Densities and Viscosities of (1,6-Hexanediamine + Ethanol) and (1,6-Hexanediamine + Ethanol + Water) Mixtures at T = (303.15 to 328.15) K

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The densities and viscosities of 1,6-hexanediamine + ethanol + water mixtures have been determined experimentally under normal atmospheric pressure over the entire molality range from (303.15 to 328.15) K. The apparent molar volumes of 1,6-hexanediamine were calculated from experimental measurements. Results were fit to obtain the appropriate parameters and standard deviations between the measured and fitted values.

Introduction

The density and viscosity data are essential for engineering designs involving chemical separations, heat transfer, mass transfer, and fluid flow and are important from practical and theoretical points of view for understanding liquid theory.[1] 1,6-Hexanediamine is an important intermediate in chemical processes, including the synthesis of nylon-type polyamide resins (nylon 66), the synthesis of oil-modified and moisture area types of urethane coatings, and the manufacture of polyamides for printing inks, paints, acids, and textiles. It is also used as a corrosion inhibitor in oil and lubricants and as a curing agent in epoxide resins. Ethanol is a necessary solvent in the preparation of 1,6-hexanediamine by catalytic hydrogenation of adiponitrile, so it is useful to know the physicochemical properties of 1,6-hexanediamine + ethanol + water mixtures in the synthesis and purification process of 1,6-hexanediamine. However, a survey of the literature shows that very few measurements have been made on the physicochemical properties of 1,6-hexanediamine + ethanol + water mixtures; only the Physical Properties Handbook of Chemistry & Chemical Engineering[2] has recorded the solubility and viscosity data of pure 1,6-hexanediamine. Nevertheless, to our knowledge, no density and viscosity data on mixtures of 1,6-hexanediamine + ethanol + water mixtures were previously reported in the literature. In this study, the densities and viscosities of 1,6-hexanediamine + ethanol + water mixtures have been measured from (303.15 to 328.15) K at atmospheric pressure (0.1 MPa). From measurements of densities, the apparent molar volumes of 1,6-hexanediamine were calculated. Results were fit to obtain the adjustable parameters and standard deviations.

Experimental Section

Materials. Analytical-grade ethanol obtained from Shanghai Chemical Reagent was degassed ultrasonically and kept in dark bottles dried over molecular sieves (3A 1/16, 4A 1/16) 2 to 3 weeks prior to their use to eliminate the residual traces of water and to avoid moisturizing. The mass fraction purity was > 0.998 for ethanol. High-grade 1,6-hexanediamine from Shengma Nylon Chemical was directly used without further purification, and its purity, 0.993 by mass, was determined by gas chromatography (type GC2010 Shimadzu) using a DB-1 capillary column with an FID detector. Water used in the experiments was double distilled; the conductivity was less than $1 \cdot 10^{-4}$ $S \cdot m^{-1}$.

Apparatus and Procedure. The density was measured with five Ostwald−Sprengel-type pycnometers having a bulb volume of 25 cm^3 and an internal capillary diameter of about 1 mm. The internal volumes of the pycnometers were calibrated with pure water at each of the measured temperatures, and the densities of water were taken from the literature.[3] The thoroughly cleaned and perfectly dried pycnometers were first weighed on an electronic balance (type AW120, Shimadzu) that was accurate to within ± 0.0001 g and were then filled with experimental liquid and immersed in a thermostat (type 501, Shanghai Laboratory Instrument Works). To improve the accuracy of the experiment, a mercury-in-glass precise thermometer was inserted into the 501 thermostat to control the temperature within ± 0.01 K. After thermal equilibrium had been achieved at the required temperature, the pycnometers were removed from the thermostat and properly cleaned, dried, and weighed. The density was then determined from the mass of the sample and the volume of the pycnometers. The readings from five pycnometers were averaged to determine the density. Uncertainties in density measurements were estimated to be within ± 0.0002 $g \cdot cm^{-3}$ on the basis of the 95 % confidence level. The errors were mainly caused by the weighing process, repeatability of the measurement, and glassware.

