Densities and Viscosities of 1,1′-(Pentane-1,5-diyl)-bis(pyridinium) Dibromide in Ethanol + Water from (293.15 to 344.15) K

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The densities and viscosities of 1,1′-(pentane-1,5-diyl)-bis(pyridinium) dibromide in ethanol + water have been determined experimentally at temperatures from (293.15 to 344.15) K. The density and viscosity data were fitted by the Vogel−Tamman−Fulcher equation. The adjustable parameters and standard deviations are obtained.

Introduction

The density and viscosity are important basic data used in chemical engineering designs, solution theory, and molecular thermodynamics. 1,1′-(Pentane-1,5-diyl)-bis(pyridinium) dibromide ($[C_5(Py)_2][Br]_2$) is a dicational ionic liquid, which can be proposed as a solvent in high-temperature reactions.[1] In the synthesis and purification process of $[C_5(Py)_2][Br]_2$, it is useful to know the physical properties of $[C_5(Py)_2][Br]_2$ + solvent. However, to our knowledge, no density and viscosity data on mixtures for $[C_5(Py)_2][Br]_2$ + ethanol + water were previously reported in the literature. In this study, the densities and viscosities of $[C_5(Py)_2][Br]_2$ + ethanol + water ternary mixtures have been measured at temperatures from (293.15 to 344.15) K. The results of measurements were fitted by the Vogel−Tamman−Fulcher equation to obtain the appropriate parameters and standard deviations between the measured and fitted values.

Experimental Section

Materials. High-grade ethanol from Tianjin Kemel Chemical Reagent Co., Ltd. was used directly without further purification, and its mass fraction purity was greater than 99 %. $[C_5(Py)_2][Br]_2$ was from our Key Laboratory. Its mass fraction purity was determined by high-performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 99 %, and it was stored under nitrogen. The molecular structure of $[C_5(Py)_2][Br]_2$ is illustrated in Figure 1. Analysis for water contamination using the Karl Fischer technique (method Titro-Line KF) for the IL showed that the mass fraction was less than 0.01 %. The melting temperature (T_m) of $[C_5(Py)_2][Br]_2$ is (470.15 to 472.15) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.). The water used in the experiments was double distilled, and the conductivity was less than $1 \cdot 10^{-4}$ S·m^{-1}.

Apparatus and Procedure. The mixtures were prepared by mass using an electronic balance (type XS104, Mettler-Toledo Co.) and were stored in ground-glass-stoppered bottles of 250 cm^3. The balance has an uncertainty of ± 0.0001 g. It was ensured that the components were adequately mixed before being transferred to the pycnometers. Uncertainty in the mass fractions is estimated to be ± 0.001.

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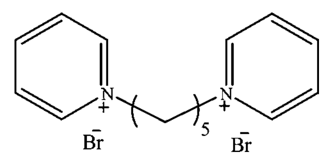

Figure 1. Molecular structure of $[C_5(Py)_2][Br]_2$.

The density was measured with five Ostwald−Sprengel-type pycnometers having a bulb volume of (25 ± 0.0001) 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.[2] The pycnometers were immersed in a water bath controlled to within ± 0.05 K. The readings from three pycnometers were averaged to determine the density. Uncertainties in density measurements were estimated to be within ± 0.0002 g·cm^{-3}.

Solution viscosity was measured in triplicate using a Ubbelohde capillary viscometer (1836-A) of 0.55 mm diameter. A water bath maintained a constant temperature (± 0.05 K). After thermal stability was attained, the flow times of the liquids were recorded with an electronic digital stopwatch. At least three repetitions of each datum 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)

Table 1. Comparison of Experimental Densities, *ρ*, and Viscosities, *η*, of Ethanol (1) + H_2O (2) with Literature Values

		ρ/g·cm^{-3}		η/mPa·s	
w_1	T/K	exptl	lit.[4]	exptl	lit.[5]
0.10	293.15	0.9818	0.9819	1.538	1.602
	303.15	0.9790	0.9788	1.160	1.263
	313.15	0.9746	0.9748	0.907	0.927
0.20	293.15	0.9682	0.9686	2.183	2.180
	303.15	0.9641	0.9640	1.553	1.687
	313.15	0.9587	0.9586	1.160	1.148
0.30	293.15	0.9536	0.9538	2.701	2.592
	303.15	0.9474	0.9474	1.870	1.980
	313.15	0.9403	0.9406	1.368	1.352
0.40	293.15	0.9355	0.9352	2.910	2.879
	303.15	0.9272	0.9277	2.020	2.161
	313.15	0.9198	0.9199	1.482	1.466
0.50	293.15	0.9139	0.9138	2.870	2.915
	303.15	0.9056	0.9058	2.022	2.133
	313.15	0.8976	0.8975	1.499	1.483

