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DATA

Densities and Excess Molar Volumes of the Ternary System $N_2O_4 + H_2O + HNO_3$ at 278.15 K, 283.15 K, 288.15 K, and 293.15 K

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ABSTRACT: The experimental data of densities for the $N_2O_4 + H_2O + HNO_3$ system were measured with the N_2O_4 mole fractions from 0 to 0.15 and H_2O mole fraction from 0.08 to 0.33 at 278.15 K, 283.15 K, 288.15 K, and 293.15 K. The excess molar volumes (V^E) at 293.15 K were obtained from the experimental results for this ternary system. The experimental results were correlated using an empirical equation. The average absolute deviations (AADs) between the calculated and experimental data were calculated.

INTRODUCTION

Recently, dinitrogen pentoxide (N_2O_5) as a green nitrating agent has many applications in the nitration of organic compounds, especially in the synthesis of energetic materials.[1,2] Electrochemical synthesis of N_2O_5 is one of the main preparation methods, and much work has been done on this method.[2−6] For this method, it is very important to develop a online composition analysis technique of the electrosynthesis solution. Usually, a mixture of N_2O_4, H_2O and HNO_3 as the catholyte and a mixture of N_2O_5, N_2O_4, and HNO_3 as the anolyte are obtained at the end of electrolysis in the electrosynthesis of N_2O_5. A variety of analytical techniques were investigated to monitoring the composition of the electrosynthesis solutions such as nuclear magnetic resonance (NMR),[5] density measurement, redox potential measurement,[6] acidity titration,[7] infrared spectrophotometry,[8] and Raman spectroscopy.[9] Among these methods, the density measurement of the electrosynthesis catholyte was used as the primary online, real-time analytical technique for most of bench- and pilot-scale electrosynthesis of N_2O_5.[6] However, this technique cannot be widely applied without the density data of the N_2O_4, H_2O, and HNO_3 ternary system at different experimental temperatures. Therefore, it is necessary to study the N_2O_4, H_2O, and HNO_3 system and construct a diagram of density of this system.

In this work, the densities for the ternary system $N_2O_4 + H_2O + HNO_3$ with N_2O_4 mole fractions from 0 to 0.15 and H_2O mole fractions from 0.08 to 0.33 were measured at 278.15 K, 283.15 K, 288.15 K, and 293.15 K. The excess molar volumes, V^E, of these mixtures at 293.15 K were also calculated and discussed.

EXPERIMENTAL SECTION

Materials. Cerium(IV) sulfate ($w > 0.995$, Huabei Special Reagent, Huabei, China), iron(II) ammonium sulfate ($w > 0.995$, Huabei Special Reagent), sodium hydroxide ($w > 0.995$, Huabei Special Reagent, Huabei, China), white fuming nitric acid ($w > 0.998$, Shandong Unite Chemical Industry, Shandong, China), and dinitrogen tetraoxide ($w > 0.998$, Jilin Chemical Industry, Jilin, China) were used as received. Deionized water was employed.

Apparatus. The solutions were prepared by a gravimetric method, which was carried out on a Libor AEG-220 balance (Germany) with a precision of 0.1 mg. Densities of solutions were measured on a Mettler Toledo DE-40 vibrating tube densimeter with an uncertainty of $\pm 1 \cdot 10^{-4}\ \mathrm{g \cdot cm^{-3}}$.

Sample Preparation and Analytical Methods. The mass of a 10 mL dry glass bottle was first determined. The cold white fuming nitric acid was introduced into the bottle, and the total mass was recorded. Then, the deionized water and dinitrogen tetroxide were introduced successively at or below 263 K to avoid the volatilization of HNO_3 and N_2O_4. The mass of each component was determined, respectively. The obtained mixture was then stirred for 12 h below 263 K. The compositions of solutions were also determined by oxidation−reduction with an acidity titration method in which the cerium(IV) sulfate, iron(II) ammonium sulfate, and sodium hydroxide were used as the oxidant, reductant, and neutralizer, respectively.[10] The uncertainties in the measurement of N_2O_4 and H_2O were ± 0.0027 and ± 0.0028, respectively.

Density Measurement. Prior to each measurement at a given temperature, the densimeter was first calibrated using dry air and distilled water as a reference substance at atmospheric pressure. The temperature was controlled by the self-contained Peltier systems of the densimeter with an uncertainty of ± 0.01 K. The sample was stabilized at the given temperature for 600 s to determine the density. At the given temperature, the density of each sample was measured three times; the average value was used.

