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Thermophysical properties of 1-hexyl-3-methylimidazolium bromide in the range of 283.15 K to 373.15 K at 0.1 MPa

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ABSTRACT

Ionic liquid are important green reagents for solvent extraction systems as well as novel chemical processes. Densities and viscosities of [HMIm]Br from 283.15 K to 373.15 K at 0.1 MPa were experimentally measured and correlated. For this ionic liquid with high viscosity, an extended van Velzen model was used. A good agreement between experimental and predicted values was observed.

KEYWORDS

Ionic liquid;
Thermophysical properties;
[HMIm]Br;
Density;
Viscosity.

INTRODUCTION

Ionic liquids are fast emerging as novel reagents for a variety of solvent extraction and other related chemical processes. Information on the thermophysical properties of many ionic liquid is severely limited. In this paper, experimentally determined and correlated density and viscosity of 1-hexyl-3-methylimidazolium bromide (hereafter referred as [HMIm]Br) at 0.1 MPa are reported.

EXPERIMENTAL WORK

General procedures

ASTM Grade-I water as per ASTM D-1193[1] with a resistivity of 18.2 MΩ·cm at 298.15 K and TOC <15ppb from a MILLIPORE Simplicity system was used in the density standard. Water for density standard was drawn from the water-purifier immediately before the experiments and it was degassed in an ultrasonic bath (TEC-110H) at 35 kHz for 60 seconds. To ensure the ripple-free power supply to all the equipments, AC supply was regulated with an uninterrupted power supply (APC), set at high sensitivity. The ambient conditions were monitored with a Cole-Parmer hygrometer (0.1%) consisting of thermometer (0.1 K) and pressure sensor (0.1 kPa).

AR grade (99%+) [HMIm]Br was procured from M/S Numex Scintifics, Mumbai. Purity was 99%+ by NMR and water content was about 0.05% as found by Karlfisher titration. Before weighing, the [HMIm]Br was kept in dessicator to prevent moisture pick-up.

Measurement of density and viscosity

Density and viscosity were measured simultaneously by a Anton Paar Stabinger Viscometer SVM-3000 with a built-in thermoelectric Peltier Element module for maintaining temperature of sample. Samples were loaded manually by using a 2 mL glass syringe in the cell input. Due to very high viscosity, these samples could not be loaded by automatic sample changers in either DMA-5000 or SVM-3000 systems. Air was dried with a drierite based drier to ensure almost complete removal of moisture. The measurement procedure followed was exactly as described in ASTM D-7042-04[2].

TABLE 1 : Density determinations as per ASTM-D 7042-04

Temperature K	Density g/mL Expt.	Density g/mL Pred.	Residual g/mL	Deviation %
283.15	1.2349	1.2353	0.0004	0.0391
288.15	1.2316	1.2319	0.0003	0.0272
293.15	1.2284	1.2285	0.0001	0.0087
298.15	1.2251	1.2251	0.0000	0.0000
303.15	1.2218	1.2217	-0.0000	-0.0072
308.15	1.2185	1.2183	-0.0001	-0.0128
313.15	1.2151	1.2149	-0.0001	-0.0086
318.15	1.2118	1.2116	-0.0001	-0.0110
323.15	1.2083	1.2083	0.0000	0.0047
328.15	1.2049	1.2050	0.0001	0.0139
333.15	1.2016	1.2017	0.0001	0.0165
338.15	1.1984	1.1985	0.0001	0.0124
343.15	1.1951	1.1953	0.0002	0.0184
348.15	1.1920	1.1921	0.0001	0.0092
353.15	1.1888	1.1889	0.0001	0.0101
358.15	1.1857	1.1857	0.0000	0.0042
363.15	1.1826	1.1826	0.0000	0.0000
368.15	1.1796	1.1794	-0.0001	-0.0110
373.15	1.1766	1.1763	-0.0002	-0.0204

RESULTS AND DISCUSSION

Densities at different temperature

The observed densities of [HMIm]Br, listed in TABLE 1, could be correlated with Eq.1. It was based on a quadratic temperature dependence on the density of pure fluid-

$$\rho = \rho_{298.15}\left(1+\alpha\left(\frac{T}{K}-298.15\right)+\beta\left(\frac{T}{K}-298.15\right)^2\right) \quad (1)$$

Where $\rho_{298.15K}$= 1.2251 g/mL Coefficients of the Eq.1 were regressed as α= -5.5474x10^{-4}, β=3.2371x10^{-7} with a mean deviation of 4.9x10^{-3}% and standard deviation of 1.49x10^{-2}%. These results are shown in Figure 1.

