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Densities, Viscosities, Heat Capacities, and Vapor−Liquid Equilibria of Ammonia + Sodium Thiocyanate Solutions at Several Temperatures

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ABSTRACT: Several thermophysical properties were experimentally measured for the ammonia + sodium thiocyanate mixtures at several temperatures: density from (269.4 to 350.9) K, dynamic viscosity from (269.8 to 369.5) K, and isobaric heat capacity from (304.17 to 364.15) K, all them at a constant pressure of 3 MPa, and vapor−liquid equilibria from (253.1 to 393.1) K. All properties were measured in a range of composition from 0.35 to 0.90 in ammonia mass fraction. The experimental techniques used were a vibrating-tube densimeter, a piston-style viscometer, a heat flux Calvet-type calorimeter, and a static method, respectively. The measured data were correlated as a function of temperature and composition using empirical equations and were compared with literature values.

INTRODUCTION

Heating and cooling absorption systems based on the NH_3 + H_2O and H_2O + LiBr working fluids have been used for many decades, despite its well-known disadvantages: the first requires rectification of the refrigerant vapor and high working pressure, while the second works at very low pressure, and it could show crystallization and corrosion. To overcome these drawbacks, research about new cycles in advanced absorption refrigeration has been carried out in recent years, as is the case of the cycle based on ammonia as refrigerant and sodium thiocyanate as absorbent (NH_3 + NaSCN). Since NaSCN is a salt (nonvolatile), this system does not require rectification (as in NH_3 + H_2O mixture), and besides, it is highly soluble in ammonia.

With ammonia + sodium thiocyanate as a working fluid, several researchers[1−7] have presented the analysis and simulations of thermodynamic cycles for a cooling system at low temperatures and heating applications with heat pumps, comparing this mixture with other, like NH_3 + H_2O and NH_3 + $LiNO_3$. All of these studies have used thermophysical properties proposed by Infante Ferreira,[8] who presented different correlations for each property based on the previous data for the NH_3 + NaSCN mixture and properties for pure ammonia. Between these works, Blytas and Daniels[9] carried out measurements of several thermodynamic and transport properties. Roberson et al.[10] reported new vapor−liquid equilibria data. Sargent and Bechman[11] measured a few data of specific heat, and Gupta et al.[12] presented measurements of thermodynamic properties. In two previous works,[13,14] we could test that the correlations presented by Infante Ferreira[8] for NH_3 + $LiNO_3$ were not sufficiently reliable, probably because the experimental data from which equations were constructed are scarce. Besides, comparing the property values between these works results in disagreements, and sometimes, the working ranges are not enough for applications as absorption refrigeration. For this reason, it is necessary to carry out new experimental measurements and propose new more reliable correlations to be used in calculations of the thermodynamic cycles.

The thermodynamic and transport properties of the working fluids used in absorption refrigeration cycles are very important when these have to be appropriately evaluated and designed. The composition range of interest for absorption refrigeration is between 0.35 to 0.65 ammonia mass fraction and 0.60 to 0.90 for power cycles. In the present study, the density, dynamic viscosity, and heat capacity of binary liquid mixtures of ammonia + sodium thiocyanate were measured at several ranges of temperature from (269 to 369) K for various compositions, and at constant pressure of 3 MPa, because this is higher than the saturation pressure across the range of measurements, to prevent the evaporation of the solvent. Vapor−liquid equilibria data for these binary mixtures were also obtained in the same composition range, from (253 to 393) K, using a static method. The vapor and liquid compositions were calculated from the total initial composition and the experimental pressure and temperature. For interpolation and limited extrapolations, the experimental data were correlated with temperature and composition using empirical correlations commonly used for pure ammonia properties. The results were compared with literature.[8−12]

Also, the uncertainties of the obtained experimental values have been calculated according to the EA-4/02 guide,[15] and they are presented in this work.

EXPERIMENTAL SECTION

Materials. The description of chemicals is summarized in Table 1. ISO 17025 certified reference standards were used as viscosity standards. All chemicals were used without further purification.

Apparatus and Experimental Procedure. *Density and Dynamic Viscosity.* The densities and dynamic viscosities of ammonia and sodium thiocyanate solutions were measured at 3 MPa

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Table 1. Sample Table

IUPAC chemical name	other name	molecular formula	CAS number	source	mass fraction purity
azane	ammonia	NH_3	7664-41-7	Carburos Metálicos	0.9998
sodium thiocyanate		NaSCN	540-72-7	Panreac	> 0.99
Milli-Q water		H_2O	7789-20-0	Millipore water	resistivity lower than 18.2 MΩ·cm
methylbenzene	toluene	C_7H_8	108-88-3	Sigma-Aldrich	> 0.995
N10 ISO 17025 certified reference standard		N/A	8042-47-5	Paragon Scientific Limited	N/A
N26 ISO 17025 certified reference standard		N/A	68037-01-4	Paragon Scientific Limited	N/A
nitrogen		N_2	7727-37-9	Carburos Metálicos	N/A

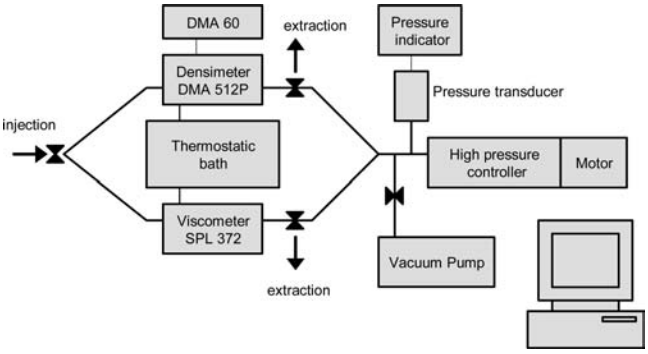

Figure 1. Scheme of the densimeter and viscometer automatic system.