RESULTS AND DISCUSSION

Experimental densities, ρ, of the $N_2O_4(1) + H_2O(2) + HNO_3(3)$ ternary system at 278.15 K, 283.15 K, 288.15 K, and 293.15 K, respectively, are listed in Tables 1 to 3. The excess molar volume, V^E, at 293.15 K was calculated from the experimental results by the following equation:[11]

$$V^E = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho} - \frac{x_1M_1}{{\rho_1}^a} - \frac{x_2M_2}{\rho_2} - \frac{x_3M_3}{{\rho_3}^b} \qquad (1)$$

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Table 1. Experimental Densities, ρ, at Various Temperatures and Excess Molar Volume, V^E, at 293.15 K for N_2O_4 (1) + H_2O (2) + HNO_3 (3)

x_1	x_2	$\rho/(g \cdot cm^{-3})$				$V^E/(cm^3 \cdot mol^{-1})$
		278.15 K	283.15 K	288.15 K	293.15 K	293.15 K
1.0000	0	-	-	-	1.448[a]	-
0	0	-	-	-	1.5128[b]	
0	1.0000	1.0000	0.9997	0.9991	0.9982	-
0.0038	0.0917	1.5353	1.5265	1.5179	1.5092	−0.480
0.0140	0.1127	1.5415	1.5328	1.5242	1.5155	−0.799
0.0231	0.1318	1.5465	1.5379	1.5293	1.5207	−1.070
0.0330	0.1522	1.5512	1.5426	1.5340	1.5254	−1.337
0.0462	0.1796	1.5570	1.5482	1.5398	1.5312	−1.675
0.0520	0.1915	1.5588	1.5502	1.5416	1.5329	−1.802
0.0759	0.2411	1.5643	1.5556	1.5469	1.5381	−2.278
0.0908	0.2719	1.5653	1.5565	1.5476	1.5387	−2.511
0.1041	0.3000	1.5634	1.5545	1.5456	1.5365	−2.662
0.1150	0.3221	1.5602	1.5512	1.5421	1.5330	−2.743
0.0021	0.3096	1.5099	1.5015	1.4931	1.4847	−1.292
0.0165	0.2869	1.5218	1.5133	1.5049	1.4963	−1.437
0.0239	0.2752	1.5280	1.5194	1.5109	1.5023	−1.517
0.0396	0.2502	1.5412	1.5326	1.5239	1.5153	−1.701
0.0448	0.2420	1.5448	1.5362	1.5276	1.5189	−1.749
0.0509	0.2322	1.5499	1.5413	1.5327	1.5240	−1.827
0.0649	0.2099	1.5604	1.5517	1.5430	1.5343	−1.979
0.0766	0.1914	1.5692	1.5605	1.5518	1.5431	−2.119
0.0816	0.1836	1.5726	1.5639	1.5552	1.5464	−2.169
0.0895	0.1707	1.5783	1.5697	1.5610	1.5523	−2.267
0.1027	0.1499	1.5877	1.5790	1.5704	1.5616	−2.424
0.1168	0.1276	1.5972	1.5885	1.5798	1.5711	−2.589
0.1445	0.0835	1.6156	1.6070	1.5983	1.5898	−2.937

[a] The data from ref 3. [b] The data from ref 12.

where ρ and ρ_i are the density of the mixture and pure component i, respectively; the superscript a and b represent the pure N_2O_4 data from ref 3 and the pure HNO_3 data from ref 12 at 293.15 K, respectively; x_i represents the mole fraction of component i of the mixture; M_i is the molecular weight of component i of the mixture. Because of the unavailability of anhydrous HNO_3 and the vigorous volatilization of N_2O_4 at the experimental temperatures, it is difficult to obtain the densities of pure HNO_3 and pure N_2O_4. Therefore, the literature data of the densities of pure HNO_3 and pure N_2O_4 were used in eq 1. The experimental densities of pure water at different temperatures (see Table 1) were used in eq 1.

