Densities and Heat Capacities of the Ammonia + Water + NaOH and Ammonia + Water + KOH Solutions

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Ammonia + water + sodium hydroxide and ammonia + water + potassium hydroxide mixtures were chosen as potential candidates for absorption chillers driven by low-temperature heat sources. Heat capacity and density were studied between (293.15 and 353.15) K at a constant pressure of 1.8 MPa for these solutions using a heat flux Calvet-type calorimeter and a vibrating-tube densimeter, respectively. Measured data were well-correlated with temperature and composition using simple polynomial equations. The relative deviations between the experimental and calculated values in the density and heat capacity measurements were 0.20 % and 0.49 % for NH₃ + H₂O + NaOH solutions and 0.10 % and 0.36 % for NH₃ + H₂O + KOH solutions, respectively. Also, two density prediction methods were checked using the experimental data. Previously, it was necessary to measure the density of ammonia and hydroxide aqueous solutions in similar conditions. The results showed that both methods are suitable for predicting the density of these solutions.

Introduction

Several researchers have suggested that the performance of an absorption refrigeration cycle that uses a mixture of ammonia and water can be improved by adding inorganic salts to reduce the vapor pressure of water and, therefore, the rectification needed to separate the ammonia from the water.^{1–4} Such additives, NaOH and KOH, are used to shift the chemical equilibrium toward a more effective separation of ammonia molecules in the ammonia–water absorption refrigeration system. In this case, hydroxide tends to salt out ammonia in the solution, simplify the design, cut the rectification load and cost of the generator, and allow the generator to operate at a lower temperature. This improves the coefficient of performance.

There are very few data in the literature about the thermophysical properties of ammonia-water-hydroxide. This information is needed in order to evaluate the potential of these selected additives and especially for designing industrial plants and solving material and energy balances required for the optimization of chemical processes. Reiner and Zaltash¹ measured the densities, viscosities, and boiling points of the solutions formed by various salts dissolved in ammonia-water solvent (4 % mass fraction of ammonia).

In our previous study,⁵ the vapor-liquid equilibria of ammonia + water + NaOH and ammonia + water + KOH solutions were measured between (293.15 and 353.15) K for mass fractions up to 0.4 ammonia and 0.2 hydroxide. In the present work, we obtain the densities and heat capacities of the proposed solutions for various compositions using a vibrating-tube densimeter and a C-80 Setaram calorimeter, respectively, in 10 K steps between (293.15 and 353.15) K.

Experimental Section

Materials. Benzene (Panreac, 99.8 %), heptane (Fluka, > 99.5 %), octane (Fluka, > 99.5 %), ammonia (Carburos Metálicos,

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99.98 %), potassium hydroxide (Aldrich, 99.99 % pellets), and sodium hydroxide (Aldrich 99.998 % pellets) were used without further purification. Only heptane, octane, and benzene were stored over molecular sieves to remove water. All solutions were prepared using Millipore water (resistivity less than 18.2 M Ω · cm). Potassium hydroxide pellets contained some residual water. The exact concentration was found by titration using an Orion 960 autochemisty system.

Apparatus and Procedure. Densities of the ammonia + water + sodium hydroxide and ammonia + water + potassium hydroxide solutions at a pressure of 1.8 MPa were measured between (293.15 and 353.15) K using an Anton Paar vibratingtube densimeter (DMA60/512P) connected to a pressure system. The experimental apparatus and procedure used for the density measurement were the same as in our previous studies.^{6,7} Pressure was applied to the system with nitrogen gas. This was controlled using a pressure generator (HiP 50-6-15) and measured with a pressure transducer SETRA C280E. The temperature of the densimeter cell was regulated using a Julabo F-20 thermostat and measured by a digital thermometer (Anton Paar MKT 100). Millipore water and nitrogen gas were used as reference fluids for the calibration of the densimeter at 1.8 MPa. A test measurement was done with benzene in the range (283.15 to 353.15) K and compared with literature data.⁸ The resulting average deviation was 0.1 %.

