Densities and Viscosities of Niacin + 3-Picoline + Water Mixtures from (293.15 to 343.15) K

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The densities and viscosities of niacin + 3-picoline + water mixtures have been determined experimentally at temperatures from 293.15 K to 343.15 K. The apparent molar volumes were calculated from experimental measurements. Results were fit to obtain the adjustable parameters and standard deviations between the measured and fit values.

Introduction

Density and viscosity data are essential for engineering applications and are important from practical and theoretical points of views in understanding liquid theory. 3-Picoline is an important material in the synthesis of niacin. In the synthesis and purification process of niacin, it is useful to know the physical properties of niacin + 3-picoline + water mixtures. The author[1] reported solubility data of niacin in 3-picoline + water. In this study, the densities and viscosities of a niacin + 3-picoline binary mixture and a niacin + 3-picoline + water ternary mixture have been measured from 293.15 K to 343.15 K. From measurements of densities, the apparent molar volumes were calculated. Results were fit to obtain the adjustable parameters and standard deviations between the measured and fit values. These quantities can be used to study the molecular interactions among the components of the mixture.

Experimental Section

Materials. Analytical-grade 3-picoline from Shanghai Chemical Reagent Co. was further purified by distillation; the purity was determined by UV spectrophotometry (type UV-2401PC, Shimadzu Co.) to be 99.7% by mass. Analytical-grade nicotinic acid (niacin) obtained from Peking Biotech. Co. Ltd. was further purified by recrystallization from aqueous solutions. After filtration and drying, its purity was determined by titration to be 99.8% by mass. The water used in experiments was deionized, and the conductivity was less than 1×10^{-4} S·m^{-1}.

Apparatus and Procedure. The mixtures were prepared by mass using an electronic balance (type AW120, Shimadzu Co.) and were stored in ground glass stoppered bottles of 200 cm^3. The balance has an uncertainty of ±0.0001 g. It was ensured that the components were adequately mixed before being transferred into the pycnometers. The possible error in the mass fractions is estimated to be ±0.00005.

Density was measured with five Ostwald−Sprengel-type pycnometers having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The internal volumes of the pycnometers were calibrated with pure water at each of the measured temperatures; the densities of water were taken from literature.[2] The thoroughly cleaned and perfectly dried pycnometers were first weighed on an electronic balance and then filled with experimental liquid and immersed in a thermostat (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) controlled within ±0.02 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 within ±0.0002 g·cm^{-3}.

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 293.15, 303.15, 313.15, 323.15, 333.15, and 343.15 K. A thoroughly cleaned and perfectly dried viscometer, filled with experimental liquid, was placed exactly vertical in an insulated jacket wherein constant temperature (±0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) 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 datum point obtained were reproducible to ±0.06 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 (90−100 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity η was then calculated from the relationship[3]

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

where η, ρ, and t and η_w, ρ_w, and t_w are the viscosities, densities, and flow time of the mixture and water, respectively. The values of the viscosity and density of pure water come from Lange's Handbook of Chemistry.[2] The uncertainty of the viscosity measurement was ±0.6%.

Results and Discussion

The measured densities of 3-picoline together with literature values are included in Table 1. The experimental densities at (293.15, 303.15, 313.15, 323.15, 333.15, and

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Table 1. Comparison of Experimental Densities, ρ, and Viscosities, η, of 3-Picoline with Literature Values

	ρ/g·cm^{-3}		η/mPa·s	
T/K	exptl	lit	exptl	lit
293.15	0.9560	0.95658[4]	0.9459	
298.15		0.95232[5]		0.8960[5]
		0.95178[6]		0.8661[6]
303.15	0.9466	0.94736[4]	0.8318	
323.15	0.9283			
323.137		0.9296[7]		