using an automatic system formed by an Anton-Paar vibrating-tube densimeter (DMA60/512P) and a piston-type viscometer (Cambridge, mod. SPL 372). Both experimental devices are connected in parallel to a vacuum/pressure system. This consists of a high pressure controller (HiP, mod. 50-6-15), a vacuum pump (Telstar), and a pressure transducer (Setra C280E). The liquid sample is directly compressed up to the required pressure by means of the high pressure controller using a stepper motor. On the other hand, the temperature of the experiment is controlled by a refrigerated/heating circulator (Julabo, mod. F20-ME) with a thermal oil bath (Baysilone Fluid M-20, Bayer) and measured with the same device, using an external Pt100 probe. A computer controls all devices and works as a data logger through the software VEE (Visual Engineering Environment), a visual and dataflow programming language developed by Agilent Technologies. A scheme of the whole device is shown in Figure 1.

The calibration of the densimeter was performed following the method proposed by Comuñas et al.,[16] using deionized water (quality Milli-Q), toluene, and vacuum as references, in a temperature range from (280.1 to 380.1) K. The density values of water and toluene were taken from Wagner and Pruss[17] and McLinden and Spleet,[18] respectively. The validity of the calibration was tested by measuring the density of *n*-heptane in the temperature range from (283.1 to 373.1) K and comparing with values presented by Span and Wagner[19] showing deviations lower than 0.1 %. The estimated expanded uncertainty (coverage factor $k = 2$) for temperature was ± 0.1 K, for pressure ± 0.002 MPa, and ± 1.0 $kg\cdot m^{-3}$ for density at temperature up to 343.1 K and ± 1.3 $kg\cdot m^{-3}$ from (343 to 380) K. It should be noted that results from (269.4 to 283.0) K could have some error, because the calibration and validation of the density was carried out from (283.1 to 373.1) K. However, the error should be negligible since the change of density with temperature can be considered linear and calibration can be extrapolated when temperature difference is small.

Experimental device and methodology for measuring the dynamic viscosity were described previously in Libotean et al.[14] In the present work, a new piston with a viscosity range from (0.25 to 5) mPa·s was used. The viscometer system was calibrated in the factory and validated using two viscosity reference standards (types N10 and N26). Deviations were lower than 2 %. The expanded uncertainty ($k = 2$) for the viscosity values was estimated at ± 0.05 mPa·s and ± 0.1 K for temperature.

Isobaric Heat Capacity. The heat capacity of the ammonia + sodium thiocyanate mixtures was determined using a differential heat flux Calvet-type calorimeter (Setaram C80 II) at a constant pressure of 3 MPa. The details of the apparatus, measurement cells, and procedure have been presented in our previous studies.[14,20] Vacuum and water were used to calibrate the device[21] and ammonia to validate the technique, comparing with Tillner-Roth et al.[22] Deviations were lower than 1.5 %. The expanded uncertainty for heat capacity values was estimated at ± 0.015 $J\cdot g^{-1}\cdot K^{-1}$ and ± 0.02 K for temperature.

Vapor−Liquid Equilibria. The vapor pressure of the ammonia + sodium thiocyanate solutions was measured by the static method. The equipment and the measurement procedure were previously described by Herraiz et al.[23] and Salavera et al.[24] It consists of an equilibrium cell, a differential pressure transducer (Ruska model 2439-702), a differential pressure null indicator (Ruska model 2416-711), a precise pressure controller (Ruska model 3891-801), and a double-walled thermostatted bath of 0.40 m^3 capacity. The temperature in the bath was controlled using two Haake proportional temperature controllers, a N3 unit for heating, and a F6 cooler for cooling. Different bath fluids were used according to the range of temperature: a water + ethylene glycol (40 % in volume) mixture from (253.1 to 293.1) K, distilled water from (293.1 to 353.1) K, and thermal oil (Baysilone Fluid M 20, Bayer) above 353 K were used. For an accurate measurement of the temperature, a digital precision thermometer (Anton Paar MKT100) was employed with a Pt100 probe. The estimated expanded uncertainty ($k = 2$) for temperature was ± 0.2 K.

An equilibrium cell made of stainless steel with a volume of 149 cm^3 was used. A weighed quantity of ammonia was transferred to the equilibrium cell, using an auxiliary high-pressure stainless steel cylinder of 150 cm^3 of capacity. The pressure was measured by three digital pressure gauges (Ruska) according to three different ranges: up to 130 kPa, from 130 kPa to 1 MPa, and from (1 to 5) MPa. The estimated expanded uncertainties ($k = 2$) for vapor pressure data were less than ± 0.2 kPa for values of vapor pressure lower than 1 MPa and ± 1.2 kPa for values of vapor pressure values higher than 1 MPa. The methodology for preparing and measuring the vapor pressure was described in a previous work.[24]

For the measurement of each property the mixtures were prepared using the same equilibrium cell used for measuring

Table 2. Experimental Values of Density ρ for the Solution Ammonia (1) + Sodium Thiocyanate (2) for the Liquid at Pressure p = 3 MPa from w_1 = 0.5 to 0.9[a]