A recently developed experimental procedure, using a differential heat flux Calvet-type calorimeter (Setaram C-80 II), was used to measure the heat capacity of the ammonia + water + NaOH and ammonia + water + KOH solutions. The experimental device used in this work was described in detail by Esteve et al.⁶ and Conesa.⁹ Special measuring and reference cells made of stainless steel with an inner volume of 11 cm³ were designed to provide a working range from room temperature up to 573 K and pressure up to 3 MPa. The cells were connected to a pressure control assembly by stainless steel capillaries with inner diameters of 1 mm. The assembly consisted of a buffer volume of 1000 cm³ filled with nitrogen,

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Table 1.	Experimental	Density	Data	for	NH ₃	(1) -	H ₂ O	(2) +
NaOH (3	8) at 1.8 MPa							

Table 3. Experimental Heat Capacity Data for NH₃ (1) + H₂O (2) + NaOH (3) at 1.8 MPa

$100 \cdot w_1$	$100 \cdot w_2$	$ ho/kg \cdot m^{-3}$	$100 \cdot w_1$	$100 \cdot w_2$	$\rho/kg \cdot m^{-3}$					
		T = 29	3.15 K							
8.43	16.54	1135.4	17.38	13.58	1060.4					
9.37	8.42	1052.1	28.88	3.97	931.1					
9.46	3.76	997.7								
	T = 303.15 K									
8.43	16.54	1129.1	17.38	13.58	1053.4					
9.37	8.42	1046.8	28.88	3.97	924.1					
9.46	3.76	993.1								
T = 313.15 K										
8.43	16.54	1122.9	17.38	13.58	1046.6					
9.37	8.42	1041.3	28.88	3.97	916.7					
9.46	3.76	988.1								
T = 323.15 K										
8.43	16.54	1116.4	17.38	13.58	1039.4					
9.37	8.42	1035.4	28.88	3.97	909.1					
9.46	3.76	982.8								
		T = 33	3.15 K							
8.43	16.54	1109.5	17.38	13.58	1031.9					
9.37	8.42	1028.9	28.88	3.97	901.0					
9.46	3.76	976.7								
		T = 34	3.15 K							
8.43	16.54	1102.6	17.38	13.58	1024.3					
9.37	8.42	1022.4	28.88	3.97	892.5					
9.46	3.76	970.5								
		T = 35	3.15 K							
8.43	16.54	1095.3	17.38	13.58	1016.3					
9.37	8.42	1015.3	28.88	3.97	883.6					
9.46	3.76	963.5								

Table 2. Experimental Density Data for $NH_3(1) + H_2O(2) + KOH$ (4), at 1.8 MPa

$100 \cdot w_1$	$100 \cdot w_4$	$ ho/kg \cdot m^{-3}$	$100 \cdot w_1$	$100 \cdot w_4$	$ ho/kg \cdot m^{-3}$				
		T = 29	3.15 K						
8.37	15.75	1103.5	32.78	16.97	995.9				
9.42	7.5	1025.5	35.35	4.5	909.9				
19.48	3.69	954.8							
T = 303.15 K									
8.37	15.75	1098.0	32.78	16.97	987.0				
9.42	7.5	1020.7	35.35	4.5	901.9				
19.48	3.69	949.1							
		T = 31	3.15 K						
8.37	15.75	1092.4	32.78	16.97	978.1				
9.42	7.5	1015.6	35.35	4.5	893.8				
19.48	3.69	943.1							
T = 323.15 K									
8.37	15.75	1086.5	32.78	16.97	969.0				
9.42	7.5	1010.1	35.35	4.5	885.3				
19.48	3.69	936.7							
		T = 33	3.15 K						
8.37	15.75	1080.1	32.78	16.97	959.3				
9.42	7.5	1003.9	35.35	4.5	876.3				
19.48	3.69	929.7							
		T = 34	3.15 K						
8.37	15.75	1073.6	32.78	16.97	949.5				
9.42	7.5	997.5	35.35	4.5	867.1				
19.48	3.69	922.5							
		T = 35	3.15 K						
8.37	15.75	1066.6	32.78	16.97	939.4				
9.42	7.5	990.5	35.35	4.5	857.2				
19.48	3.69	914.7							

which served to reduce pressure pulses generated in the system. Pressure in the system was measured by a pressure transducer SETRA C280E. The change in pressure during one run of experiments was below 0.02 MPa. This is negligible as compared to the pressure dependence of the heat capacity of measured compounds.