The densities of the N_2O_4 + H_2O + HNO_3 ternary system varying with composition at 293.15 K are shown in Figure 1. It could be seen that the density increased first and then decreased with the simultaneous increase of N_2O_4 and H_2O at a constant temperature, which was consistent with the electrosynthesis result of Harrar et al.[6]

The effect of N_2O_4 on the density and excess molar volume were listed in Table 2, in which the mole fraction of water was kept in the range of 0.0835 to 0.0931 or 0.3096 to 0.3221, respectively. The results with water mole fraction at 0.0835 to 0.0931 were plotted in Figure 2. It could be seen that the density of this ternary system increased with the increase of N_2O_4. The excess molar volumes versus N_2O_4 mole fraction were plotted in Figure 3. As shown in Figure 3, the V^E decreased with N_2O_4 increasing at 293.15 K. N_2O_4 had much more influence on the V^E of this ternary system at low water mole fractions than at high water mole fractions.

Table 2. Experimental Densities, ρ, at Various Temperatures and Excess Molar Volume, V^E, at 293.15 K for the N_2O_4 (1) + H_2O (2) + HNO_3 (3) System

x_1	x_3	$\rho/(g \cdot cm^{-3})$				$V^E/(cm^3 \cdot mol^{-1})$
		278.15 K	283.15 K	288.15 K	293.15 K	293.15 K
		$x_2 = 0.0835 - 0.0931$				
0.1445	0.7720	1.6156	1.6070	1.5983	1.5896	−2.932
0.1332	0.7824	1.6107	1.6021	1.5935	1.5847	−2.772
0.1195	0.7950	1.6046	1.5960	1.5874	1.5787	−2.578
0.1088	0.8051	1.5995	1.5909	1.5824	1.5737	−2.418
0.0984	0.8149	1.5944	1.5858	1.5772	1.5685	−2.256
0.0867	0.8254	1.5883	1.5797	1.5711	1.5625	−2.070
0.0851	0.8272	1.5873	1.5787	1.5701	1.5615	−2.039
0.0759	0.8355	1.5822	1.5736	1.5650	1.5564	−1.884
0.0661	0.8446	1.5768	1.5683	1.5597	1.5510	−1.720
0.0577	0.8524	1.5716	1.5631	1.5545	1.5458	−1.565
0.0486	0.8609	1.5662	1.5576	1.5491	1.5404	−1.403
0.0373	0.8715	1.5589	1.5503	1.5417	1.5331	−1.188
0.0266	0.8814	1.5517	1.5430	1.5345	1.5258	−0.974
0.0148	0.8921	1.5434	1.5348	1.5262	1.5175	−0.733
		$x_2 = 0.3096 - 0.3221$				
0.1150	0.5629	1.5603	1.5512	1.5421	1.5330	−2.743
0.1063	0.5737	1.5579	1.5489	1.5399	1.5309	−2.659
0.0981	0.5816	1.5557	1.5468	1.5379	1.5289	−2.591
0.0909	0.5898	1.5536	1.5448	1.5359	1.5270	−2.524
0.0725	0.6101	1.5469	1.5381	1.5294	1.5206	−2.319
0.0620	0.6216	1.5428	1.5341	1.5253	1.5166	−2.194
0.0568	0.6276	1.5402	1.5316	1.5229	1.5142	−2.124
0.0496	0.6353	1.5370	1.5283	1.5197	1.5110	−2.029
0.0449	0.6407	1.5345	1.5259	1.5173	1.5087	−1.962
0.0375	0.6490	1.5308	1.5223	1.5137	1.5051	−1.858
0.0321	0.6549	1.5278	1.5193	1.5107	1.5022	−1.776
0.0251	0.6627	1.5239	1.5153	1.5068	1.4983	−1.667
0.0207	0.6675	1.5213	1.5128	1.5042	1.4958	−1.597
0.0158	0.6731	1.5183	1.5098	1.5013	1.4929	−1.517
0.0082	0.6816	1.5135	1.5050	1.4966	1.4881	−1.387
0.0021	0.6883	1.5099	1.5015	1.4931	1.4847	−1.292