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Table 2. Densities, ρ, and Viscosities, η, at Different Temperatures and $[C_5(Py)_2][Br]_2$ Concentrations (m) in Binary Mixtures of (w) Ethanol (1) and (1 − w) Water (2), Where w = 0.10

T/K	ρ/g·cm^{-3}	η/mPa·s	T/K	ρ/g·cm^{-3}	η/mPa·s
		m = 0.10 mol·kg^{-1}			
293.65	1.0022	1.596	324.15	0.9799	0.741
298.65	0.9977	1.347	328.15	0.9789	0.692
303.35	0.9930	1.181	334.15	0.9768	0.619
309.15	0.9870	1.034	339.15	0.9754	0.573
314.15	0.9834	0.915	344.15	0.9745	0.537
319.15	0.9816	0.823			
		m = 0.20 mol·kg^{-1}			
294.15	1.0064	1.658	323.15	0.9869	0.835
299.65	1.0023	1.440	328.15	0.9843	0.753
304.15	0.9985	1.280	333.15	0.9814	0.693
309.15	0.9951	1.113	338.15	0.9794	0.630
314.15	0.9927	1.008	343.15	0.9771	0.585
318.15	0.9898	0.908			
		m = 0.30 mol·kg^{-1}			
293.15	1.0163	1.737	323.15	0.9974	0.874
299.15	1.0132	1.508	328.15	0.9944	0.786
303.15	1.0108	1.379	333.15	0.9915	0.725
308.15	1.0071	1.227	338.15	0.9883	0.657
313.15	1.0034	1.078	343.15	0.9861	0.599
319.15	1.0003	0.951			
		m = 0.40 mol·kg^{-1}			
299.15	1.0244	1.824	323.15	1.0071	0.969
303.15	1.0210	1.639	328.15	1.0038	0.862
308.15	1.0173	1.447	333.15	0.9999	0.757
313.15	1.0141	1.269	338.15	0.9966	0.686
318.15	1.0103	1.102	343.15	0.9937	0.618
		m = 0.50 mol·kg^{-1}			
299.15	1.0375	1.931	323.15	1.0169	0.983
303.15	1.0323	1.684	328.15	1.0146	0.886
308.15	1.0278	1.466	333.15	1.0126	0.790
313.15	1.0228	1.263	338.15	1.0108	0.736
318.15	1.0197	1.160	343.15	1.0091	0.672

Table 3. Densities, ρ, and Viscosities, η, at Different Temperatures and $[C_5(Py)_2][Br]_2$ Concentrations (m) in Binary Mixtures of (w) Ethanol (1) and (1 − w) Water (2), Where w = 0.20

T/K	ρ/g·cm^{-3}	η/mPa·s	T/K	ρ/g·cm^{-3}	η/mPa·s
		m = 0.10 mol·kg^{-1}			
293.15	0.979	2.3414	323.15	0.9581	0.975
299.15	0.979	1.8684	327.15	0.9560	0.901
303.15	0.972	1.6358	335.15	0.9526	0.765
308.15	0.968	1.4043	338.15	0.9522	0.736
313.15	0.965	1.2359	343.15	0.9496	0.667
318.15	0.961	1.0968			
		m = 0.20 mol·kg^{-1}			
293.15	0.9909	2.422	323.15	0.9713	1.009
298.15	0.9873	2.032	327.15	0.9685	0.927
303.15	0.9837	1.706	333.15	0.9651	0.827
308.15	0.9807	1.455	338.15	0.9618	0.754
313.15	0.9772	1.289	343.15	0.9592	0.699
318.15	0.9745	1.139			
		m = 0.30 mol·kg^{-1}			
293.15	1.0045	2.497	323.15	0.9822	1.088
298.15	1.0006	2.115	328.15	0.9796	0.960
303.15	0.9965	1.760	333.15	0.9774	0.883
308.15	0.9923	1.559	338.15	0.9751	0.801
313.15	0.9889	1.369	343.15	0.9732	0.747
318.15	0.9854	1.195			
		m = 0.40 mol·kg^{-1}			
293.15	1.0193	2.513	323.15	0.9913	1.105
298.15	1.0146	2.134	328.15	0.9879	1.018
303.15	1.0091	1.807	333.15	0.9836	0.934
308.15	1.0048	1.547	338.15	0.9795	0.863
313.15	1.0005	1.382	343.15	0.9751	0.804
318.15	0.9957	1.227			
		m = 0.50 mol·kg^{-1}			
297.15	1.0274	2.326	323.15	1.0081	1.158
303.15	1.0232	1.909	328.15	1.0047	1.034
308.15	1.0199	1.645	333.15	1.0018	0.938
313.15	1.0157	1.450	338.15	0.9987	0.878
318.15	1.0122	1.279	343.15	0.9964	0.823