The viscosity was measured using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter calibrated with double-distilled water at temperatures of (303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in an insulated jacket, wherein constant temperature (± 0.01 K) was maintained by circulating water from a thermostatically controlled water bath at the required temperature. After thermal stability was attained, the flow times of the liquids were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each data point obtained were reproducible to ± 0.05 s, and the results were averaged. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length (100 mm), the kinetic energy and end corrections were found

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Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of Ethanol with Literature Values

	10^{-3} ρ/kg·m^{-3}		η/mPa·S	
T/K	exptl	lit	exptl	lit
303.15	0.7808	0.78089[5]	0.9790	0.9870[9]
308.15	0.7765	0.77655[6]	0.8877	0.906[10]
313.15	0.7703	0.77200[7]	0.8086	0.829[11]
318.15	0.7652	0.76762[8]	0.7335	0.759[8]
323.15	0.7603	0.76324[5]	0.6677	0.694[3]
328.15	0.7545	0.75860[8]	0.6104	0.641[7]

to be negligible. The viscosity, η, was then calculated from the relationship[4]

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \tag{1}$$

where η, ρ, and t and η_w, ρ_w, and t_w are the viscosities, densities, and flow times of the mixture and water, respectively. The values of the viscosity and density of pure water come from the literature.[3] The overall uncertainty of the viscosity measurements is dependent on the equilibrium stability of the viscometer, the time of flow, and the change in density, and viscosity values are uncertain to within the range ± 0.0030 mPa·s.

Results and Discussion

The measured densities and viscosities of ethanol together with literature values are included in Table 1, and it is clear from Table 1 that the experimental results show good agreement with the literature data. The experimental densities and viscosities at (303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K are listed in Tables 2, 3, 4, and 5, which showed the dependencies of density and viscosity on temperature and concentration, respectively. It can be found that the density and viscosity increase with increasing concentration of 1,6-hexanediamine at constant temperature and decrease with increasing temperature at a fixed concentration of 1,6-hexanediamine. The dependence of density and viscosity on temperature and concentration has been calculated by means of the Vogel−Tamman−Fulcher (VTF) equation[12]

$$F = P_1 \exp\left(\frac{P_2 + P_3 m}{T - P_4}\right) \tag{2}$$

where $F = (\rho$ or $\eta)$, ρ and η are the density and viscosity of solution, respectively, m is the molality of 1,6-hexanediamine, T is the absolute temperature, and P_1, P_2, P_3, and P_4 obtained by applying the nonlinear least-squares method are the curve-fit coefficients. The values are listed in Table 6 along with standard deviations. The standard deviation is defined by

$$\sigma = [\sum_{i=1}^{p} ((Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2/(p - n))]^{1/2} \tag{3}$$

where p is the number of experimental points and n is the number of parameters. Y^{calcd} and Y^{exptl} refer to the calculated values from the equation and to the experimental value. On the basis of the obtained standard deviation values, we conclude that eq 2 can be successfully used for the correlation of the investigated physical properties.

Table 2. Density (ρ), Viscosity (η), and Apparent Molar Volumes ($V_{\Phi,2}$) of 1,6-Hexanediamine + Ethanol Binary Mixtures from T = (303.15 to 328.15) K