Table 2. Experimental Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of Niacin + 3-Picoline Binary Mixtures from T = 293.15 K to 343.15 K

m	ρ	$V_{\Phi,2}$	η
mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	mPa·s
	T/K = 293.15		
0	0.9560		0.9459
0.02469	0.9567	97.68	0.9504
0.1070	0.9595	92.65	0.9659
0.2134	0.9641	86.52	0.9908
0.3190	0.9695	81.32	1.0155
0.4240	0.9758	76.10	1.0504
0.5284	0.9830	70.87	1.1066
	T/K = 303.15		
0	0.9466		0.8318
0.02469	0.9473	98.34	0.8363
0.1070	0.9501	93.21	0.8514
0.2134	0.9546	87.48	0.8764
0.3190	0.9600	82.01	0.9018
0.4240	0.9664	76.34	0.9368
0.5284	0.9735	71.22	0.9891
	T/K = 313.15		
0	0.9377		0.7352
0.02469	0.9384	98.97	0.7399
0.1070	0.9412	93.74	0.7553
0.2134	0.9457	87.90	0.7804
0.3190	0.9510	82.70	0.8048
0.4240	0.9575	76.56	0.8396
0.5284	0.9647	71.13	0.8961
	T/K = 323.15		
0	0.9283		0.6565
0.02469	0.9290	99.64	0.6610
0.1070	0.9318	94.30	0.6762
0.2134	0.9363	88.35	0.7014
0.3190	0.9415	83.41	0.7265
0.4240	0.9478	77.62	0.7613
0.5284	0.9552	71.47	0.8173
	T/K = 333.15		
0	0.9193		0.5936
0.02469	0.9200	100.3	0.5981
0.1070	0.9228	94.85	0.6134
0.2134	0.9272	89.34	0.6381
0.3190	0.9325	83.75	0.6632
0.4240	0.9387	78.13	0.6983
0.5284	0.9462	71.58	0.7541
	T/K = 343.15		
0	0.9103		0.5390
0.02469	0.9110	100.9	0.5434
0.1070	0.9138	95.40	0.5594
0.2134	0.9182	89.79	0.5833
0.3190	0.9235	84.09	0.6086
0.4240	0.9297	78.36	0.6431
0.5284	0.9372	71.69	0.6997

343.15) K are listed in Tables 2 to 4 and Figure 1. The density increases with increasing concentration of niacin at constant temperature and decreases with increasing temperature at a fixed concentration of niacin.

The apparent molar volume of niacin, $V_{\Phi,2}$, is given by the following equation

$$V_{\Phi,2} = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \tag{2}$$

where M and m are the molar mass and molality of niacin,

Table 3. Experimental Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of Niacin + H_2O + 15 Mass % 3-Picoline Mixtures at from T = 293.15 K to 343.15 K

m	ρ	$V_{\Phi,2}$	η
mol·kg^{-1}	g·cm^{-3}	cm^3·mol^{-1}	mPa·s
	T/K = 293.15		
0	0.9975		1.4476
0.0687	1.0006	77.83	1.4846
0.1107	1.0025	77.64	1.5100
0.2371	1.0082	77.23	1.5880
0.4610	1.0184	76.26	1.7459
0.8739	1.0373	74.67	2.0734
1.2458	1.0545	73.25	2.4906
	T/K = 303.15		
0	0.9937		1.1429
0.0687	0.9968	77.95	1.1674
0.1107	0.9987	77.76	1.1856
0.2371	1.0044	77.35	1.2402
0.4610	1.0146	76.37	1.3487
0.8739	1.0335	74.77	1.5710
1.2458	1.0507	73.35	1.8651
	T/K = 313.15		
0	0.9892		0.9152
0.0687	0.9923	78.09	0.9330
0.1107	0.9942	77.90	0.9448
0.2371	0.9999	77.50	0.9828
0.4610	1.0101	76.51	1.0595
0.8739	1.0290	74.90	1.2314
1.2458	1.0462	73.46	1.4390
	T/K = 323.15		
0	0.9837		0.7673
0.0687	0.9868	78.27	0.7809
0.1107	0.9887	78.08	0.7895
0.2371	0.9944	77.67	0.8194
0.4610	1.0046	76.67	0.8804
0.8739	1.0235	75.05	1.0104
1.2458	1.0407	73.60	1.1625
	T/K = 333.15		
0	0.9777		0.6568
0.0687	0.9808	78.46	0.6674
0.1107	0.9827	78.27	0.6744
0.2371	0.9884	77.85	0.6979
0.4610	0.9986	76.85	0.7480
0.8739	1.0175	75.21	0.8492
1.2458	1.0347	73.75	0.9683
	T/K = 343.15		
0	0.9717		0.5712
0.0687	0.9748	78.65	0.5798
0.1107	0.9767	78.46	0.5856
0.2371	0.9824	78.04	0.6047
0.4610	0.9926	77.02	0.6421
0.8739	1.0115	75.38	0.7278
1.2458	1.0287	73.90	0.8249