was far less than its length (100 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity η was then calculated from the relationship[3]

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \qquad (1)$$

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 the literature.[2] The uncertainty in the viscosity measurement is estimated to be ± 0.0030 mPa·s.

Results and Discussion

The measured densities and viscosities of the mass fraction of (10, 20, and 30) % ethanol + H_2O mixture together with literature values[4,5] are included in Table 1. The measured

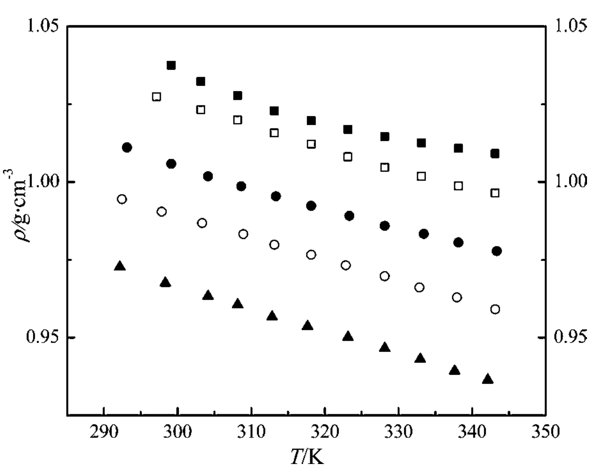

Figure 2. Dependence of the densities (ρ) on the content of ethanol (w) in the binary mixtures of ethanol + water, where $m([C_5(Py)_2][Br]_2)$ = 0.50 mol·kg^{-1}. ■, w = 0.10; □, w = 0.20; ●, w = 0.30; ○, w = 0.40; ▲, w = 0.50.

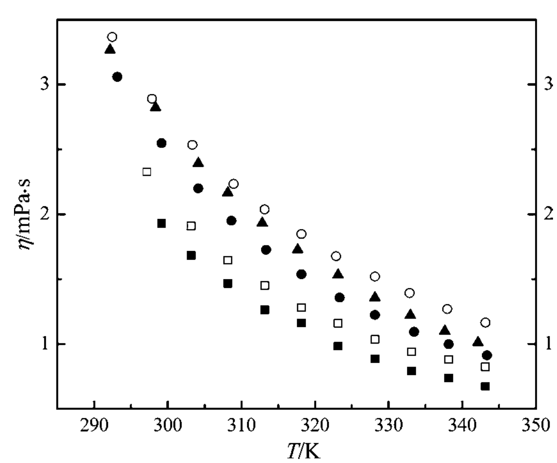

Figure 3. Dependence of the viscosities (η) on the content of ethanol (w) in the binary mixtures of ethanol + water, where $m([C_5(Py)_2][Br]_2)$ = 0.50 mol·kg^{-1}. ■, w = 0.10; □, w = 0.20; ●, w = 0.30; ○, w = 0.40; ▲, w = 0.50.

Table 4. Densities, ρ, and Viscosities, η, at Different Temperatures and $[C_5(Py)_2][Br]_2$ Concentrations (m) in Binary Mixtures of (w) Ethanol (1) and (1 − w) Water (2), Where w = 0.30