T/K	w_1	ρ/kg·m^{-3}
270.5	0.4998	965.7
275.0	0.4998	962.2
279.5	0.4998	959.3
284.1	0.4998	955.9
288.7	0.4998	952.2
293.4	0.4998	948.2
298.2	0.4998	944.6
303.0	0.4998	941.0
307.7	0.4998	937.1
312.4	0.4998	933.3
317.2	0.4998	929.3
321.9	0.4998	925.5
326.7	0.4998	921.4
331.5	0.4998	917.4
336.3	0.4998	913.3
341.2	0.4998	909.2
346.0	0.4998	905.1
350.9	0.4998	900.9
270.4	0.6140	896.5
274.8	0.6140	892.6
279.4	0.6140	888.8
284.0	0.6140	884.9
288.6	0.6140	881.6
293.3	0.6140	878.3
298.1	0.6140	875.8
302.8	0.6140	870.0
307.6	0.6140	866.2
312.4	0.6140	862.3
317.0	0.6140	857.4
321.8	0.6140	852.4
326.6	0.6140	846.9
331.4	0.6140	843.1
336.2	0.6140	838.1
341.1	0.6140	832.6
346.0	0.6140	826.5
270.4	0.6824	850.0
274.9	0.6824	848.0
279.3	0.6824	844.0
283.8	0.6824	839.0
288.6	0.6824	834.0
293.3	0.6824	831.0
298.0	0.6824	828.0
302.9	0.6824	821.0
307.6	0.6824	817.0
312.3	0.6824	811.0
317.2	0.6824	807.0
321.9	0.6824	800.5
326.7	0.6824	795.0
331.4	0.6824	792.0
336.3	0.6824	783.1
341.1	0.6824	775.2
270.5	0.7970	772.7
274.8	0.7970	767.4
279.4	0.7970	761.7
283.9	0.7970	756.4
288.6	0.7970	750.7
293.4	0.7970	745.1
302.9	0.7970	734.7
307.6	0.7970	729.5
312.4	0.7970	724.2
317.1	0.7970	718.9
321.8	0.7970	713.6
326.6	0.7970	708.4
331.4	0.7970	701.0
336.2	0.7970	692.7
341.0	0.7970	686.7
269.4	0.8921	707.7
275.2	0.8921	699.9
284.2	0.8921	686.6
293.5	0.8921	674.0
303.0	0.8921	660.5
312.4	0.8921	648.1
322.0	0.8921	635.4

[a] Combined uncertainties are $U_c(T)$ = 0.1 K, $U_c(w)$ = 0.0002, $U_c(p)$ = 0.002 MPa, and $U_c(\rho)$ = 1 kg·m^{-3} at $T \leq$ 343.1 K and $U_c(\rho)$ = 1.3 kg·m^{-3} at T > 343.1 K, with a 0.95 level of confidence ($k \approx 2$).

vapor pressure. The components were weighed on a balance (Metter Toledo PR2003DR) with a resolution of 10^{-3} g. The expanded uncertainty (k = 2) for mass fraction was estimated to be ± 0.0002 for density, viscosity, and heat capacity experiments and ± 0.001 for the phase compositions in vapor—liquid equilibria measurements.

RESULTS

The density and dynamic viscosity of ammonia + sodium thiocyanate mixtures were measured at T = (269.4 to 350.9) K and T = (269.8 to 350.9) K, respectively, and at constant pressure of 3 MPa. Several samples were measured with ammonia mass fractions between 0.50 and 0.90, taking into account the solubility and saturation pressure limits.[9] The experimental results for density and dynamic viscosity are presented in Tables 2 and 3, respectively.

The heat capacity for NH_3 + NaSCN mixtures was measured in a range of temperatures from (304.17 to 364.15) K, at 3 MPa, in an ammonia mass fraction range from 0.5 to 1.0. Results are presented in Table 4. Pure ammonia results were used to validate the methodology, comparing the experimental data with reported data in literature.[22] The maximum deviation found was 0.4 %.

The vapor pressure of the NH_3 + NaSCN solutions was measured from (253.1 to 393.1) K, at steps of 10 K, varying the total ammonia mass fraction from 0.35 to 0.90, taking into account the solubility limit[9] and a maximum pressure of approximately 3 MPa. The liquid-phase composition was determined isothermally using Barker's method. This method was previously described.[24] The vapor phase nonideality was modeled using a virial equation. Second virial coefficients used for NH_3 were taken from Rumf et al.[25] and were validated comparing pure

Table 3. Experimental Values of Dynamic Viscosity η for the Solution Ammonia (1) + Sodium Thiocyanate (2) for the Liquid at Pressure p = 3 MPa from w_1 = 0.5 to 0.9[a]

