JOURNAL OF CHEMICAL & ENGINEERING DATA

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Density, Speed of Sound, Refractive Index, Viscosity, Surface Tension, and Excess Volume of *N*-Methyl-2-pyrrolidone + 1-Amino-2-propanol {or Bis(2-hydroxypropyl)amine} from *T* = (293.15 to 323.15) K

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ABSTRACT: The density, speed of sound, refractive index, viscosity, and surface tension values of binary mixtures formed by *N*-methyl-2-pyrrolidone (NMP) + 1-amino-2-propanol (MIPA) {or bis(2-hydroxypropyl)amine (DIPA)} were determined at several temperatures from (293.15 to 323.15) K. The excess volumes were determined using the density values, and the calculated data have been fitted with a Redlich−Kister equation.

INTRODUCTION

The use of mixtures of two alkanolamines (mainly a tertiary alkanolamine with a primary or secondary alkanolamine) has also been proposed by different studies in the past few years, with the aim of substituting at the industrial level the aqueous solutions of a single alkanolamine for carbon dioxide capture.[1,2] To fully characterize the physicochemical behavior of new formulations of solvents, it is important to create a database on those thermophysical properties that are relevant for the design, operation, and optimization of acid gas treatment plants. 1-Amino-2-propanol (MIPA) and bis(2-hydroxypropyl)amine (DIPA) are considered in different studies[3−5] as interesting compounds for their presence in the liquid phase in absorption processes for acid gas separation.

The blend of this kind of alkanolamines in the presence of a physical solvent such as *N*-methyl-2-pyrrolidone (widely recommended for the acid gas capture process[6] by physical absorption) could be considered as an alternative way for capture and/or separation of acid gases with higher loading and selectivity than conventional processes.

In this work, several physical properties (density, speed of sound, refractive index, viscosity, and surface tension) of binary systems using blends of an amine and an amide, MIPA (or DIPA) with NMP, were measured over the temperature range employed in this work (293.15 to 323.15) K. Also, the present study includes the analysis of the influence of composition and temperature upon the previously commented physical properties.

EXPERIMENTAL SECTION

Materials. MIPA (CAS Registry No. 2799-16-8) was supplied by Merck, with a purity of ≥ 98 %; DIPA (CAS Registry No. 110-97-4) was supplied by Sigma Aldrich, with a purity of ≥ 98 %, and NMP (CAS No. 872-50-4) with a mass purity of ≥ 99 % was supplied by Fluka. The uncertainty of the samples preparation in mole fraction was ± 0.0008. Double-distilled water was used to prepare the amine aqueous solutions.

Methods. *Density and Speed of Sound.* The densities 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 $\pm\ 2\cdot10^{-4}\ g\cdot cm^{-3}$ and $\pm\ 1.3\ m\cdot s^{-1}$, respectively.

Viscosity. The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through capillary Ubbelohde viscosimeters supplied by Schott, capillary numbers I, Ia, Ic, and II, and using eq 1 for viscosity calculations on the basis of transit time.

$$\nu = K\cdot(t - \theta) \tag{1}$$

where t is the efflux time; K is the characteristic constant of the capillary viscosimeter; 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 viscosimeter was used. Each measurement was repeated at least five times, and the uncertainty of this measurement is $\pm\ 0.0024\ mm^2\cdot s^{-1}$. 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 2 for each mixture composition.

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

Refractive Index. 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

Received: February 1, 2011
Accepted: May 12, 2011
Published: May 18, 2011

Table 1. Density, ρ/g·cm^{-3}, of NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	0.9608	0.9528	0.9447	0.9365
0.1034	0.9682	0.9600	0.9517	0.9432
0.2008	0.9753	0.9669	0.9584	0.9498
0.3001	0.9828	0.9742	0.9656	0.9569
0.4002	0.9895	0.9808	0.9721	0.9633
0.4978	0.9965	0.9877	0.9788	0.9699
0.5943	1.0033	0.9945	0.9856	0.9767
0.7000	1.0109	1.0020	0.9931	0.9842
0.7993	1.0181	1.0092	1.0003	0.9914
0.8913	1.0250	1.0161	1.0072	0.9982
1.0000	1.0336	1.0247	1.0157	1.0068
		NMP (1) + DIPA (2)		
0.0000				0.9841
0.1049				0.9840
0.1898				0.9844
0.2764			0.9931	0.9851
0.3733			0.9945	0.9864
0.4695		1.0060	0.9978	0.9882
0.5721		1.0073	0.9989	0.9906
0.6754		1.0108	1.0023	0.9935
0.7804	1.0219	1.0134	1.0048	0.9968
0.8882	1.0268	1.0182	1.0094	1.0007
1.0000	1.0336	1.0247	1.0157	1.0068