Table 3 shows the effect of H_2O on the density and excess molar volume, in which the mole fractions of N_2O_4 were kept in the range of 0.0023 to 0.0038, 0.0629 to 0.0743, and 0.1150 to 0.1399, respectively. The variation of density with water increasing was shown in Figure 4. The density decreased gradually with the increase of water. The excess molar volumes versus the mole fraction of water were influenced significantly by the N_2O_4 content (see Figure 5). As shown in Figure 5, with the increase of water mole fraction, the excess molar volume decreased at N_2O_4 mole fractions below ca. 0.08, and the reverse was obtained at N_2O_4 mole fractions above ca. 0.08. When the N_2O_4 mole fraction was nearly at ca. 0.08, the excess molar volumes have hardly been affected by the variation of water mole fraction. This phenomenon might happen because N_2O_4 in nitric acid was ionized to form nitrosonium cation and nitrate ion at low N_2O_4 mole fractions; meanwhile, it was only partly ionized at high N_2O_4 mole fractions.[5]

The variations of V^E with the mole fraction of N_2O_4 and water at 293.15 K were shown in Figure 6. The excess molar volumes were negative over the measured composition range for the investigated N_2O_4 + H_2O + HNO_3 ternary system. This indicated that volume contraction took place due to the attractive interaction when the compounds were mixed.

From the result of Figures 2 and 4, it was found the density of the N_2O_4 + H_2O + HNO_3 ternary system varied with the temperature constantly at a rate of ca. 0.00174 $g \cdot cm^{-3} \cdot T^{-1}$.

Table 3. Experimental Densities, ρ, at Various Temperatures and Excess Molar Volume, V^E, at 293.15 K for N_2O_4 (1) + H_2O (2) + HNO_3 (3)

x_2	x_3	$\rho/(g\cdot cm^{-3})$				$V^E/(cm^3\cdot mol^{-1})$
		278.15 K	283.15 K	288.15 K	293.15 K	293.15 K
		$x_1 = 0.0023-0.0038$				
0.0917	0.9045	1.5353	1.5265	1.5179	1.5092	−0.480
0.1065	0.8897	1.5341	1.5254	1.5168	1.5081	−0.544
0.1297	0.8667	1.5314	1.5228	1.5142	1.5062	−0.640
0.1557	0.8409	1.5288	1.5202	1.5116	1.5030	−0.725
0.1966	0.8004	1.5242	1.5156	1.5070	1.4984	−0.870
0.2167	0.7804	1.5222	1.5136	1.5051	1.4965	−0.954
0.2474	0.7500	1.5185	1.5099	1.5014	1.4929	−1.068
0.2615	0.7360	1.5165	1.5080	1.4995	1.4911	−1.118
0.2844	0.7132	1.5132	1.5048	1.4963	1.4879	−1.197
		$x_1 = 0.0629-0.0743$				
0.1137	0.8120	1.5791	1.5704	1.5618	1.5532	−1.932
0.1383	0.7889	1.5754	1.5668	1.5581	1.5495	−1.970
0.1569	0.7713	1.5726	1.5639	1.5553	1.5466	−1.997
0.1744	0.7549	1.5698	1.5611	1.5525	1.5438	−2.023
0.2097	0.7217	1.5639	1.5552	1.5465	1.5378	−2.071
0.2478	0.6861	1.5568	1.5481	1.5394	1.5307	−2.117
0.2680	0.6670	1.5528	1.5441	1.5354	1.5267	−2.140
0.2777	0.6579	1.5508	1.5421	1.5334	1.5247	−2.151
0.3018	0.6353	1.5456	1.5369	1.5282	1.5195	−2.174
		$x_1 = 0.1150-0.1399$				
0.1211	0.7390	1.6082	1.5995	1.5908	1.5819	−2.903
0.1732	0.6934	1.5982	1.5894	1.5806	1.5716	−2.888
0.2113	0.6599	1.5896	1.5808	1.5718	1.5629	−2.860
0.2381	0.6365	1.5830	1.5742	1.5652	1.5561	−2.832
0.2526	0.6238	1.5798	1.5708	1.5618	1.5528	−2.828
0.2714	0.6073	1.5748	1.5659	1.5568	1.5477	−2.806
0.2810	0.5989	1.5721	1.5631	1.5541	1.5450	−2.794
0.2976	0.5843	1.5669	1.5579	1.5489	1.5399	−2.765
0.3221	0.5629	1.5602	1.5512	1.5421	1.5330	−2.743