respectively, ρ is the density of the solution, and ρ_0 is the density of 3-picoline or the solvent mixture of 3-picoline + water. The values of the apparent molar volume of niacin in solvent mixtures are also listed in Tables 2 to 4. It was found that $V_{\Phi,2}$ varied linearly with the molality of niacin over the range studied and could be analyzed by fitting to

$$V_{\Phi,2} = V^0{}_{\Phi,2} + S_v m \tag{3}$$

where $V^0{}_{\Phi,2}$ is the infinite dilution apparent molar volume that is equal in value to the standard partial molar volume and S_v is the experimental slope. The values of $V^0{}_{\Phi,2}$ and S_v obtained by least-squares analysis for the niacin in solvent mixtures are listed in Table 5, along with their standard deviations. The standard deviations is defined by

$$\sigma = \left[\sum_{i=1}^{p} \frac{(Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2}{p - n}\right]^{1/2} \tag{4}$$

Table 4. Experimental Densities, ρ, Viscosities, η, and Apparent Molar Volumes, $V_{\Phi,2}$, of Niacin + H_2O + 10 Mass % 3-Picoline Mixtures from T = 293.15 K to 343.15 K

m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,2}$ / cm^3·mol^{-1}	η / mPa·s
	T/K = 293.15		
0	0.9978		1.2913
0.1158	1.0032	76.13	1.3454
0.1994	1.0072	75.32	1.3926
0.3432	1.0140	74.76	1.4689
0.4822	1.0207	73.98	1.5548
0.6166	1.0272	73.33	1.6387
0.7468	1.0335	72.76	1.7257
	T/K = 303.15		
0	0.9944		1.0015
0.1158	0.9998	76.23	1.0413
0.1994	1.0038	75.42	1.0741
0.3432	1.0106	74.85	1.1341
0.4822	1.0173	74.07	1.1900
0.6166	1.0238	73.41	1.2501
0.7468	1.0301	72.84	1.3176
	T/K = 313.15		
0	0.9902		0.8117
0.1158	0.9956	76.35	0.8422
0.1994	0.9996	75.53	0.8648
0.3432	1.0064	74.96	0.9080
0.4822	1.0131	74.18	0.9529
0.6166	1.0196	73.52	0.9997
0.7468	1.0259	72.94	1.0519
	T/K = 323.15		
0	0.9852		0.6796
0.1158	0.9906	76.50	0.7035
0.1994	0.9946	75.67	0.7218
0.3432	1.0014	75.09	0.7550
0.4822	1.0081	74.30	0.7921
0.6166	1.0146	73.64	0.8260
0.7468	1.0209	73.06	0.8681
	T/K = 333.15		
0	0.9796		0.5794
0.1158	0.9850	76.66	0.5985
0.1994	0.9890	75.82	0.6137
0.3432	0.9958	75.24	0.6411
0.4822	1.0025	74.44	0.6700
0.6166	1.0090	73.77	0.6981
0.7468	1.0153	73.19	0.7307
	T/K = 343.15		
0	0.9737		0.5053
0.1158	0.9791	76.82	0.5207
0.1994	0.9831	75.98	0.5343
0.3432	0.9899	75.39	0.5571
0.4822	0.9966	74.59	0.5814
0.6166	1.0031	73.91	0.6050
0.7468	1.0094	73.33	0.6324

where p is the number of experimental points and n is the number of parameters. Y_i^{calcd} and Y_i^{exptl} refer to the calculated values from the equation and to the experimental value.