T/K	ρ/g·cm⁻³	η/mPa·s	T/K	ρ/g·cm⁻³	η/mPa·s
		m = 0.10 mol·kg⁻¹			
294.15	0.9631	2.745	323.15	0.9424	1.145
298.15	0.9578	2.368	328.15	0.9392	1.023
303.15	0.9547	1.988	333.15	0.9366	0.918
308.15	0.9512	1.696	338.15	0.9320	0.822
313.15	0.9481	1.478	343.15	0.9298	0.751
318.15	0.9443	1.302			
		m = 0.20 mol·kg⁻¹			
293.15	0.9702	2.907	323.15	0.9503	1.233
299.15	0.9656	2.340	328.15	0.9477	1.104
303.15	0.9626	2.048	333.15	0.9454	0.953
308.15	0.9589	1.755	338.95	0.9420	0.872
313.15	0.9559	1.535	343.15	0.9403	0.788
317.85	0.9529	1.384			
		m = 0.30 mol·kg⁻¹			
294.15	0.9922	2.874	323.15	0.9661	1.215
299.15	0.9873	2.387	327.15	0.9638	1.109
304.15	0.9806	1.994	332.95	0.9612	0.987
308.15	0.9772	1.758	337.85	0.9584	0.903
313.15	0.9735	1.545	343.15	0.9568	0.803
318.15	0.9697	1.364			
		m = 0.40 mol·kg⁻¹			
296.15	0.9939	2.805	323.15	0.9754	1.320
304.15	0.9876	2.204	328.15	0.9714	1.177
308.15	0.9846	1.976	333.35	0.9681	1.027
313.35	0.9811	1.712	337.65	0.9659	0.911
318.45	0.9778	1.497	343.15	0.9631	0.829
		m = 0.50 mol·kg⁻¹			
293.15	1.0111	3.060	323.35	0.9891	1.357
299.15	1.0058	2.548	328.15	0.9859	1.223
304.15	1.0018	2.199	333.45	0.9833	1.093
308.65	0.9986	1.950	338.15	0.9806	0.997
313.35	0.9954	1.726	343.35	0.9778	0.912
318.15	0.9923	1.537			

Table 5. Densities, ρ, and Viscosities, η, at Different Temperatures and $[C_5(Py)_2][Br]_2$ Concentrations (m) in Binary Mixtures of (w) Ethanol (1) and (1 − w) Water (2), Where w = 0.40

T/K	ρ/g·cm⁻³	η/mPa·s	T/K	ρ/g·cm⁻³	η/mPa·s
		m = 0.10 mol·kg⁻¹			
297.65	0.9398	2.589	323.35	0.9168	1.212
303.15	0.9333	2.093	328.35	0.9145	1.096
309.15	0.9278	1.739	333.15	0.9118	1.004
313.35	0.9252	1.546	337.95	0.9084	0.919
318.45	0.9216	1.352	343.35	0.9061	0.847
		m = 0.20 mol·kg⁻¹			
297.35	0.9473	2.739	323.15	0.9248	1.278
303.65	0.9402	2.198	327.95	0.9213	1.157
308.75	0.9357	1.866	333.15	0.9173	1.035
313.15	0.9315	1.649	338.15	0.9126	0.939
317.15	0.9290	1.489	343.25	0.9091	0.859
		m = 0.30 mol·kg⁻¹			
292.95	0.9674	3.116	322.95	0.9457	1.358
297.65	0.9638	2.730	328.45	0.9424	1.218
303.15	0.9591	2.283	333.15	0.9393	1.103
309.15	0.9552	1.964	338.35	0.9357	0.976
313.15	0.9519	1.737	343.45	0.9325	0.893
318.35	0.9481	1.518			
		m = 0.40 mol·kg⁻¹			
294.15	0.9799	3.168	323.15	0.9604	1.490
297.95	0.9775	2.888	328.15	0.957	1.339
304.95	0.9725	2.357	333.35	0.9542	1.215
308.65	0.9701	2.138	338.15	0.9511	1.099
313.35	0.9670	1.903	342.95	0.9484	1.006
318.35	0.9632	1.698			
		m = 0.50 mol·kg⁻¹			
292.45	0.9944	3.367	322.85	0.9732	1.677
297.85	0.9905	2.890	328.15	0.9697	1.519
303.35	0.9868	2.535	332.85	0.9661	1.391
308.95	0.9832	2.234	337.95	0.9629	1.269
313.15	0.9798	2.036	343.15	0.9591	1.164
318.15	0.9766	1.847			

Table 6. Densities, ρ, and Viscosities, η, at Different Temperatures and $[C_5(Py)_2][Br]_2$ Concentrations (m) in Binary Mixtures of (w) Ethanol (1) and (1 − w) Water (2), Where w = 0.50