T/K	w_1	η/mPa·s
269.8	0.8921	0.27
275.4	0.8921	0.25
284.3	0.8921	0.22
293.5	0.8921	0.20
302.8	0.8921	0.18
312.2	0.8921	0.16
321.6	0.8921	0.15
331.0	0.8921	0.13
270.8	0.7970	0.44
275.0	0.7970	0.40
279.4	0.7970	0.37
284.1	0.7970	0.35
288.7	0.7970	0.33
293.4	0.7970	0.31
302.7	0.7970	0.28
307.5	0.7970	0.26
312.2	0.7970	0.24
316.8	0.7970	0.23
321.5	0.7970	0.22
326.4	0.7970	0.21
331.1	0.7970	0.20
335.7	0.7970	0.19
340.6	0.7970	0.18
270.6	0.6824	0.82
274.9	0.6824	0.77
279.4	0.6824	0.70
284.0	0.6824	0.65
288.7	0.6824	0.61
293.3	0.6824	0.57
298.0	0.6824	0.52
302.8	0.6824	0.49
307.5	0.6824	0.46
312.2	0.6824	0.43
317.0	0.6824	0.40
321.7	0.6824	0.38
326.5	0.6824	0.36
331.2	0.6824	0.35
336.0	0.6824	0.33
340.8	0.6824	0.31
270.6	0.6140	1.41
274.9	0.6140	1.27
279.4	0.6140	1.14
284.0	0.6140	1.06
293.4	0.6140	0.89
298.0	0.6140	0.83
302.8	0.6140	0.76
307.5	0.6140	0.71
312.3	0.6140	0.66
317.0	0.6140	0.62
321.7	0.6140	0.57
326.5	0.6140	0.53
331.2	0.6140	0.51
336.1	0.6140	0.47
340.8	0.6140	0.46
345.6	0.6140	0.43
350.2	0.6140	0.40
270.8	0.4998	3.47
275.0	0.4998	3.08
279.5	0.4998	2.75
284.1	0.4998	2.43
288.7	0.4998	2.20
293.4	0.4998	1.95
298.1	0.4998	1.73
302.9	0.4998	1.57
307.6	0.4998	1.41
312.3	0.4998	1.27
317.1	0.4998	1.15
321.8	0.4998	1.06
326.6	0.4998	1.00
331.4	0.4998	0.92
336.3	0.4998	0.87
341.1	0.4998	0.82
345.9	0.4998	0.77
350.4	0.4998	0.73
359.7	0.4998	0.65
369.5	0.4998	0.58

[a] Combined uncertainties are $U_c(T)$ = 0.1 K, $U_c(w)$ = 0.0002, $U_c(p)$ = 0.002 MPa, and $U_c(\eta)$ = 0.05 mPa·s, with a 0.95 level of confidence ($k \approx 2$).

ammonia vapor pressure with ref 22. The deviations were better than 0.4 % in the range of temperature from (253.1 to 393.1) K. The vapor pressure and liquid-phase composition obtained at each temperature for the binary mixtures are shown in Table 5.

To correlate the experimental data, DIPPR correlations[26] were used for each property (eqs 1 to 4). The number 105 DIPPR equation was used for fitting the density values, the number 100 DIPPR equation was used for fitting the heat capacity values, and the number 101 DIPPR equation was used for correlating the dynamic viscosity and vapor pressure values.

$$\rho/\mathrm{kg\cdot m^{-3}} = \frac{A/\mathrm{kg\cdot m^{-3}}}{B^{[1+(1-T/T_c)^D]}} \tag{1}$$

$$\ln(\eta/\mathrm{mPa\cdot s}) = A + \frac{B}{\left(\frac{T}{\mathrm{K}}\right)} + C\ln\left(\frac{T}{\mathrm{K}}\right) + D\cdot T^E \tag{2}$$

$$\begin{aligned} C_p/\mathrm{J\cdot g^{-1}\cdot K^{-1}} = {} & A/\mathrm{J\cdot g^{-1}\cdot K^{-1}} + (B/\mathrm{J\cdot g^{-1}\cdot K^{-2}})\left(\frac{T}{\mathrm{K}}\right) \\ & + (C/\mathrm{J\cdot g^{-1}\cdot K^{-3}})\left(\frac{T}{\mathrm{K}}\right)^2 \\ & + (D/\mathrm{J\cdot g^{-1}\cdot K^{-4}})\left(\frac{T}{\mathrm{K}}\right)^3 \\ & + (E/\mathrm{J\cdot g^{-1}\cdot K^{-5}})\left(\frac{T}{\mathrm{K}}\right)^4 \end{aligned} \tag{3}$$

Table 4. Experimental Values of Heat Capacity C_p for the Solution Ammonia (1) + Sodium Thiocyanate (2) for the Liquid at Pressure p = 3 MPa from w_1 = 0.5 to 1[a]

		C_p
T/K	w_1	$\mathrm{J\cdot g^{-1}\cdot K^{-1}}$
304.17	0.4992	2.253
304.17	0.5988	2.910
304.17	0.7013	3.443
304.17	0.9000	4.409
304.17	1.0000	4.842
314.14	0.4992	2.293
314.14	0.5988	2.900
314.14	0.7013	3.487
314.14	0.7961	3.997
314.14	0.9000	4.431
314.14	1.0000	4.900
324.11	0.4992	2.294
324.11	0.5988	2.893
324.11	0.7013	3.493
324.11	0.7961	4.047
324.11	0.9000	4.530
324.11	1.0000	5.040
334.09	0.4992	2.316
334.09	0.5988	2.907
334.09	0.7013	3.507
334.09	0.7961	4.079
334.09	0.9000	4.647
334.09	1.0000	5.247
344.07	0.4992	2.340
344.07	0.5988	2.940
344.07	0.7013	3.553
354.06	0.4992	2.388
354.06	0.5988	2.973
364.15	0.4992	2.495

[a] Combined uncertainties are $U_c(T)$ = 0.02 K, $U_c(w)$ = 0.0002, $U_c(p)$ = 0.002 MPa, and $U_c(C_p)$ = 0.015 $\mathrm{J\cdot g^{-1}\cdot K^{-1}}$, with a 0.95 level of confidence ($k \approx 2$).

$$\ln(p/\mathrm{kPa}) = A + \frac{B}{T} + C\ln\left(\frac{T}{\mathrm{K}}\right) + D\left(\frac{T}{\mathrm{K}}\right)^{E} \qquad (4)$$

In eqs 1 to 4, ρ means density, η is dynamic viscosity, C_p is isobaric heat capacity, p is pressure, T is absolute temperature, and T_c is the critical temperature of the ammonia.

