a positive and negative charged species.

The isentropic compressibilities of these aqueous mixtures have been determined using eq 1, and this system shows an interesting trend (see Figure 3). This kind of trend, as suggested by different authors,[12] holds over this very narrow interval of concentration where the compressibility isotherms cross one another and point to formation of a clathrate-like structure with the stoichiometry corresponding to the concentration at which

Table 5. Fit Parameters Corresponding to the Redlich−Kister Equation for Water (1) + 1-Ethyl-2-pyrrolidinone (2) from $T = (293$ to $323)$ K

	T/K				
parameter	293	298	303	313	323
			V^E/cm^3·mol^{-1}		
A_1	−1.26	1.41	3.56	3.85	5.17
A_2	−34.48	−44.93	−54.48	−52.27	−55.65
A_3	67.57	82.58	97.97	93.01	96.88
A_4	−35.14	−42.51	−50.67	−48.08	−49.74
σ	0.02	0.03	0.04	0.04	0.04
			$\Delta\eta$/mPa·s		
A_1	−5.82	5.44	5.76	9.97	5.70
A_2	274.10	156.67	121.36	46.55	34.80
A_3	−578.19	−351.31	−278.77	−126.78	−87.06
A_4	319.07	195.17	157.34	73.14	48.93
σ	0.10	0.08	0.08	0.07	0.07
			Δu/m·s^{-1}		
A_1	−401.92	−360.55	−321.23	−261.13	−211.15
A_2	1242.88	1112.07	985.18	809.86	668.91
A_3	−1391.83	−1238.37	−1086.06	−894.54	−743.12
A_4	543.59	480.72	417.05	343.44	285.68
σ	0.12	0.11	0.14	0.08	0.08
			Δn_D		
A_1	0.913	1.205	0.914	1.151	1.131
A_2	−1.243	−2.656	−1.249	−2.501	−2.441
A_3	0.137	2.302	0.102	2.091	2.013
A_4	0.345	−0.720	0.400	−0.597	−0.571
σ	0.001	0.001	0.003	0.001	0.001
			$\Delta k_s \cdot 10^{11}$/Pa^{-1}		
A_1	−42.22	−37.29	−32.61	−25.19	−18.87
A_2	133.42	117.45	101.99	79.37	60.51
A_3	−151.10	−134.01	−117.12	−95.07	−77.34
A_4	59.41	53.34	47.18	40.35	35.16
σ	0.009	0.009	0.010	0.011	0.014

the crossing occurs. The structure is relatively temperature-resistant, and consequently, the rigidity of mixture is almost independent of temperature. Attending to our results, this structure for water is created at molar fraction 0.05 (a proportion of approximately 19:1 molecules). It is possible to consider that the change observed for the structure of this kind of mixture produces the behavior observed for the different properties commented previously, as well as the important deviations obtained for each of them.

With regard to the values obtained for the other deviations obtained in the present study (viscosity, isentropic compressibility, and refractive index), positive deviations for viscosity and refractive index have been obtained like in previous studies,[8] whereas in the case of the isentropic compressibility, negative deviations have been obtained.

The values calculated for excess molar volumes, isentropic compressibility, and the viscosity and refractive index deviations were fitted using a Redlich−Kister type equation (eq 7). The results obtained for fitting parameters are shown in Table 5.

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

The Redlich−Kister equation fits satisfactorily (see Figure 2) the excess properties and all deviation values calculated from experimental data in the present work.

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Supporting Information Available:

Data of excess volume and isentropic compressibility deviation. This material is available free of charge via the Internet at http://pubs.acs.org.

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