$100 \cdot w_1$	$100 \cdot w_3$	$C_p/J \cdot g^{-1} \cdot K^{-1}$	$100 \cdot w_1$	$100 \cdot w_3$	$C_p/J \cdot g^{-1} \cdot K^{-1}$				
T = 302.74 K									
8.67	16.28	3.632	24.09	3.79	4.095				
9.16	10.68	3.838	34.23	15.55	4.001				
10.37	3.93	4.020	35.82	10.52	4.100				
18.91	16.95	3.832	36.71	3.83	4.216				
T = 312.66 K									
8.67	16.28	3.676	24.09	3.79	4.158				
9.16	10.68	3.872	34.23	15.55	4.039				
10.37	3.93	4.052	35.82	10.52	4.154				
18.91	16.95	3.873	36.71	3.83	4.300				
T = 322.57 K									
8.67	16.28	3.713	24.09	3.79	4.208				
9.16	10.68	3.895	34.23	15.55	4.070				
10.37	3.93	4.073	35.82	10.52	4.200				
18.91	16.95	3.898	36.71	3.83	4.363				
		T = 33	2.47 K						
8.67	16.28	3.745	24.09	3.79	4.256				
9.16	10.68	3.919	34.23	15.55	4.098				
10.37	3.93	4.101	35.82	10.52	4.254				
18.91	16.95	3.920	36.71	3.83	4.421				
		T = 34	2.38 K						
8.67	16.28	3.781	24.09	3.79	4.305				
9.16	10.68	3.940	34.23	15.55	4.125				
10.37	3.93	4.128	35.82	10.52	4.306				
18.91	16.95	3.945	36.71	3.83	4.486				
		T = 35	2.28 K						
8.67	16.28	3.813	24.09	3.79	4.337				
9.16	10.68	3.950	35.82	10.52	4.367				
10.37	3.93	4.147	36.71	3.83	4.544				
18.91	16.95	3.959							

Table 4. Experimental Heat Capacity Data for $NH_{3}\left(1\right)$ + $H_{2}O\left(2\right)$

+ KOH (4) at 1.8 MPa								
$100 \cdot w_1$	$100 \cdot w_4$	$C_p/J \cdot g^{-1} \cdot K^{-1}$	$100 \cdot w_1$	$100 \cdot w_4$	$C_p/J \cdot g^{-1} \cdot K^{-1}$			
		T = 30	2.74 K					
8.25	16.80	3.449	23.12	4.60	4.020			
8.92	10.73	3.678	33.29	16.32	3.740			
9.77	3.89	3.930	35.32	3.74	4.169			
20.67	16.60	3.579	36.12	10.49	3.942			
22.03	10.68	3.776						
		T = 31	2.66 K					
8.25	16.80	3 486	23.12	4.60	4 083			
8.92	10.73	3,720	33.29	16.32	3.790			
9.77	3.89	3 958	35.32	3 74	4 246			
20.67	16.60	3 625	36.12	10.49	4 009			
22.03	10.68	3.835	50.12	10.17	1.009			
		T = 32	2 57 K					
8 25	16.80	3 510	2.37 K	4.60	4 131			
8.02	10.00	3 746	23.12	16.32	3 828			
9.72	3.80	3 98/	35.27	3 74	1 315			
20.67	16.60	3.660	36.12	10.49	4.058			
22.03	10.00	3 869	50.12	10.47	4.050			
22.05	10.00	5.007						
		T = 33	2.47 K					
8.25	16.80	3.531	23.12	4.60	4.181			
8.92	10.73	3.770	33.29	16.32	3.865			
9.77	3.89	4.019	35.32	3.74	4.374			
20.67	16.60	3.694	36.12	10.49	4.102			
22.03	10.68	3.899						
		T = 34	2.38 K					
8.25	16.80	3.552	23.12	4.60	4.232			
8.92	10.73	3.797	33.29	16.32	3.906			
9.77	3.89	4.054	35.32	3.74	4.441			
20.67	16.60	3.729	36.12	10.49	4.156			
22.03	10.68	3.936						
		T = 35	2.28 K					
8.25	16.80	3.574	23.12	4.60	4.271			
8.92	10.73	3.822	33.29	16.32	3.943			
9.77	3.89	4.080	35.32	3.74	4.498			
20.67	16.60	3.760	36.12	10.49	4.203			
22.03	10.68	3.969						