From the pure ammonia coefficients (A, B, C, D, and E in eqs 1 to 4), some of these were considered as composition-dependent parameters (eqs 5 to 8), such that if sodium thiocyanate composition is zero, equations reduce to the pure ammonia DIPPR correlations. The parameters for pure ammonia have been taken from the DIPPR database.[26]

$$A = \sum_{i=0}^{n} a_i \cdot w_2^i \qquad (5)$$

$$B = \sum_{i=0}^{n} b_i \cdot w_2^i \qquad (6)$$

Table 5. Experimental VLE Data for Temperature T, Pressure p, and for the Solution Ammonia (1) + Sodium Thiocyanate (2) for Ammonia Mass Fraction w_1 from 0.35 to 0.90[a]

T/K	w_1	p/kPa
253.1	0.606	112.0
253.1	0.701	151.6
253.1	0.722	156.6
253.1	0.803	174.2
253.1	0.898	185.0
263.1	0.605	169.3
263.1	0.702	230.7
263.1	0.721	239.4
263.1	0.806	267.4
263.1	0.898	280.3
273.1	0.604	252.0
273.1	0.700	338.8
273.1	0.801	392.4
273.1	0.898	414.1
283.1	0.699	491.2
283.1	0.720	512.0
283.1	0.805	565.1
293.1	0.352	93.0
293.1	0.420	185.5
293.1	0.597	535.8
293.1	0.635	608.8
293.1	0.696	686.6
293.1	0.718	718.1
293.1	0.795	779.7
293.1	0.897	825.2
303.1	0.351	135.5
303.1	0.418	254.2
303.1	0.483	415.9
303.1	0.536	582.2
303.1	0.592	734.5
303.1	0.633	836.0
303.1	0.694	932.5
303.1	0.717	968.1
303.1	0.792	1052.0
303.1	0.897	1124.0
313.1	0.349	195.0
313.1	0.417	351.2
313.1	0.481	560.1
313.1	0.534	761.1
313.1	0.590	958.0
313.1	0.632	1096.0
313.1	0.688	1228.2
313.1	0.716	1284.0
313.1	0.783	1394.2
313.1	0.896	1492.8
323.1	0.348	271.2
323.1	0.415	470.1
323.1	0.479	732.2
323.1	0.532	1015.1
323.1	0.588	1248.9
323.1	0.630	1438.0
323.1	0.684	1591.0

Table 5. Continued

T/K	w_1	p/kPa
323.1	0.714	1677.0
323.1	0.778	1810.5
323.1	0.896	1965.8
333.1	0.346	361.2
333.1	0.412	619.8
333.1	0.476	943.5
333.1	0.529	1305.0
333.1	0.585	1582.0
333.1	0.627	1840.0
333.1	0.679	2015.0
333.1	0.711	2145.0
333.1	0.771	2312.0
333.1	0.895	2518.8
343.1	0.343	475.3
343.1	0.408	816.8
343.1	0.472	1209.0
343.1	0.527	1625.0
343.1	0.581	2026.0
343.1	0.624	2308.0
343.1	0.674	2457.0
343.1	0.708	2695.0
343.1	0.764	2890.0
343.1	0.895	3192.8
353.1	0.340	615.1
353.1	0.405	1046.2
353.1	0.468	1516.6
353.1	0.524	1970.0
353.1	0.577	2531.0
353.1	0.621	2810.0
353.1	0.665	3120.0
353.1	0.705	3340.0
353.1	0.755	3538.0
353.1	0.894	3980.0
363.1	0.337	776.5
363.1	0.400	1287.0
363.1	0.464	1848.0
373.1	0.333	962.0
373.1	0.397	1529.0
373.1	0.458	2240.0
383.1	0.329	1180.0
383.1	0.392	1830.0
393.1	0.324	1410.0
393.1	0.387	2150.0

[a] Combined uncertainties are $U_c(T) = 0.2$ K, $U_c(w) = 0.001$, $U_c(p) = 0.2$ kPa at $p \leq 1$ MPa, and $U_c(p) = 1.2$ kPa at $p > 1$ MPa, with a 0.95 level of confidence ($k \approx 2$).

$$C = \sum_{i=0}^{n} c_i \cdot w_2^i \qquad (7)$$

$$D = \sum_{i=0}^{n} d_i \cdot w_2^i \qquad (8)$$

In eqs 5 to 8, w_2 is the sodium thiocyanate mass fraction. The coefficients a_0, b_0, c_0, d_0, and E agree with pure ammonia parameters for the DIPPR correlations,[26] and the others ($i \neq 0$) are the regressed parameters, where n is the polynomial degree which depends on the correlation and the property. Units for A to D are shown in eqs 1 to 4. All of the parameters are presented in Table 6 for each property, and the maximum deviation (δ_{max} %) and the root-mean-square deviation (rmsd, eq 9) between calculated (X_c) and experimental (X_e) data are also shown.