Table 2. Speed of Sound, u/m·s^{-1}, of NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	1560.8	1528.3	1495.7	1462.9
0.1034	1553.5	1519.6	1486.0	1452.1
0.2008	1549.1	1514.7	1480.5	1446.0
0.3001	1547.5	1511.8	1476.6	1441.6
0.4002	1546.0	1510.0	1474.8	1440.5
0.4978	1546.2	1509.4	1472.8	1436.8
0.5943	1547.4	1510.3	1473.5	1436.8
0.7000	1550.9	1512.8	1475.4	1438.4
0.7993	1554.8	1516.8	1479.1	1441.7
0.8913	1559.4	1520.6	1482.6	1445.1
1.0000	1567.9	1529.7	1491.2	1454.6
		NMP (1) + DIPA (2)		
0.0000				1420.3
0.1049				1414.2
0.1898				1411.8
0.2764			1443.5	1412.2
0.3733			1445.0	1413.0
0.4695		1483.8	1450.8	1415.4
0.5721		1486.6	1453.3	1419.6
0.6754		1494.7	1460.3	1424.3
0.7804	1535.6	1499.4	1463.7	1428.6
0.8882	1548.8	1511.9	1474.9	1438.7
1.0000	1567.9	1529.7	1491.2	1454.6

Table 3. Refractive Index, n_D, of NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	1.4480	1.4442	1.4401	1.4360
0.1034	1.4503	1.4464	1.4423	1.4382
0.2008	1.4523	1.4484	1.4445	1.4401
0.3001	1.4545	1.4505	1.4464	1.4421
0.4002	1.4567	1.4527	1.4488	1.4442
0.4978	1.4585	1.4547	1.4506	1.4464
0.5943	1.4607	1.4567	1.4528	1.4482
0.7000	1.4632	1.4591	1.4548	1.4506
0.7993	1.4655	1.4614	1.4572	1.4529
0.8913	1.4675	1.4635	1.4594	1.4552
1.0000	1.4688	1.4657	1.4621	1.4579
		NMP (1) + DIPA (2)		
0.0000				1.4512
0.1049				1.4510
0.1898				1.4511
0.2764			1.4558	1.4520
0.3733			1.4563	1.4524
0.4695		1.4608	1.4567	1.4528
0.5721		1.4616	1.4576	1.4535
0.6754		1.4623	1.4582	1.4541
0.7804	1.4675	1.4635	1.4594	1.4553
0.8882	1.4682	1.4648	1.4607	1.4565
1.0000	1.4688	1.4657	1.4621	1.4579

Table 4. Viscosity, η/mPa·s, of NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	31.670	17.710	10.648	6.961
0.1034	18.957	11.487	7.301	4.793
0.2008	12.719	8.051	5.308	3.499
0.3001	8.746	5.780	4.045	2.939
0.4002	7.694	5.210	3.725	2.649
0.4978	6.542	4.723	3.448	2.438
0.5943	5.578	4.271	3.375	2.731
0.7000	4.249	3.395	2.775	2.317
0.7993	3.533	2.909	2.458	2.073
0.8913	3.098	2.576	2.168	1.861
1.0000	1.899	1.592	1.353	1.170
		NMP (1) + DIPA (2)		
0.0000				125.730
0.1049				61.135
0.1898				35.414
0.2764			38.269	20.934
0.3733			21.142	12.670
0.4695		20.251	11.236	7.412
0.5721		10.566	7.051	5.022
0.6754		6.229	4.495	3.420
0.7804	4.857	3.694	2.890	2.330
0.8882	2.943	2.371	1.943	1.631
1.0000	1.899	1.592	1.353	1.170

refractometer. This procedure was repeated at least three times, and the uncertainty of the measurement was $\pm\ 1.3 \cdot 10^{-4}$. The average of these readings was taken for the refractive index values.