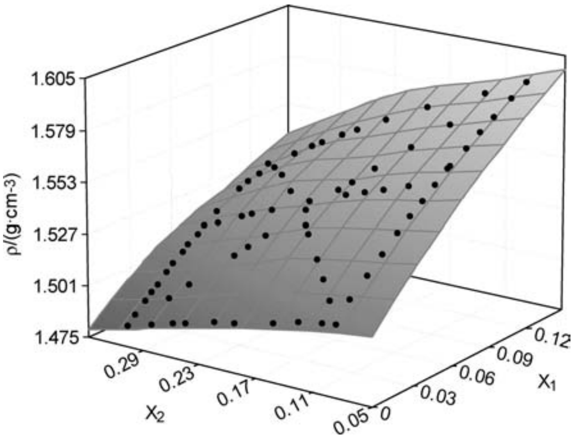

Figure 1. Experimental density, ρ, of N_2O_4 (1) + H_2O (2) + HNO_3 (3) ternary mixtures at 293.15 K.

The experimental densities were correlated as functions of temperature by the following equations:[13]

$$\rho/g\cdot cm^{-3} = A + B(293.15 - T/K) \tag{2}$$

where ρ and T are the experimental density and temperature, respectively; A and B are the undetermined parameters which are the function of mole fraction of N_2O_4 (x_1) and H_2O (x_2), respectively. It can be expressed as follows:

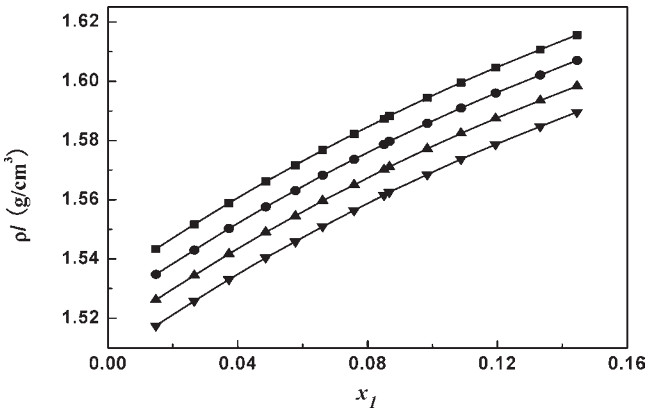

Figure 2. Experimental density, ρ, for N_2O_4 (1) + H_2O (2) + HNO_3 (3) with the mole fraction of water at 0.0237 to 0.0283: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K.

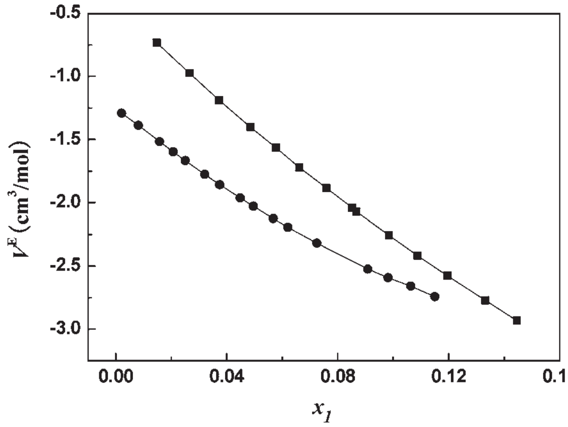

Figure 3. Excess molar volume, V^E, of N_2O_4 (1) + H_2O (2) + HNO_3 (3) at 293.15 K: ■, water mole fraction at 0.0237 to 0.0283; ●, water mole fraction at 0.3096 to 0.3221.

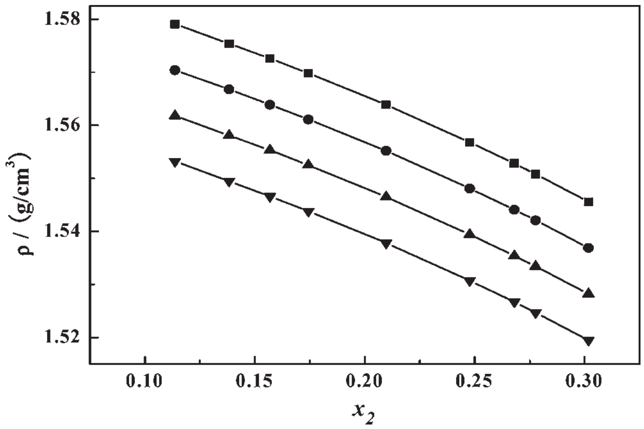

Figure 4. Experimental density of N_2O_4 (1) + H_2O (2) + HNO_3 (3) with the mole fraction of N_2O_4 at 0.0629 to 0.0743: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K.