Table 6. Parameters and Deviations of eqs 1 to 8 for Ammonia + Sodium Thiocyanate

parameter	density	viscosity	heat capacity	vapor pressure
a_0[a]	$6.025725 \cdot 10^{1}$	$1.6476 \cdot 10^{-1}$	$6.3576 \cdot 10^{1}$	$8.35752 \cdot 10^{1}$
a_1	$3.638 \cdot 10^{2}$	$-1.604 \cdot 10^{2}$	$-1.073 \cdot 10^{2}$	$-3.87 \cdot 10^{-2}$
a_2	$9.692 \cdot 10^{2}$	$-1.250 \cdot 10^{2}$	$9.119 \cdot 10^{1}$	$6.2386 \cdot 10^{0}$
a_3	0	$1.144 \cdot 10^{2}$	0	$-5.464 \cdot 10^{0}$
b_0[a]	$2.5443 \cdot 10^{-1}$	$5.983 \cdot 10^{2}$	$-9.1257 \cdot 10^{-1}$	$-4.6697 \cdot 10^{3}$
b_1	$8.204 \cdot 10^{-1}$	$8.365 \cdot 10^{3}$	$7.104 \cdot 10^{-1}$	$3.6464 \cdot 10^{2}$
b_2	$-2.99 \cdot 10^{-2}$	$3.824 \cdot 10^{3}$	$-6.662 \cdot 10^{-1}$	$2.99 \cdot 10^{-2}$
b_3	0	$1.800 \cdot 10^{3}$	0	$-1.3164 \cdot 10^{3}$
c_0[a]	-	$-7.341 \cdot 10^{-1}$	$5.22672 \cdot 10^{-3}$	$-1.1607 \cdot 10^{1}$
c_1	-	$2.373 \cdot 10^{1}$	$-1.214 \cdot 10^{-3}$	$-2.795 \cdot 10^{-1}$
c_2	-	$2.064 \cdot 10^{1}$	$1.172 \cdot 10^{-3}$	0
c_3	-	$-2.143 \cdot 10^{1}$	0	0
d_0[a]	$2.888 \cdot 10^{-1}$	$-3.7 \cdot 10^{-27}$	$-1.32196 \cdot 10^{-5}$	$1.7194 \cdot 10^{-2}$
d_1	0	0	0	0
d_2	0	0	0	0
d_3	0	0	0	0
E[a]	-	10	$1.25285 \cdot 10^{-8}$	1
rmsd %	0.2	1.7	1.0	2.5
δ_{max} %	0.5	4.1	2.4	7.3

[a] DIPPR equation parameters for pure ammonia.[26]

$$\text{rmsd} = \sqrt{\sum_{N} \frac{\left(\dfrac{X_c - X_e}{X_e}\right)^2}{N}} \cdot 100 \qquad (9)$$

where N is the total number of values compared.

Experimental results and calculated values using eqs 1 to 8 are shown in Figures 2 to 5. In the case of the vapor–liquid equilibria, only some isotherms are presented, and the literature[22] vapor pressure for pure ammonia is shown for consistency assessment. The deviations in Table 6 and Figures 2 to 5 show that there are deviations between some experimental data and the calculated values using the correlations. This should take into account that DIPPR equations are correlations for pure components, while in this work these equations have been used for mixtures. Different analytical equations were used for fitting the experimental data, some of them with better results, but we chose DIPPR equations for a better agreement between pure ammonia and ammonia + sodium thiocyanate mixture.

The experimental data for each property were compared with the scarce values reported in the literature.[8,9]

For the density of NH_3 + NaSCN, Blytas and Daniels[9] measured several mixtures with a composition from 0.49 to 0.90 in ammonia mass fraction and temperatures from (208.15 to 373.15) K. The mean deviation was 1.4 %, and the maximum deviation was 2.6 %, when the experimental values were compared with the reported data.[9] On the other hand, Infante Ferreira[8] correlated the values of ref 9 together with pure ammonia density

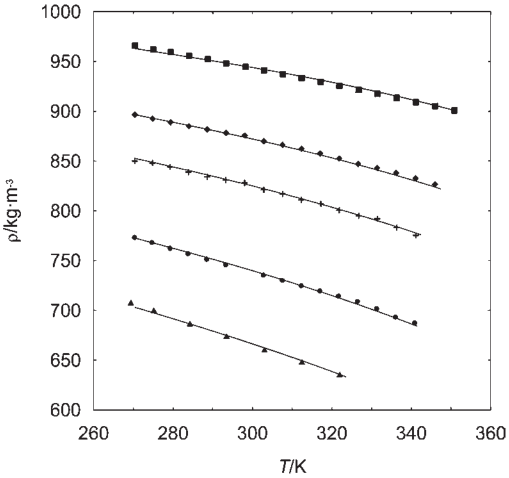

Figure 2. Density for the ammonia + sodium thiocyanate mixture at 3 MPa, several temperatures, and ammonia mass fractions: ■, 0.4998; ♦, 0.6140; +, 0.6824; ●, 0.7970; ▲, 0.8921; —, calculated values by eq 1.

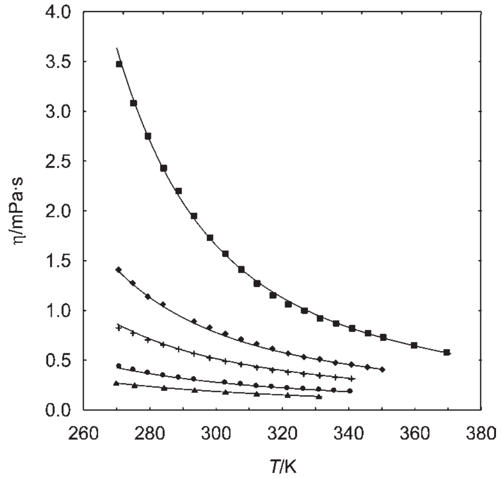

Figure 3. Viscosity for the ammonia + sodium thiocyanate mixture at 3 MPa, several temperatures, and ammonia mass fractions: ■, 0.4998; ♦, 0.6140; +, 0.6824; ●, 0.7970, ▲, 0.8921; —, calculated values by eq 2.

values. Comparing the experimental values of the present work with those calculated using the Infante Ferreira's correlation, the mean deviation was 2.0 %, and the maximum deviation was 3.9 %, so our values acceptably agree with Infante Ferreira's correlation and better with experimental data reported by Blytas and Daniels.[9] Deviations are shown in Figure 6.