m	$10^{-3}\rho$	$10^6 V_{\Phi,m}$	η	m	$10^{-3}\rho$	$10^6 V_{\Phi,m}$	η
mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mPa·S	mol·kg^{-1}	kg·m^{-3}	m^3·mol^{-1}	mPa·S
T = 303.15 K							
0.0000	0.7808		0.9790	0.6113	0.7886	126.64	1.1620
0.1293	0.7823	129.56	1.0111	0.7834	0.7911	125.61	1.2022
0.2808	0.7842	128.41	1.0526	0.9637	0.7938	124.63	1.2583
0.4406	0.7863	127.46	1.1022				
T = 308.15 K							
0.0000	0.7765		0.8877	0.6113	0.7847	126.08	1.0460
0.1293	0.7779	131.46	0.9157	0.7834	0.7873	125.06	1.0807
0.2808	0.7797	130.22	0.9505	0.9637	0.7901	124.08	1.1331
0.4406	0.7819	128.44	0.9928				
T = 313.15 K							
0.0000	0.7703		0.8086	0.6113	0.7772	130.67	0.9437
0.1293	0.7716	133.69	0.8341	0.7834	0.7793	129.98	0.9750
0.2808	0.7733	132.34	0.8606	0.9637	0.7815	129.40	1.0188
0.4406	0.7752	131.29	0.8994				
T = 318.15 K							
0.0000	0.7652		0.7335	0.6113	0.7714	133.47	0.8571
0.1293	0.7664	135.81	0.7569	0.7834	0.7733	132.80	0.8816
0.2808	0.7679	134.97	0.7849	0.9637	0.7753	132.22	0.9201
0.4406	0.7696	134.04	0.8154				
T = 323.15 K							
0.0000	0.7603		0.6677	0.6113	0.7660	135.70	0.7761
0.1293	0.7614	137.93	0.6866	0.7834	0.7678	134.95	0.7980
0.2808	0.7628	137.00	0.7105	0.9637	0.7697	134.31	0.8301
0.4406	0.7643	136.42	0.7356				
T = 328.15 K							
0.0000	0.7545		0.6104	0.6113	0.7599	137.52	0.7013
0.1293	0.7555	140.25	0.6275	0.7834	0.7616	136.81	0.7227
0.2808	0.7568	139.21	0.6485	0.9637	0.7634	136.19	0.7564
0.4406	0.7583	138.18	0.6737				

Table 3. Density (ρ), Viscosity (η), and Apparent Molar Volumes ($V_{\Phi,2}$) of 1,6-Hexanediamine + Ethanol + Water (Mass Fraction is 25 %) Mixtures from T = (303.15 to 328.15) K

m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S	m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S
T = 303.15 K							
0.0000	0.8488		1.6111	1.9954	0.8650	123.29	2.7547
0.5002	0.8530	124.64	1.8643	2.5009	0.8689	122.85	3.0809
1.0020	0.8571	124.20	2.1418	3.0004	0.8727	122.41	3.4519
1.5027	0.8611	123.76	2.4319				
T = 308.15 K							
0.0000	0.8430		1.4016	1.9954	0.8584	124.71	2.3488
0.5002	0.8470	126.00	1.6129	2.5009	0.8621	124.29	2.6140
1.0020	0.8509	125.58	1.8435	3.0004	0.8657	123.87	2.9058
1.5027	0.8547	125.16	2.0857				
T = 313.15 K							
0.0000	0.8382		1.2294	1.9954	0.8535	125.44	2.0279
0.5002	0.8420	127.25	1.4111	2.5009	0.8574	124.86	2.2485
1.0020	0.8458	126.70	1.6066	3.0004	0.8613	124.26	2.4890
1.5027	0.8497	126.02	1.8053				
T = 318.15 K							
0.0000	0.8336		1.0851	1.9954	0.8481	126.75	1.7607
0.5002	0.8372	128.50	1.2409	2.5009	0.8518	126.18	1.9461
1.0020	0.8408	127.96	1.4036	3.0004	0.8555	125.60	2.1506
1.5027	0.8445	127.30	1.5749				
T = 323.15 K							
0.0000	0.8275		0.9573	1.9954	0.8415	128.02	1.5295
0.5002	0.8310	129.67	1.0880	2.5009	0.8451	127.45	1.6855
1.0020	0.8345	129.14	1.2275	3.0004	0.8486	126.93	1.8531
1.5027	0.8380	128.60	1.3714				
T = 328.15 K							
0.0000	0.8225		0.8538	1.9954	0.8364	128.81	1.3490
0.5002	0.8259	130.70	0.9659	2.5009	0.8400	128.22	1.4773
1.0020	0.8294	130.02	1.0861	3.0004	0.8436	127.62	1.6194
1.5027	0.8329	129.42	1.2112				