Modeling of experimental viscosities

Andrade equation, for viscosity of liquids, can be written as

$$\ln\frac{\eta}{mPa.s} = A + \frac{B}{T/K} \quad (2)$$

At a given reference temperature $T=T_o$, the equation can be written as

$$\ln\frac{\eta_o}{mPa.s} = A + \frac{B}{T_o/K} \quad (3)$$

If T_o is selected such as at $T=T_o$, η=1 mPa.s (cP), then

$$A = -\frac{B}{T_o/K} \quad (4)$$

On substituting this value in Eq. 2, one may write

$$\ln\frac{\eta}{mPa.s} = B\left(\frac{1}{T/K}-\frac{1}{T_o/K}\right) \quad (5)$$

The Eq.5 was proposed by van Velzen *et al.*[3]. Generally coefficients B and T_o are estimated by group contribution techniques. For most of the low viscosity liquids and gases, T_o is a merely fictional value at the reference viscosity of 1 mPa.s. To deal with extended temperature ranges, if a higher order extension of Eq.2 in temperature is desired, then one may write

$$\ln\frac{\eta}{mPa.s} = A + \frac{B}{T/K} + \frac{C}{(T/K)^2} \quad (6)$$

At $T=T_{ref}$, $\eta=\eta_{ref}$ and

$$\ln\frac{\eta_{ref}}{mPa.s} = A + \frac{B}{T_{ref}/K} + \frac{C}{(T_{ref}/K)^2} \quad (6a)$$

On combining Eqs.6 and 7, we have

$$\ln\left(\frac{\eta}{\eta_{ref}}\right) = \left[B\left(\frac{1}{T/K}-\frac{1}{T_{ref}/K}\right)+C\left(\frac{1}{(T/K)^2}-\frac{1}{(T_{ref}/K)^2}\right)\right] \quad (7)$$

Coefficients B and C of the Eq.7 may be estimated either with group-contribution technique or simply by regression of experimental results. Effect of the temperature on viscosities is embedded in Eq.7. The basic difference between Eq.7 and model of van Velzen *et al.*[3] is treatment of T_o and viscosity at T_o. In the model of Van velzen *et al.* at $T=T_o$, the viscosity is assumed to have a unit value which may or may not be observable in the practical cases. However in Eq. 7, at $T=T_{ref}$, the reference viscosity value is an observed value, having physical significance.

The observed viscosities of [HMIm]Br, are listed in TABLE 2. Eq.7 was used to correlate the experimental data with the reference viscosity being taken at the reference temperature of 298.15K. Coefficients of the Eq.7 were regressed as B=-0.0109x10^6, C=2.9237x10^6 with a mean deviation of 0.01% and standard deviation of 1.20%.

CONCLUSIONS

Densities and viscosities of [HMIm]Br from 283.15

K to 373.15 K at 0.1 MPa were experimentally measured and modeled. Extended van Velzen model was used for correlating the experimental viscosity data and the agreement between experimental and predicted values was good.

TABLE 2 : Viscosity determinations as per ASTM-D 7042-04

Temperature *K*	Dynamic Viscosity mPa.s (Expt.)	Dynamic Viscosity mPa.s (Pred.)	Deviation $100\left(\frac{\text{Pred.} - \text{Expt.}}{\text{Expt.}}\right)$
283.15	22725	21553.78	5.1539
288.15	12154	11985.33	-1.3878
293.15	6955.1	6942.67	-0.1787
298.15	4176.5	4176.50	0
303.15	2601.5	2601.8	0.0115
308.15	1678.9	1674.25	-0.2770
313.15	1116.2	1110.21	-0.5366
318.15	762.94	757.00	-0.7786
323.15	535.52	529.71	-1.0849
328.15	384.69	379.70	-1.2971
333.15	281.66	278.34	-1.1787
338.15	211.02	208.34	-1.2700
343.15	161.03	159.01	-1.2544
348.15	124.94	123.589	-1.0813
353.15	98.41	97.69	-0.7316
358.15	78.65	78.46	-0.2416
363.15	63.71	63.95	0.3767
368.15	52.25	52.85	1.1483
373.15	43.33	44.25	2.1232