From Table 5, we find that the infinite dilution apparent molar volumes are positive and increase as temperature increases for all systems examined; however, S_v is negative and decreases as temperature increases.

Over the temperature range under the investigation, the variation of density values with the concentration of niacin at constant temperature can be expressed by the polynomial equation

$$\rho = \sum_{i=0}^{n} B_j m^j \qquad (5)$$

Table 5. Parameters of Equation 3 and Standard Deviation, σ, for $V_{\Phi,2}$ from T = 293.15 K to 343.15 K

T / K	$V^0_{\Phi,2}$ / cm^3·mol^{-1}	S_V / cm^3·kg^{-1}	σ / cm^3·mol^{-1}
	Niacin + 3-Picoline		
293.15	98.41	−52.77	0.48
303.15	99.20	−53.56	0.35
313.15	99.92	−54.76	0.34
323.15	100.5	−54.72	0.46
333.15	101.3	−55.72	0.42
343.15	102.0	−56.70	0.42
	Niacin + H_2O + 15 Mass % 3-Picoline		
293.15	78.10	−3.90	0.039
303.15	78.22	−3.92	0.041
313.15	78.37	−3.95	0.043
323.15	78.55	−3.98	0.043
333.15	78.74	−4.02	0.041
343.15	78.93	−4.05	0.044
	Niacin + H_2O + 10 Mass % 3-Picoline		
293.15	76.53	−5.16	0.14
303.15	76.64	−5.20	0.14
313.15	76.76	−5.22	0.15
323.15	76.91	−5.27	0.15
333.15	77.07	−5.31	0.15
343.15	77.24	−5.35	0.15

Table 6. Parameters of Equation 5 and Standard Deviation, σ, for ρ from T = 293.15 K to 343.15 K

T/K	B_0	B_1	B_2	$10^5\sigma$/g·cm^{-3}
	Niacin + 3-Picoline			
293.15	0.9560	0.02901	0.04192	4.82
303.15	0.9466	0.02861	0.04242	4.93
313.15	0.9377	0.02798	0.04382	4.99
323.15	0.9283	0.02748	0.04404	8.25
333.15	0.9193	0.02700	0.04483	9.45
343.15	0.9103	0.02700	0.04483	9.45
	Niacin + H_2O + 15 Mass % 3-Picoline			
293.15	0.9974	0.04574		9.28
303.15	0.9936	0.04574		9.28
313.15	0.9891	0.04574		9.28
323.15	0.9836	0.04574		9.28
333.15	0.9776	0.04574		9.28
343.15	0.9716	0.04574		9.28
	Niacin + H_2O + 10 Mass % 3-Picoline			
293.15	0.9977	0.04784		8.63
303.15	0.9943	0.04784		8.63
313.15	0.9901	0.04784		8.63
323.15	0.9851	0.04784		8.63
333.15	0.9795	0.04784		8.63
343.15	0.9736	0.04784		8.63

Fitting parameters B_i were obtained by an unweighted least-squares method, and the optimum number of parameters n was determined using an F test.[8] Table 6 shows the fitting parameters and the standard deviations for each system. These parameters were used to obtain the calculated curves shown in Figure 1.

The viscosity data for all systems at (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K are also listed in Tables 2 to 4 and Figure 2. For all systems, the viscosity increases with increasing niacin concentration at constant temperature and decreases with increasing temperature at a fixed concentration of niacin. The viscosity data can be represented with the following polynomial[9]