$ \mathbf{A} = \mathbf{A} =$	Table 5.	Coefficients	of Equation	4 for the	Density of NH ₃	$+ H_2O +$	- NaOH	at 1.8 MPa
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coeff a_{ij}		$\operatorname{coeff} b_{ij}$		coeff c_{ij}	
kg•m ⁻³	value	$kg \cdot m^{-3} \cdot K^{-1}$	value	$\overline{\text{kg}}\cdot\text{m}^{-3}\cdot\text{K}^{-2}$	value
<i>a</i> ₀₀	8.211×10^{2}	b_{00}	1.416×10^{0}	C ₀₀	-2.856×10^{-3}
a_{01}	2.338×10^{1}	b_{01}	-6.568×10^{-2}	C ₀₁	8.706×10^{-5}
a_{10}	1.986×10^{0}	b_{10}	-2.203×10^{-2}	C10	1.606×10^{-5}
a_{11}	-4.131×10^{-2}	b_{11}	-7.400×10^{-4}	c_{11}	1.315×10^{-6}

Table 6. Coefficients of Equation 4 for the Density of NH₃ + H₂O + KOH at 1.8 MPa

coeff a_{ij}		coeff b_{ij}		coeff c_{ij}	
kg·m ⁻³	value	$kg \cdot m^{-3} \cdot K^{-1}$	value	$\overline{\text{kg}}\cdot\text{m}^{-3}\cdot\text{K}^{-2}$	value
<i>a</i> ₀₀	8.153×10^{2}	b_{00}	1.393×10^{0}	C ₀₀	-2.803×10^{-3}
a_{01}	1.964×10^{1}	b_{01}	-5.423×10^{-2}	c_{01}	7.521×10^{-5}
a_{10}	2.610×10^{0}	b_{10}	-2.423×10^{-2}	c_{10}	1.921×10^{-5}
a_{11}	-1.933×10^{-1}	b_{11}	5.123×10^{-4}	c_{11}	-8.998×10^{-7}

Table 7.	Coefficients	of Equation	4 for th	e Heat	Capacity	of NH ₃	+ H	-0+	NaOH at	1.8 MPa
	000000000000000000000000000000000000000	or highertron			Capacity			2 -2 -		TIO 1111 44

coeff a_{ij}		$\operatorname{coeff} b_{ij}$		coeff c_{ij}	
$\overline{\mathbf{J}}\cdot\mathbf{g}^{-1}\cdot\mathbf{K}^{-1}$	value	$\overline{\mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-2}}$	value	$\overline{\mathbf{J} \cdot \mathbf{g}^{-3} \cdot \mathbf{K}^{-3}}$	value
<i>a</i> ₀₀	1.085×10^{0}	b_{00}	1.776×10^{-2}	C00	-2.636×10^{-5}
a_{01}	-1.716×10^{-1}	b_{01}	7.487×10^{-4}	c_{01}	-9.297×10^{-7}
a_{10}	-8.566×10^{-2}	b_{10}	3.920×10^{-4}	C_{10}	-2.973×10^{-7}
a_{11}	1.921×10^{-2}	b_{11}	-1.059×10^{-4}	c_{11}	1.452×10^{-7}

Table 8. Coefficients of Equation 4 for the Heat Capacity of $NH_3 + H_2O + KOH$ at 1.8 MPa