$$C = C_0 + C_1x_1 + C_2x_2 + C_3{x_1}^2 + C_4{x_2}^2 + C_5x_1x_2 \tag{3}$$

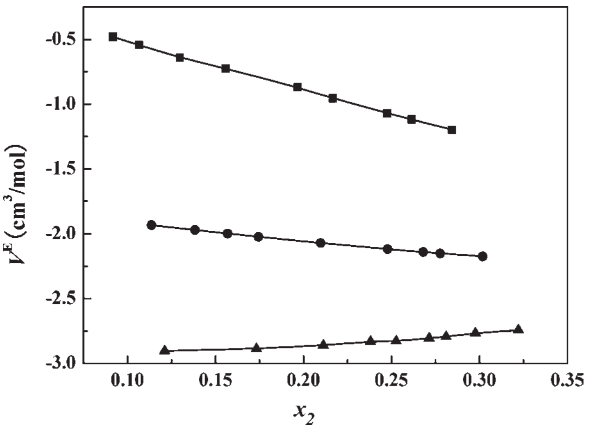

Figure 5. Excess molar volume, V^E, of N_2O_4 (1) + H_2O (2) + HNO_3 (3) at 293.15 K: ■, N_2O_4 mole fraction at 0.0023 to 0.0038; ●, N_2O_4 mole fraction at 0.0629 to 0.0743; ▲, N_2O_4 mole fraction at 0.1150 to 0.1399.

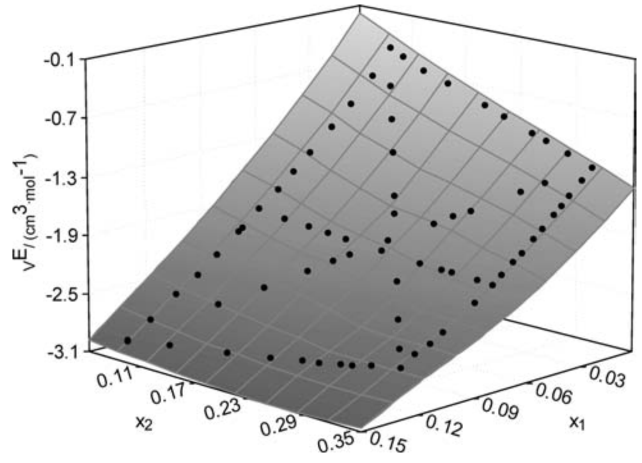

Figure 6. Excess molar volume, V^E, for N_2O_4(1) + H_2O(2) + HNO_3(3) ternary mixtures at 293.15 K.

Table 4. Parameters of eqs 2 and 3

	C_0	C_1	C_2	C_3	C_4	C_5
10A	15.0909	8.4419	−0.1621	−14.9452	−2.1716	−6.5983
10^4B	17.5562	−9.6937	−1.7801	30.6186	−1.8292	55.3711

where C stands for parameters A or B and C_i for A_i or B_i (i = 1 to 5), respectively. The average absolute deviations (AADs) were calculated as a measure of agreement between experimental density and calculated values. The AAD was defined in the following form:

$$\mathrm{AAD} = \frac{1}{n}\sum\frac{|\rho_{\mathrm{cal}} - \rho|}{\rho} \qquad (4)$$

The obtained parameters for eqs 2 and 3 are shown in Table 4. The calculated AAD for the experimental density and calculated values was 0.0419 %.

■ CONCLUSIONS

The density data for the N_2O_4 + H_2O + HNO_3 ternary system with mole fractions of N_2O_4 ranging from 0 to 0.15 and H_2O ranging from 0.08 to 0.33, at different temperatures were measured. The density of this ternary system increased with the increase of N_2O_4 and decreased with water increasing at 278.15 K, 283.15 K, 288.15 K, and 293.15 K. The excess molar volume V^E decreased with the N_2O_4 increase and with the increase of water mole fraction at low N_2O_4 mole fractions, while the reverse was obtained at high N_2O_4 mole fractions. The experimental density values were correlated with an empirical equation. The AAD between experimental density and calculated values was 0.0419 %.

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Funding Sources

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