The kinematic viscosity for NH_3 + NaSCN was measured by Blytas and Daniels,[9] but no data are shown in this paper; only a plot of dynamic viscosity versus temperature at several compositions is presented. For this reason, approximated values were obtained by interpolation in this figure and compared with experimental values of the present work, being the mean deviation of 32.7 % and the maximum deviation of 53.8 %. Besides, Infante Ferreira[8] correlated those data of ref 9 together with pure ammonia data. The mean deviation between the experimental data of present work and Infante Ferreira's correlation was 30.4 %, and the maximum deviation was 71.6 %. Deviations are shown in Figure 7. Our experimental viscosity data show large deviation with literature data, and generally they are higher values. Probably, the deviations between this work and literature values is due to the very different methodology used for measuring the viscosity. While we have used a closed viscometer with temperature and pressures controlled, keeping the sample compressed and liquid, Blytas and Daniels[9] used a viscometer with no constant pressure at different temperatures, while the composition changed with temperature due to the vaporization of ammonia. For this reason, a correction had to be applied. Also, experimental data are not reported by Blytas and Daniels;[9] only two plots are shown.

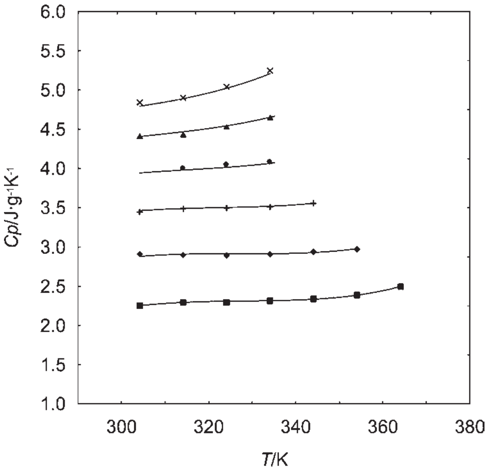

Figure 4. Isobaric heat capacity for the ammonia + sodium thiocyanate mixture at 3 MPa, several temperatures, and ammonia mass fractions: ■, 0.4992; ♦, 0.5988; +, 0.7013; ●, 0.7961; ▲, 0.9000; ×, 1.0000; —, calculated values by eq 3.

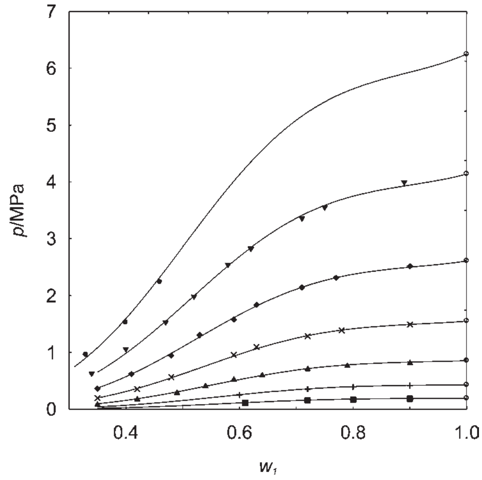

Figure 5. Vapor pressure for the ammonia + sodium thiocyanate mixture as a function of ammonia mass fractions w_1, at several temperatures: ■, 253.15 K; +, 273.15 K; ▲, 293.15 K; ×, 313.15 K; ♦, 333.15 K; ▼, 353.15 K; ●, 373.15 K; ○, literature[22] vapor pressure for pure ammonia; —, calculated values by eq 4.

Isobaric heat capacity was measured by Sargent and Beckman[11] (data not available) and by Blytas and Daniels,[9] who measured only four compositions at (273.15 and 298.15) K, and Infante Ferreira[8] used these data for correlating together with pure ammonia data. The range of temperature of the present work does not intersect with literature experimental data.[9,11] For this reason, a comparison was only carried out with Infante Ferreira's correlation.[8] The mean absolute and maximum deviations were 7.8 % and 13.9 %, respectively. In Figure 8 deviations

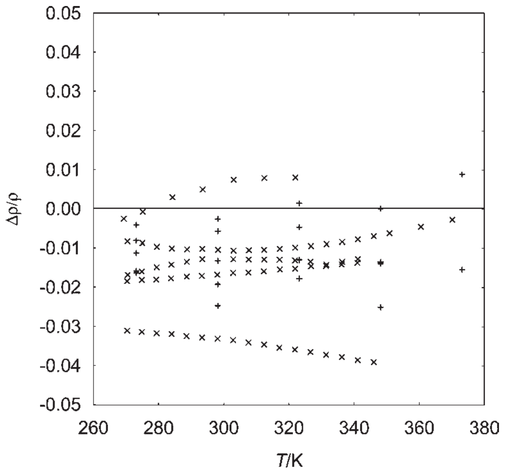

Figure 6. Relative deviations $\Delta\rho/\rho = [\rho(\text{exp}) - \rho(\text{calc})]/[\rho(\text{calc})]$ of the experimental densities $\rho(\text{exp})$ from values $\rho(\text{calc})$ estimated from literature data, for the mixture ammonia + sodium thiocyanate. +, ref 9; ×, ref 8.