$\operatorname{coeff} a_{ij}$		$\operatorname{coeff} b_{ij}$		coeff c_{ij}	
$\overline{\mathbf{J}}\cdot\mathbf{g}^{-1}\cdot\mathbf{K}^{-1}$	value	$\overline{\mathbf{J}} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-2}$	value	$\overline{J \cdot g^{-3} \cdot K^{-3}}$	value
<i>a</i> ₀₀	2.612×10^{0}	b_{00}	6.676×10^{-3}	C ₀₀	-7.191×10^{-6}
a_{01}	4.297×10^{-1}	b_{01}	-2.855×10^{-3}	c_{01}	4.364×10^{-6}
a_{10}	1.606×10^{-2}	b_{10}	-1.710×10^{-4}	C_{10}	4.895×10^{-7}
a_{11}	-2.241×10^{-2}	b_{11}	1.424×10^{-4}	c_{11}	-2.257×10^{-7}

To calibrate the experimental technique, we took measurements with three calibrating substances for which experimental data are available: vacuum, water, and heptane. The reference vessel was kept under vacuum for all the experiments. Measurements were taken from (293.15 to 353.15) K at 1.8 MPa. A step method was used to determine the heat capacity of the sample. The measurement procedure (step in temperature) was completely controlled by a computer. In all the experiments, the heating rate was $0.3 \text{ K} \cdot \text{min}^{-1}$. The charge of the measuring vessel with ammonia + water + salt was the same as that described by Salavera et al.⁵ The performance of the calorimeter was checked by measuring the heat capacity of octane for identical conditions to those in the present study. The results

were compared with Zábranský et al.,¹⁰ and the deviation of the measured values was less than 0.4%.

Uncertainties of Measurement. Standard uncertainty of temperature to both experimental devices was \pm 0.01 K according to the respective calibration certificates. The standard uncertainty of the pressure transducer was 0.11 % FS. For estimating the uncertainty of compositions, we calculated the difference between initial and calculated composition according to previous studied⁵ resulting a standard uncertainty in the mass fraction of \pm 0.0005 for ammonia and \pm 0.0001 for the hydroxides. Combined standard uncertainties of density and heat capacity were \pm 0.3 kg·m⁻³ and \pm 0.006 kJ·kg⁻¹·K⁻¹, respectively.



Figure 1. Density of NH₃ (1) + H₂O (2) + NaOH (3) solution at 1.8 MPa and (293.15 to 353.15)K: -, calculated data using eq 1; \blacktriangle , $w_1 = 0.0843$, $w_3 = 0.1654$; \blacksquare , $w_1 = 0.1738$, $w_3 = 0.1358$; \blacklozenge , $w_1 = 0.2888$, $w_3 = 0.0397$; \diamondsuit , $w_1 = 0.0946$, $w_3 = 0.0376$.



Figure 2. Density of NH₃ (1) + H₂O (2) + KOH (4) solution at 1.8 MPa and (293.15 to 353.15)K: -, calculated data using eq 1; \blacklozenge , $w_1 = 0.0837$, $w_4 = 0.1575$; \blacksquare , $w_1 = 0.0942$, $w_4 = 0.0750$; \blacklozenge , $w_1 = 0.3278$, $w_4 = 0.1697$; \blacklozenge , $w_1 = 0.1948$, $w_4 = 0.0369$; **X**, $w_1 = 0.3535$, $w_4 = 0.0450$.



Figure 3. Heat capacity of NH₃ (1) + H₂O (2) + NaOH (3) solution at 1.8 MPa and (293.15 to 353.15) K: -, calculated data using eq 1: \blacklozenge , $w_1 = 0.3671$, $w_3 = 0.0383$; \blacksquare , $w_1 = 0.2409$, $w_3 = 0.0379$; \blacklozenge , $w_1 = 0.1037$, $w_3 = 0.0393$.