Surface Tension. The surface tension was determined by employing a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned and flame-dried before each measurement. The uncertainty of the measurement was $\pm$ 0.2 mN·m^{-1}. Each surface tension value reported came from an average of five measurements. The samples were thermostatted in a closed stirring vessel before the surface tension measurements.

Table 5. Surface Tension, σ/mN·m^{-1}, NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	37.6	36.9	36.3	35.9
0.1034	38.1	37.3	36.8	36.2
0.2008	38.5	37.8	37.3	36.6
0.3001	39.0	38.3	37.7	37.1
0.4002	39.5	38.8	38.1	37.6
0.4978	40.0	39.2	38.7	38.0
0.5943	40.7	39.5	39.0	38.4
0.7000	41.2	40.1	39.5	38.8
0.7993	41.5	40.7	40.2	39.2
0.8913	42.1	41.0	40.4	39.5
1.0000	42.7	41.5	40.8	40.0
		NMP (1) + DIPA (2)		
0.0000				34.5
0.1049				34.9
0.1898				35.1
0.2764			36.0	35.1
0.3733			36.2	35.3
0.4695		37.1	36.7	36.0
0.5721		37.6	37.2	36.5
0.6754		38.3	37.9	37.1
0.7804	39.7	39.0	38.5	37.7
0.8882	41.3	40.0	39.5	38.7
1.0000	42.7	41.3	41.0	39.8

RESULTS AND DISCUSSION

Density, speed of sound, refractive index, viscosity, and surface tension corresponding to the binary systems of NMP + MIPA (or DIPA) have been determined for temperatures from (293.15 to 323.15) K, and the experimental data are shown in Tables 1 to 5. In these tables it is possible to observe that the physical properties have not been determined on the entire concentration range for the system NMP + DIPA due to the melting point of this kind of mixtures.

In relation with the values of density for these systems, a similar behavior has been found for both mixtures observing an increase in the value of this physical property when NMP concentration increases in the mixture (see Figures 1 and 2).

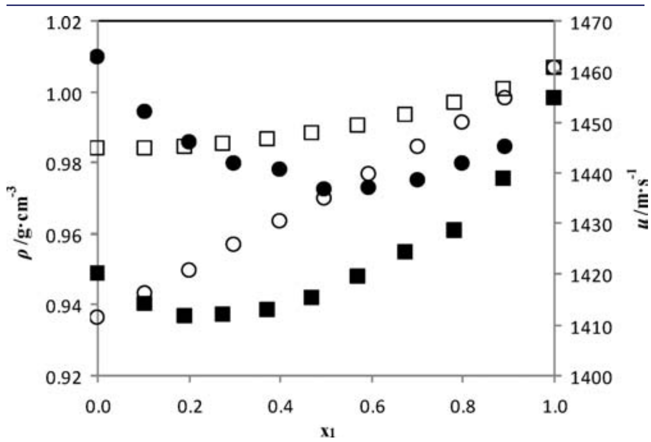

Figure 2. Influence of mixture composition on density and speed of sound. NMP (1) + MIPA (2): ○, density; ●, speed of sound. NMP (1) + DIPA (2): □, density; ■, speed of sound. T = 323.15 K.