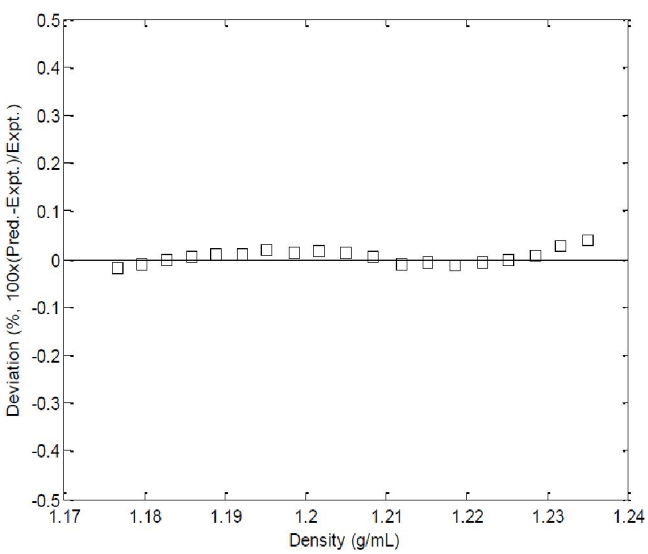

Figure 1 : Plot of deviations for densities of [HMIm]Br at different temperatures

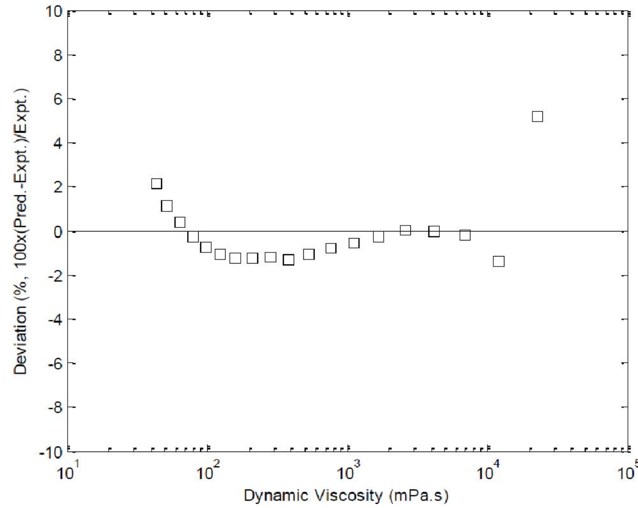

Figure 2 : Plot of deviations for viscosities of [HMIm]Br at different temperatures

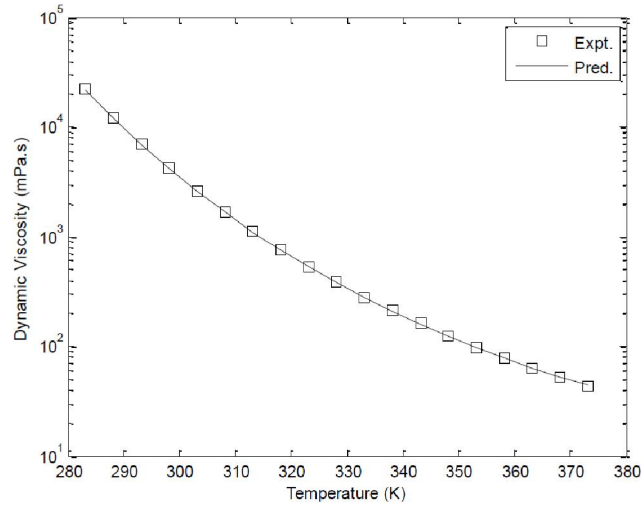

Figure 3 : Comparison of experimental and predicted viscosities of [HMIm]Br from 283.15 K to 373.15 K Solid line represents Eq.7

NOMENCLATURE

T Temperature (K), B, C Adjustable coefficients

Greek

ρ Density, g/mL, η Dynamic Viscosity, mPa.s

REFERENCES

[1] ASTM Standard D-1193, Specification for Reagent Water, **(2006)**.

[2] ASTM Standard D-7042, Standard test method for kinematic viscosity and density of liquids by stabinger viscometer, **(2004)**.

[3] D.Van Velzen, R.L.Cardozo, H.Langenkamp; Ind.Eng.Chem.Fund., **11**, 20–25 **(1972)**.