Figure 4. Heat capacity of NH₃ (1) + H₂O (2) + KOH (4) solution at 1.8 MPa and (293.15 to 353.15) K: -, calculated data using eq 1: \blacklozenge , $w_1 = 0.3532$, $w_4 = 0.0374$; \blacksquare , $w_1 = 0.2312$, $w_4 = 0.0460$; \blacklozenge , $w_1 = 0.0977$, $w_4 = 0.0389$.

Table 9. Experimental Density Data for $NH_3\ (1)+H_2O\ (2)$ at 1.8 MPa

$100 \cdot w_1$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_1$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_1$	$ ho/kg\cdot m^{-3}$				
		T = 2	93.15 K						
7.69	967.2	16.32	936.8	29.54	895.4				
13.55	946.5	23.06	916.6	39.43	865.5				
T = 303.15 K									
7.69	963.7	16.32	932.0	29.54	888.8				
13.55	942.2	23.06	910.9	39.43	857.4				
		T = 3	13.15 K						
7.69	959.6	16.32	926.7	29.54	881.7				
13.55	937.3	23.06	904.8	39.43	849.0				
T = 323.15 K									
7.69	954.6	16.32	921.1	29.54	874.3				
13.55	931.9	23.06	898.2	39.43	840.3				
		T = 3	33.15 K						
7.69	949.2	16.32	914.6	29.54	866.3				
13.55	925.8	23.06	891.0	39.43	831.1				
		T = 3	43.15 K						
7.69	943.4	16.32	907.8	29.54	858.1				
13.55	919.3	23.06	883.7	39.43	821.5				
		T = 3	53.15 K						
7.69	936.8	16.32	900.3	29.54	849.2				
13.55	912.2	23.06	875.7	39.43	811.4				

Table 10. Experimental Density Data for NaOH (3) + H_2O (2) at 1.8 MPa

$100 \cdot w_3$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_3$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_3$	$ ho/{\rm kg}{ m \cdot}{\rm m}^{-3}$		
3.97	1042.6	T = 2 11.85 16.00	293.15 K 1132.7 1179 3	20.01	1225.0		
3.97	1039.0	T = 3 11.85	03.15 K 1127.7	20.01	1219.3		
7.98	1084.5	16.00 T = 3	1173.9				
3.97 7.98	1034.9 1079.9	11.85 16.00	1122.6 1168.4	20.01	1213.6		
3.97 7.98	1030.2 1074.9	T = 3 11.85 16.00	23.15 K 1117.1 1162.6	20.01	1207.9		
3.97	1024.9	T = 3 11.85 16.00	33.15 K 1111.1 1156 3	20.01	1202.4		
T = 343.15 K 3.97 1019.1 11.85 1105.1 20.01 1196.8							
7.98 1063.3 16.00 1149.9 $T = 353.15 \text{ K}$							
3.97 7.98	1012.9 1057.1	11.85 16.00	1098.7 1143.3	20.01	1190.5		

Results and Discussion

The densities and heat capacity of the ammonia + water + NaOH and ammonia + water + KOH solutions were measured for temperatures between (293.15 and 353.15) K, ammonia mass fraction from 0.1 to 0.4, and mass fraction range of hydroxides from 0.04 to 0.20. All data are presented in Tables 1 to 4. Density and heat capacity data were regressed by similar equations:

$$\rho/\text{g}\cdot\text{cm}^{-3} = A + B(T/\text{K}) + C(T/\text{K})^2$$
 (1)

$$C_p / \mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{K}^{-1} = A + B(T/\mathbf{K}) + C(T/\mathbf{K})^2$$
 (2)

where ρ is the density of the mixture; C_p is the heat capacity; T is the absolute temperature; and A, B, and C are parameters