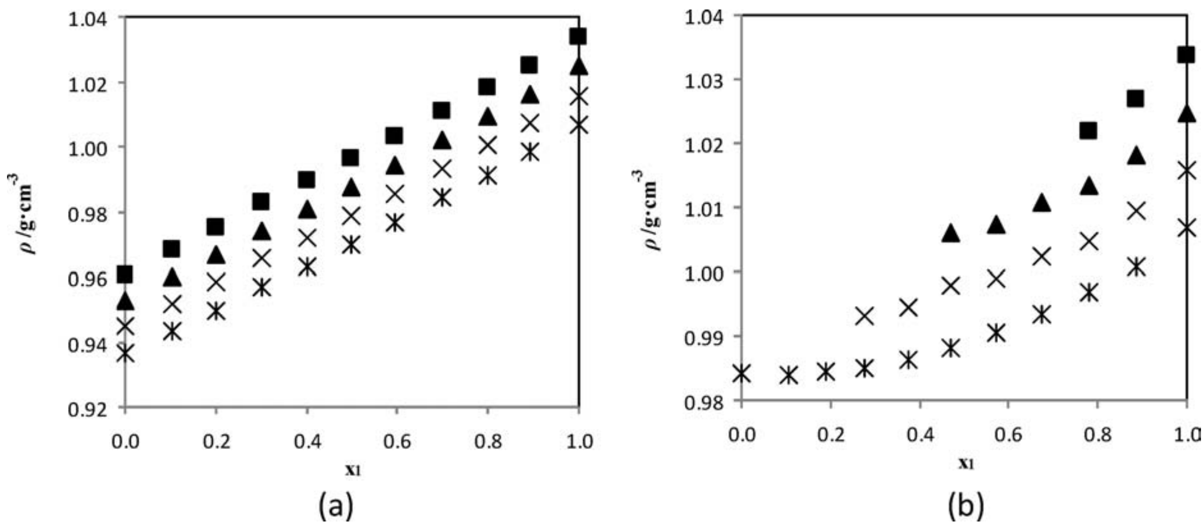

Figure 1. Influence of mixture composition and temperature on density: (a) NMP (1) + MIPA (2); (b) NMP (1) + DIPA (2). ■, T = 293.15 K; ▲, T = 303.15 K; ×, T = 313.15 K; ∗, T = 323.15 K.

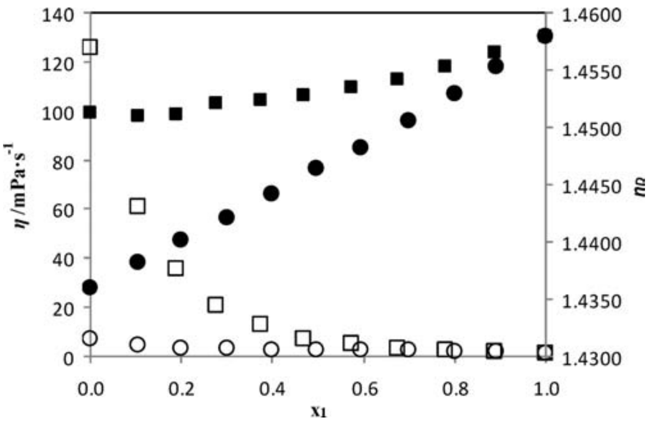

Figure 3. Influence of mixture composition on viscosity and refractive index. NMP (1) + MIPA (2): ○, viscosity; ●, refractive index. NMP (1) + DIPA (2): □, viscosity; ■, refractive index. T = 323.15 K.

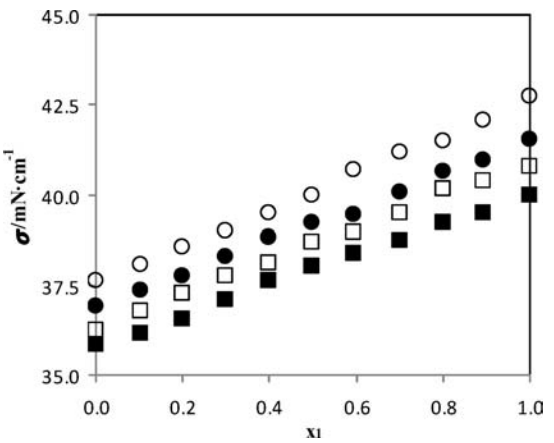

Figure 4. Influence of mixture composition and temperature on surface tension for NMP (1) + MIPA (2). ○, T = 293.15 K; ●, T = 303.15 K; □, T = 313.15 K; ■, T = 323.15 K.

Also, an increase in temperature produces a clear decrease in the values of density.

Figure 2 also shows the influence of both mixture compositions upon the speed of sound value. The same behavior was also obtained with a minimum in the value of speed of sound. This minimum in the case of NMP + MIPA system is reached in the MIPA poor region, but the opposite behavior is obtained for the NMP + DIPA mixture. Previous studies analyzing mixtures of DIPA with other amines[7] found different influences but not a minimum in the value of speed of sound. More specifically, the mixture with triethanolamine (TEA) shows a maximum in the value of speed of sound at TEA-rich mixtures. In relation with the influence of temperature, the same behavior was obtained for both systems, and it is in agreement with other MIPA based systems,[7] consisting in a decrease in the speed of sound when temperature increases. A previous work that analyzes the system NMP + MEA (monoethanolamine)[8] shows a different behavior without the presence of a minimum in the speed of sound value, and its trend is a monotonic decrease when NMP concentration increases in the mixture.