Table 4. Density (ρ), Viscosity (η), and Apparent Molar Volumes ($V_{\Phi,2}$) of 1,6-Hexanediamine + Ethanol + Water (Mass Fraction is 20 %) Mixtures from T = (303.15 to 328.15) K

m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S	m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S
T = 303.15 K							
0.0000	0.8360		1.5109	1.6011	0.8516	122.78	2.3929
0.4002	0.8399	124.48	1.6761	2.0000	0.8555	122.21	2.6135
0.8017	0.8438	123.93	1.9009	2.4010	0.8595	121.59	2.9100
1.2003	0.8477	123.33	2.0874				
T = 308.15 K							
0.0000	0.8318		1.3321	1.6011	0.8472	123.52	2.0602
0.4002	0.8357	125.04	1.4691	2.0000	0.8510	123.00	2.2436
0.8017	0.8396	124.48	1.6581	2.4010	0.8549	122.40	2.4923
1.2003	0.8434	124.01	1.8137				
T = 313.15 K							
0.0000	0.8271		1.1739	1.6011	0.8429	125.67	1.7907
0.4002	0.8310	125.67	1.2879	2.0000	0.8470	124.91	1.9454
0.8017	0.8350	124.91	1.4485	2.4010	0.8510	124.36	2.1581
1.2003	0.8389	124.36	1.5811				
T = 318.15 K							
0.0000	0.8210		1.0250	1.6011	0.8372	124.09	1.5637
0.4002	0.8250	126.10	1.1344	2.0000	0.8412	123.52	1.6944
0.8017	0.8290	125.50	1.2722	2.4010	0.8451	123.04	1.8685
1.2003	0.8331	124.75	1.3845				
T = 323.15 K							
0.0000	0.8146		0.9113	1.6011	0.8308	124.93	1.3648
0.4002	0.8187	126.58	1.0009	2.0000	0.8349	124.27	1.4744
0.8017	0.8228	125.98	1.1197	2.4010	0.8391	123.57	1.6234
1.2003	0.8268	125.46	1.2150				
T = 328.15 K							
0.0000	0.8091		0.8123	1.6011	0.8254	125.55	1.2056
0.4002	0.8132	127.33	0.8905	2.0000	0.8294	124.99	1.2992
0.8017	0.8173	126.72	0.9927	2.4010	0.8333	124.51	1.4314
1.2003	0.8213	126.20	1.0765				

The apparent molar volume of 1,6-hexanediamine, $V_{\Phi,m}$, is given by the following equation

where M is the molar mass of 1,6-hexanediamine, ρ is the density of the solution, and ρ_0 is the density of pure solvent.

Table 5. Density (ρ), Viscosity (η), and Apparent Molar Volumes ($V_{\Phi,2}$) of 1,6-Hexanediamine + Ethanol + Water (Mass Fraction is 15 %) Mixtures from T = (303.15 to 328.15) K