Table 11. Experimental Density Data for KOH (4) + H_2O (2) at 1.8 MPa

$100 \cdot w_4$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_4$	$ ho/kg\cdot m^{-3}$	$100 \cdot w_4$	$ ho/kg\cdot m^{-3}$				
T = 293.15 K									
3.37	1029.3	10.41	1087.7	17.31	1152.3				
6.96	1058.7	13.93	1118.8						
T = 303.15 K									
3.37	1026.1	10.41	1083.8	17.31	1147.7				
6.96	1055.2	13.93	1114.5						
T = 313.15 K									
3.37	1022.2	10.41	1079.3	17.31	1142.7				
6.96	1050.9	13.93	1109.8						
T = 323.15 K									
3.37	1017.9	10.41	1074.6	17.31	1137.7				
6.96	1046.3	13.93	1104.8						
T = 333.15 K									
3.37	1012.8	10.41	1069.4	17.31	1132.2				
6.96	1041.2	13.93	1099.6						
T = 343.15 K									
3.37	1007.4	10.41	1063.8	17.31	1126.6				
6.96	1035.8	13.93	1093.9						
T = 353.15 K									
3.37	1001.2	10.41	1057.7	17.31	1120.5				
6.96	1029.7	13.93	1087.9						

dependent on the ammonia and hydroxide compositions:

$$A = \sum_{0}^{1} a_{i}(100 \cdot w_{1})^{i} \quad B = \sum_{0}^{1} b_{i}(100 \cdot w_{1})^{i} \quad C = \sum_{0}^{1} c_{i}(100 \cdot w_{1})^{i}$$
(3)

where w_1 is the ammonia mass fraction, and a_i , b_i , and c_i are hydroxide composition dependent parameters:

$$a_{i} = \sum_{j=0}^{1} a_{ij} (100 \cdot w_{3})^{j} \quad b_{i} = \sum_{j=0}^{1} b_{ij} (100 \cdot w_{3})^{j}$$
$$c_{i} = \sum_{j=0}^{1} c_{ij} (100 \cdot w_{3})^{j} \quad (4)$$

where w_3 is the mass fraction of the hydroxide.

The parameters a_{ij} , b_{ij} , and c_{ij} were obtained by correlating the experimental data using a least-squares method. The values of the parameters are shown in Tables 5 to 8. The root mean standard deviations for the densities of the NH₃ (1) + H₂O (2) + NaOH (3) and NH₃ (1) + H₂O (2) + KOH (4) solutions were 0.20 % and 0.10 %, respectively. The root mean standard deviations for the heat capacities were 0.49 % and 0.36 %, respectively.

Figures 1 and 2 show the densities (experimental and calculated) of the two ternary systems. The density of ammonia + water + hydroxide solution decreases as the temperature and hydroxide content increase. Figures 3 and 4 show the experimental and calculated values of heat capacity for the NH₃ + H₂O + NaOH and NH₃ + H₂O + KOH systems, respectively, for different ammonia mass fraction and a hydroxide mass fraction of 0.04. Heat capacity increases as the temperature and ammonia composition increase and decreases as the hydroxide composition decreases.

Two prediction methods were used to estimate the densities of the ternary mixture from the binary systems. One of these methods, which was proposed by Young and Smith,¹¹ was described in a previous study.⁷ The other method was recently proposed by Laliberté and Cooper.¹² These methods were selected because only the densities of the aqueous solution of each component were necessary. The densities of ammonia, sodium hydroxide, and potassium hydroxide aqueous solutions were therefore measured in the same ranges of temperature and concentration for the ternary systems. Tables 9 to 11 show the experimental densities for NH₃ (1) + H₂O (2), NaOH (3) + H₂O (2), and KOH (4) + H₂O (2). The root mean standard deviations between experimental and estimated values for the NH₃ + H₂O + NaOH and NH₃ + H₂O + KOH systems were 0.83 % and 1.67 %, respectively, with Young and Smith's method and 0.29 % and 0.55 %, respectively, with Laliberté and Cooper's method.

Conclusions

We have developed new working fluids for absorption chillers using the optimally mixed hydroxide in the ammonia + water system. As a potential solution mixture, we tested the ammonia + water + NaOH and ammonia + water + KOH systems in which hydroxides are used as additives. The densities and heat capacities of these ternary solutions were measured over useful ranges of concentration and temperature. The data for each property were correlated with a regression equation. The calculated values showed good agreement with the measured values. We tested two methods to estimate the densities of the ternary solutions and found that the method of Laliberté and Cooper was more suitable for these solutions.

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