T/K	ρ/g·cm⁻³	η/mPa·s	T/K	ρ/g·cm⁻³	η/mPa·s
		m = 0.10 mol·kg⁻¹			
294.15	0.9205	2.797	323.45	0.8936	1.102
297.75	0.9175	2.452	327.35	0.8915	1.001
303.15	0.9111	1.975	332.75	0.8883	0.889
308.15	0.9074	1.678	337.65	0.8834	0.799
312.65	0.9030	1.458	342.95	0.8807	0.726
317.95	0.8997	1.256			
		m = 0.20 mol·kg⁻¹			
294.15	0.9370	2.808	323.45	0.9126	1.175
297.75	0.9333	2.507	327.35	0.9107	1.071
303.15	0.9284	2.115	332.75	0.9062	0.927
308.15	0.9257	1.822	337.65	0.9033	0.820
312.65	0.9226	1.598	342.95	0.9004	0.731
317.95	0.9178	1.374			
		m = 0.30 mol·kg⁻¹			
293.75	0.9460	2.908	323.15	0.9230	1.202
297.85	0.9435	2.555	327.65	0.9196	1.083
303.15	0.9391	2.094	332.55	0.9161	0.952
308.15	0.9348	1.823	338.15	0.9115	0.851
313.15	0.9311	1.572	343.15	0.9076	0.795
317.15	0.9281	1.389			
		m = 0.40 mol·kg⁻¹			
293.15	0.9625	3.157	322.15	0.9411	1.425
297.15	0.9591	2.729	327.65	0.9375	1.261
303.15	0.9547	2.287	332.45	0.9345	1.162
308.15	0.9511	1.965	337.15	0.9317	1.049
312.15	0.9485	1.783	342.15	0.9279	0.947
317.95	0.9441	1.544			
		m = 0.50 mol·kg⁻¹			
292.15	0.9727	3.267	323.15	0.9501	1.533
298.35	0.9675	2.824	328.15	0.9466	1.356
304.15	0.9633	2.393	332.95	0.9431	1.220
308.15	0.9606	2.166	337.65	0.9393	1.099
312.85	0.9567	1.933	342.15	0.9364	1.012
317.65	0.9536	1.728			

Table 7. Coefficients of Equation 2 for $[C_5(Py)_2][Br]_2$ in Binary Mixtures of (w) Ethanol + (1 − w) Water

systems		P_1	P_2	P_3	P_4	100σ
w = 0.10	ρ/g·cm⁻³	0.858	30.102	23.909	63.084	0.20
	η/mPa·s	0.157	140.123	69.117	229.425	0.55
w = 0.20	ρ/g·cm⁻³	0.829	34.438	30.804	88.709	0.21
	η/mPa·s	0.201	137.677	25.559	235.745	0.38
w = 0.30	ρ/g·cm⁻³	0.817	33.540	31.140	64.654	0.26
	η/mPa·s	0.214	149.762	22.276	234.346	0.71
w = 0.40	ρ/g·cm⁻³	0.792	33.254	37.530	68.580	0.36
	η/mPa·s	0.238	159.250	38.610	227.109	1.05
w = 0.50	ρ/g·cm⁻³	0.759	39.958	36.084	64.176	0.32
	η/mPa·s	0.215	153.337	33.373	231.687	1.10

densities and viscosities of the solutions are reported in Tables 2 to 6. The dependence of density and viscosity on temperature and concentration has been calculated by the Vogel−Tamman−Fulcher (VTF) equation[6]

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

where $F = (\rho \text{ or } \eta)$; ρ and η are the density and viscosity of solution, respectively; m is the molality of $[C_5(Py)_2][Br]_2$; T is the absolute temperature; and P_1, P_2, P_3, and P_4 are the curve-fit coefficients. The values are listed in Table 7 along with standard deviations. The standard deviation is defined by

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

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 eq 2 and to the experimental value.

From Tables 2 to 7, we can draw the following conclusions: (a) the density and viscosity are functions of temperature and decrease with increasing temperature. As the temperature increases, volume increases, and the density decreases. At the same time, as the temperature increases, the force between molecules decreases, and the viscosity decreases. (b) The calculated densities and viscosities from eq 2 are in good agreement with the experimental data, which indicate that the VTF equation can be used to correlate the density and viscosity data of $[C_5(Py)_2][PF_6]_2$ in the ethanol + water system.

By using the data shown in Tables 2 to 6, the dependence of the densities and viscosities on the content of ethanol (w) in the mixtures for $[C_5(Py)_2][Br]_2$ + ethanol + water ($m = 0.50$) is given in Figures 2 and 3. From the results shown in Tables 2 to 6 and Figures 2 and 3, it can be seen that the density decreases with the increase of the amount of ethanol in the mixtures, and the viscosity has a maximum value with the increase of the amount of ethanol at the same temperature.

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