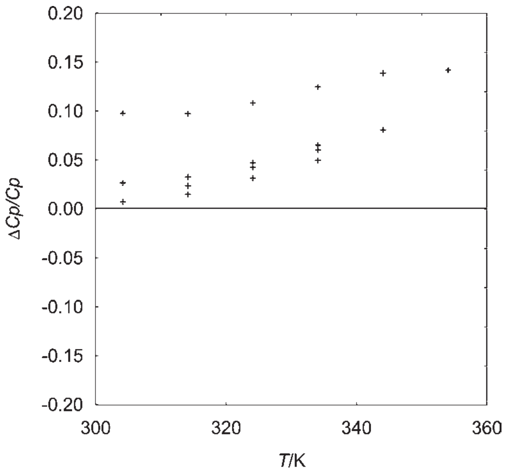

Figure 8. Relative deviations $\Delta C_p/C_p = [C_p(\text{exp}) - C_p(\text{calc})]/[C_p(\text{calc})]$ of the experimental heat capacities $C_p(\text{exp})$ from values $C_p(\text{calc})$ estimated from literature data, ref 8, for the mixture ammonia + sodium thiocyanate.

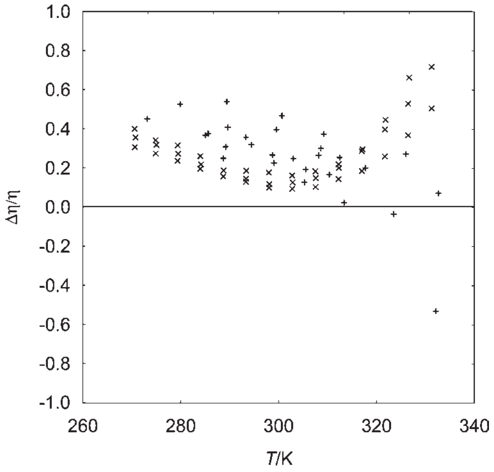

Figure 7. Relative deviations $\Delta\eta/\eta = [\eta(\text{exp}) - \eta(\text{calc})]/[\eta(\text{calc})]$ of the experimental dynamic viscosities $\eta(\text{exp})$ from values $\eta(\text{calc})$ estimated from literature data, for the mixture ammonia + sodium thiocyanate. +, ref 9; ×, ref 8.

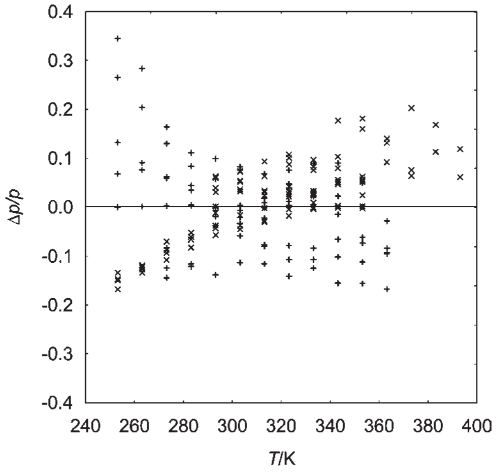

Figure 9. Relative deviations $\Delta p/p = [p(\text{exp}) - p(\text{calc})]/[p(\text{calc})]$ of the experimental vapor pressures $p(\text{exp})$ from values $p(\text{calc})$ estimated from literature data, for the mixture ammonia + sodium thiocyanate. +, ref 9; ×, ref 8.

are presented. Our results are higher that the values calculated with Infante Ferreira's correlation. Experimental data used by Infante Ferreira were not available; therefore, his correlation cannot be assessed.

Finally, for vapor pressure, Blytas and Daniels[9] measured in a range of ammonia mass fraction from 0.343 to 0.730 and temperatures from (253.15 to 363.15) K. Infante Ferreira[8] correlated these data together with Roberson and Lee[10] data and ammonia pure data. Roberson and Lee's data are not available. A comparison with the Blytas and Daniels[9] results, only in the range of temperature of the present work, shows mean absolute and maximum deviations of 10.0 % and 34.4 %, respectively. Compared with Infante Ferreria's correlation,[8] the mean absolute deviation was 8.5 %, and the maximum deviation was 20.2%. Deviations are shown in Figure 9. As it can be seen in Figure 9, deviations between reported data in literature are large. Differences between the experimental procedures used for measuring the vapor pressure could be the reason for the shown deviations. Blytas and Daniels[9] reported problems of condensation of ammonia in the gauge and the connecting tubes that could affect the results in the measurement. In our equipment, the use of the differential pressure transducer allows us to avoid condensation of vapor in the gauge because the equilibrium cell and the sensor remain immersed into the thermostatted liquid during the measurement.

■ CONCLUSIONS

The density, dynamic viscosity, and heat capacity of NH_3 + NaSCN solutions were measured at several ranges of temperature from (269.4 to 369.5) K at fixed pressure of 3 MPa and vapor pressure from (253.1 to 393.1) K, for ammonia mass fractions between 0.3 to 0.9. The experimental data were correlated with temperature and composition using empirical equations based on commonly used correlations for pure ammonia. Finally, the experimental data were compared with the literature data.

Only the density results were in agreement with literature data.[8,9] The rest of properties presented large deviations from the literature data, especially the viscosity and heat capacity, although the latter should not be compared because Blytas and Daniels[8] only measured four compositions of ammonia + sodium thiocyanate at (273.15 and 298.15) K.

Our results will be useful for the simulation of absorption refrigeration and power cycles with NH_3 + NaSCN working fluid.

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