Figure 3 shows the experimental behaviors obtained for these mixtures for refractive index and viscosity. An increase in refractive index is observed when mixtures are enriched in NMP.

Table 6. Excess Molar Volume, V^E/cm^3·mol^{-1}, of NMP (1) + MIPA (2) (or DIPA) from T/K = 293.15 to 323.15

x_1	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
0.0000	0.0000	0.0000	0.0000	0.0000
0.1034	0.1322	0.1457	0.1592	0.1729
0.2008	0.2210	0.2442	0.2676	0.2913
0.3001	0.2602	0.2898	0.3190	0.3485
0.4002	0.3466	0.3794	0.4114	0.4430
0.4978	0.3724	0.4074	0.4410	0.4742
0.5943	0.3740	0.4059	0.4372	0.4676
0.7000	0.3428	0.3696	0.3944	0.4189
0.7993	0.2811	0.3002	0.3177	0.3350
0.8913	0.1879	0.1973	0.2054	0.2140
1.0000	0.0000	0.0000	0.0000	0.0000
		NMP (1) + DIPA (2)		
0.0000				0.0000
0.1049				0.2612
0.1898				0.3973
0.2764				0.5031
0.3733				0.5670
0.4695				0.5731
0.5721				0.5465
0.6754				0.4793
0.7804				0.3981
0.8882				0.2811
1.0000				0.0000

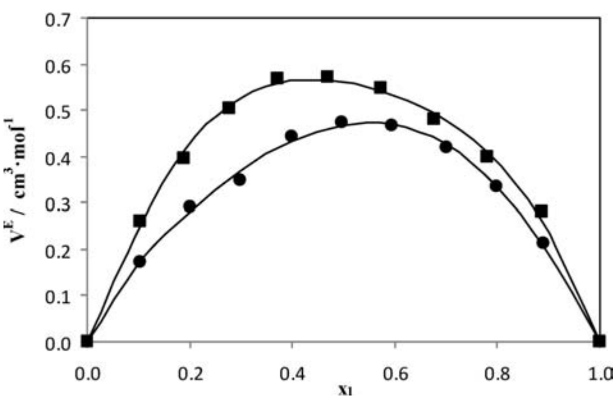

Figure 5. Effect of mixture composition upon excess volume. ●, NMP (1) + MIPA (2); ■, NMP (1) + DIPA (2). T = 323.15 K.

The opposite behavior is observed for the other property shown in Figure 3. An increase in viscosity is observed when MIPA or DIPA concentration increases in the system. For the NMP + DIPA system, a higher increase is observed in the viscosity in DIPA concentration reach region. An increase in temperature produces a decrease in both physical properties.

In relation with the value of surface tension (Table 5 and Figure 4), a linear influence is caused by the composition, with a rise in the value of this property when NMP concentration increases in both systems. The temperature causes a slight decrease in the values of surface tension.

Table 7. Fit Parameters Corresponding to the Redlich−Kister Equation for Excess Volume V^E from T/K = 293.15 to 323.15

parameter	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15
		NMP (1) + MIPA (2)		
A_0	2.471	2.719	2.987	3.215
A_1	−5.296	−5.871	−6.540	−6.957
A_2	7.194	8.218	9.397	10.106
A_3	−2.408	−3.019	−3.728	−4.170
σ	0.009	0.009	0.009	0.008
		NMP (1) + DIPA (2)		
A_0				0.292
A_1				15.122
A_2				−29.685
A_3				17.261
σ				0.016

The excess molar volumes of mixtures (V^E) were calculated from density measurements by applying eq 3

$$V^E = \sum_{i=1}^{2} x_i \cdot M_i \cdot (\rho^{-1} - \rho_i^{-1}) \qquad (3)$$