$$\ln\left(\frac{\eta}{\eta_0}\right) = \sum_{k=1}^{2} A_k m^k \qquad (6)$$

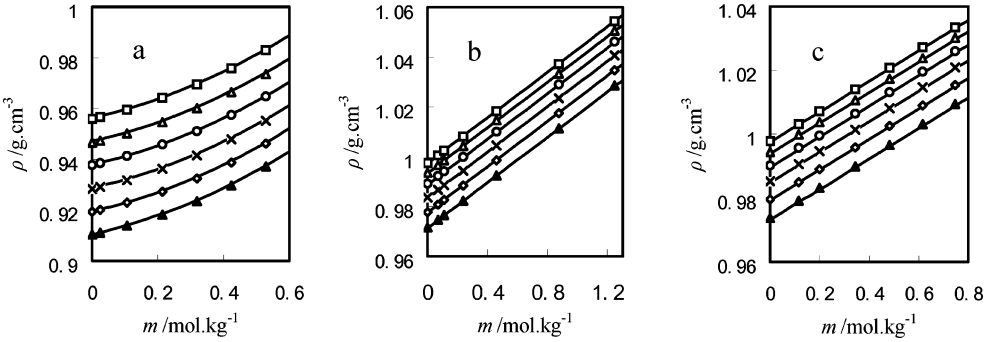

Figure 1. Variation of densities with molality at □, 293.15 K; △, 303.15 K; ○, 313.15 K; ×, 323.15 K; ◇, 333.15 K; and ▲, 343.15 K for the following mixtures: (a) niacin + 3-picoline, (b) niacin + H_2O + 15 mass % 3-picoline, and (c) niacin + H_2O + 10 mass % 3-picoline. Solid line, calculated from eq 5.

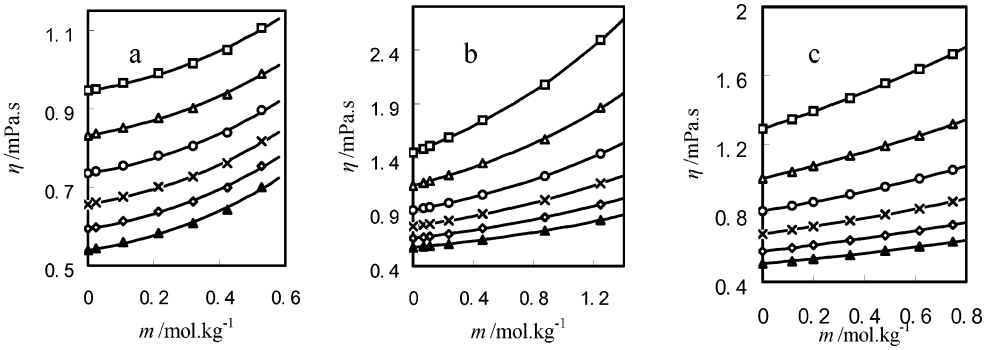

Figure 2. Variation of viscosities with molality at □, 293.15 K; △, 303.15 K; ○, 313.15 K; ×, 323.15 K; ◇, 333.15 K; and ▲, 343.15 K for the following mixtures: (a) niacin + 3-picoline, (b) niacin + H_2O + 15 mass % 3-picoline, and (c) niacin + H_2O + 10 mass % 3-picoline. Solid line, calculated from eq 6.

Table 7. Coefficient of Equation 6 and Standard Deviation, σ, for η from T = 293.15 K to 343.15 K

T/K	A_1	A_2	$10^3\sigma$/mPa·s
	Niacin + 3-Picoline		
293.15	0.1382	0.2875	3.95
303.15	0.1655	0.2963	2.98
313.15	0.1823	0.3472	4.01
323.15	0.2055	0.3791	3.66
333.15	0.2268	0.4101	3.56
343.15	0.2518	0.4373	3.79
	Niacin + H_2O + 15 Mass % 3-Picoline		
293.15	0.3761	0.04655	6.00
303.15	0.3242	0.05377	5.73
313.15	0.2869	0.06117	0.797
323.15	0.2709	0.05034	1.25
333.15	0.2543	0.04606	1.49
343.15	0.2298	0.05269	0.626
	Niacin + H_2O + 10 Mass % 3-Picoline		
293.15	0.3695	0.02634	1.90
303.15	0.3460	0.02669	1.86
313.15	0.3079	0.05141	0.617
323.15	0.2918	0.04637	1.17
333.15	0.2804	0.03949	0.608
343.15	0.2690	0.04116	0.650

where η is the viscosity of the solution, η_0 is the viscosity of pure 3-picoline or solvent mixtures of 3-picoline + water, and m is the molality of niacin. The values of the polynomial coefficients A_k are listed in Table 7, along with standard deviations for viscosity.

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