m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S	m / mol·kg^{-1}	$10^{-3}\rho$ / kg·m^{-3}	$10^{6}V_{\Phi,m}$ / m^3·mol^{-1}	η / mPa·S
T = 303.15 K							
0.0000	0.8227		1.3832	1.4019	0.8378	123.08	2.0878
0.3502	0.8266	124.21	1.5684	1.7498	0.8414	122.68	2.2555
0.7008	0.8304	123.86	1.7182	2.1998	0.8457	122.39	2.5098
1.0503	0.8341	123.51	1.9069				
T = 308.15 K							
0.0000	0.8184		1.2223	1.4019	0.8339	123.16	1.8128
0.3502	0.8224	124.34	1.3784	1.7498	0.8376	122.73	1.9614
0.7008	0.8263	123.97	1.5174	2.1998	0.8419	122.53	2.1707
1.0503	0.8301	123.60	1.6638				
T = 313.15 K							
0.0000	0.8131		1.0850	1.4019	0.8289	123.48	1.5873
0.3502	0.8172	124.59	1.2233	1.7498	0.8327	123.01	1.7131
0.7008	0.8212	124.20	1.3469	2.1998	0.8371	122.80	1.8930
1.0503	0.8251	123.81	1.4625				
T = 318.15 K							
0.0000	0.8071		0.9649	1.4019	0.8236	123.39	1.3956
0.3502	0.8113	124.92	1.0840	1.7498	0.8276	122.88	1.5019
0.7008	0.8154	124.52	1.1870	2.1998	0.8322	122.65	1.6532
1.0503	0.8195	123.96	1.2895				
T = 323.15 K							
0.0000	0.8014		0.8601	1.4019	0.8180	124.00	1.2280
0.3502	0.8057	125.22	0.9577	1.7498	0.8220	123.50	1.3182
0.7008	0.8099	124.80	1.0413	2.1998	0.8266	123.29	1.4465
1.0503	0.8140	124.37	1.1352				
T = 328.15 K							
0.0000	0.7969		0.7734	1.4019	0.8139	124.09	1.0921
0.3502	0.8013	125.35	0.8614	1.7498	0.8180	123.57	1.1707
0.7008	0.8056	124.92	0.9601	2.1998	0.8227	123.37	1.2834
1.0503	0.8098	124.47	1.0162				

Table 6. Coefficient of Equation *2* and Standard Deviation, σ, for ρ (kg·m^{-3}) and η (mPa·S) for Different Systems

system		P_1	P_2	P_3	P_4	$10^2\sigma$
1,6-hexanediamine + ethanol	ρ	0.2251	1025.2000	12.4790	−520.0500	0.084
	η	0.0019	1863.3000	75.7910	4.7757	0.47
1,6-hexanediamine + ethanol + 25 % water	ρ	0.3734	503.5100	5.4885	−309.5300	0.048
	η	0.0158	726.8800	38.2580	147.1600	2.37
1,6-hexanediamine + ethanol + 20 % water	ρ	0.0240	9806.8000	33.0210	−2458.8000	0.082
	η	0.0062	1070.4000	52.2860	108.9900	1.55
1,6-hexanediamine + ethanol + 15 % water	ρ	0.0279	9360.4000	37.6810	−2464.3000	0.072
	η	0.0107	888.5900	46.7300	121.7000	2.04

$$V_{\phi,m} = [M/\rho] - [(\rho - \rho_0)/(m\rho\rho_0)] \quad (4)$$

The values of the apparent molar volume of 1,6-hexanediamine in solvent mixtures have also been given in Tables 2, 3, 4, and 5, which are important because they form the basis for understanding molecular interactions. The apparent molar volume increases as temperature increases at fixed concentration of 1,6-hexanediamine and decreases with concentration at the same temperature.

According to Fort and Moore,[13] the viscosity of mixtures increases with their increasing interaction force. In the system of (1,6-hexanediamine + ethanol + water), the self-association of ethanol and water molecules is realized through their hydrogen bonds; the neighbor 1,6-hexanediamine molecules also have the self-association character that can form a N−H···N bond. The cross-association can be formed among the ethanol, water, and 1,6-hexanediamine molecules through the O−H···N bond, whose contribution is much more than the disassociation of the same molecules and some other physical factors. Therefore, the viscosity that increases with increasing concentration of 1,6-hexanediamine is predictable. With the rising temperature, the effect of the hydrogen bond becomes weaker, resulting in the values of viscosity decreasing.

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