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

In relation with the calculated values for excess volume (Table 6), Figure 5 shows that for both systems, positive values of this parameter have been obtained. The same behavior has been obtained in previous studies that analyze the systems formed by MIPA and other amines such as 2-amino-1-methyl-1-propanol (AMP) or diethanolamine (DEA), but also a negative deviation has been obtained for other systems with TEA.[7] The positive deviations indicate the breaking of hydrogen -bonds between the compounds. This behavior is the opposite than the corresponding one for aqueous mixtures of this amines (MIPA and DIPA)[9,10] and for NMP,[11] but it is in agreement with the data previously obtained for the NMP + MEA system.[8]

The values calculated for excess molar volumes were fitted using a Redlich−Kister type equation (eq 4). The results obtained for fitting parameters are shown in Table 7 for the systems studied in this work. This equation fits satisfactorily the excess molar volume calculated from experimental data in present work (see Figure 5 and Table 7).

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

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■ REFERENCES

(1) Mandal, B. P.; Biswas, A. K.; Bandyopadhyay, S. S. Absorption of Carbon Dioxide into Aqueous Blends of 2-Amino-2-Methyl-1-Propanol and Diethanolamine. *Chem. Eng. Sci.* **2003**, *58*, 4137–4144.

(2) Bishnoi, S.; Rochelle, G. T. Absorption of Carbon Dioxide in Aqueous Piperazine/Methyldiethanolamine. *AIChE J.* **2002**, *48*, 2788–2799.

(3) Camacho, F.; Sánchez, S.; Pacheco, R.; Sánchez, A.; La Rubia, M. D. Absorption of Carbon Dioxide at High Partial Pressures in Aqueous Solutions of Di-isopropanolamine. *Ind. Eng. Chem. Res.* **2005**, *44*, 7451–7457.

(4) Versteeg, G. F.; van Dijck, L. A. J.; van Swaaij, W. P. M. On the Kinetics between CO_2 and Alkanolamines both in Aqueous and Non-aqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113–158.

(5) Camacho, F.; Sanchez, S.; Pacheco, R. Absorption of Carbon Dioxide at High Partial Pressures in 1-Amino-2-Propanol Aqueous Solution. Considerations of Thermal Effects. *Ind. Eng. Chem. Res.* **1997**, *36*, 4358–4364.

(6) Hochgesand, G. Rectisol and Purisol. Efficient Acid Gas Removal for High Pressure Hydrogen and Syngas Production. *Ind. Eng. Chem.* **1970**, *62*, 37–43.

(7) Álvarez, E.; Cerdeira, F.; Gómez-Díaz, D.; Navaza, J. M. Density, Speed of Sound, Isentropic Compressibility, and Excess Volume of Binary Mixtures of 1-Amino-2-propanol or 3-Amino-1-propanol with 2-Amino-2-methyl-1-propanol, Diethanolamine, or Triethanolamine from (293.15 to 323.15) K. *J. Chem. Eng. Data* **2010**, *55*, 2567–2575.

(8) García-Abuín, A.; Gómez-Díaz, D.; La Rubia, M. D.; Navaza, J. M. Density, Speed of Sound, Viscosity, Refractive Index and Excess Volume of N-Methyl-2-pyrrolidone + Ethanol (or Water or Ethanolamine) from T = (293.15 to 323.15) K. *J. Chem. Eng. Data* **2011**, *56*, 646–651.

(9) Rayer, A. V.; Kadiwala, S.; Narayanaswamy, K.; Henni, A. Volumetric Properties, Viscosities, and Refractive Indices for Aqueous 1-Amino-2-Propanol (Monoisopropanolamine (MIPA)) Solutions from (298.15 to 343.15) K. *J. Chem. Eng. Data* **2010**, *55*, 5562–5568.

(10) Henni, A.; Hromek, J. J.; Tontiwachwuthikul, P.; Chakma, A. Volumetric Properties and Viscosities for Aqueous Diisopropanolamine Solutions from 25 to 70 °C. *J. Chem. Eng. Data* **2003**, *48*, 1062–1067.

(11) George, J.; Sastry, N. V. Densities, Viscosities, Speeds of Sound, and Relative Permittivities for Water + Cyclic Amides (2-Pyrrolidinone, 1-Methyl-2-pyrrolidinone, and 1-Vinyl-2-pyrrolidinone) at Different Temperatures. *J. Chem. Eng. Data* **2004**, *49*, 235–242.