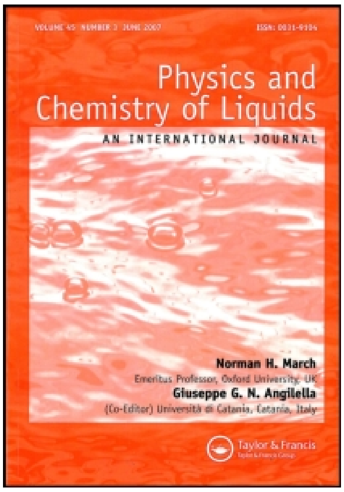

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Viscometric studies of molecular interactions of nicotine in aqueous and aqueous ethanol at 298.15, 303.15 and 308.15 K

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Precise densities and viscosities at 298.15, 303.15, and 308.15 K for solutions of nicotine in water and in 0.02 mmol aqueous ethyl alcohol were measured for limiting apparent molal volume and *B*-coefficients calculations, respectively. These data are rationalized to illustrate hydrophilic and hydrophobic interactions between various functional groups present in these solutions.

Keywords: Apparent molal volume; Viscosity *B*-coefficient; Nicotine; Ethyl alcohol; Temperature dependence

1. Introduction

Currently major efforts are devoted to the physicochemical properties of the biomolecules in mixed solvent due to the binding trends of such molecules with the medium. As is cited in the literature, little attention has been paid to the solution properties of aqueous nicotine and in ethanol solutions despite their physiological importance. Recently, measurements of enthalpy, entropy, and free energy along with their regression constants have been reported [1] for studies of solute–solvent interactions, but no substantial work is undertaken on densities, partial molal volumes, and viscosities as a function of temperature. In our present article, we report the variation of volumes and viscosities of nicotine in water + ethyl alcohol with concentration of nicotine at 298.15, 303.15, and 308.15 K. Information on aqueous nicotine is of interest as it causes linkages with substrates due to molecular interactions with media that influence the activity of the solute. So under prescribed conditions its solutions must have definite densities, apparent molal volumes, and reduced viscosities [2] that infer structure breaking or the making effect on the medium. As these are fundamental properties and can reveal information about the activity, nicotine–water

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and nicotine–ethanol interactions, so V_{ϕ}^{0} render elementary information and studies are focussed to gather information on ethanol–nicotine interactions here, which may be of some use to unfold the origin of the effects of a combination of smoking followed by ethanol intake.

2. Experimental

2.1. *Materials*

Nicotine (Sigma, 9765) and AR ethanol (E. Merck) were used and water (specific conductivity $\sim 10^{-4}\,\mathrm{S\,m^{-1}}$) was deionized and distilled, and degassed prior to making solutions w/w. The solutions were prepared with a precision of $\pm 1 \times 10^{-5}\,\mathrm{kg}$ on a Dhona balance (India, Model 100DS). Uncertainties in solution concentration were estimated at $\pm 2 \times 10^{-2}\,\mathrm{mmol\,kg^{-1}}$ in calculations. The concentrations of aqueous nicotine in ethyl alcohol were in the range 0.02–0.64 $\mathrm{mmol\,kg^{-1}}$, while that of the aqueous nicotine in 0.02 $\mathrm{mmol\,kg^{-1}}$ aqueous ethanol were 0.0202–0.0208 $\mathrm{mmol\,kg^{-1}}$.

2.2. *Apparatus and procedure*

Densities (ρ) were measured with bicapillary pyknometer of total volume $12 \times 10^{-3}\,\mathrm{dm^3}$ with capillary of $1 \times 10^{-3}\,\mathrm{m}$ internal diameter, with reproducibility better than $\pm 3 \times 10^{-2}\,\mathrm{kg\,m^{-3}}$. Thermostatically controlled well-stirred water bath with ±0.01°C control in temperature was maintained and calibration of viscometer was checked with aqueous 2 BSA solutions at 298.15 K. Kinetic correction to energy of viscometer was calculated and found to be 1.898×10^{-4}, 2.327×10^{-5}, and 2.326×10^{-6} at 298.15, 303.15, and 308.15 K, respectively. It depicts a negligible shear and not able to interfere the natural flow of the solution.

2.3. *Theoretical*

The ρ values were calculated from relation:

$$\rho = \left(\frac{W - W_e}{W_0 - W_e}\right)\rho_0 + 0.0012\left(1 - \frac{W - W_0}{W_0 - W_e}\right)$$

where ρ solution, ρ_0 solvent, and $0.0012\,\mathrm{kg\,mm^{-1}}$ are air densities, respectively, $[1 - (W - W_e)/(W_0 - W_e)]$ is buoyancy correction for air, m molality, W_e, W_0, and W are weights of empty, solvent, and solution-filled pyknometer, respectively. Errors in ρ data are calculated from equations given subsequently.

$$\sqrt{\left(\frac{W - W_0}{10^5}\right)^2 + \left(\frac{W_e}{10^5}\right)^2} \approx \pm S_n$$

$$\sqrt{\left(\frac{W_0 - W_e}{10^5}\right)^2 + \left(\frac{W_e}{10^5}\right)^2} \approx \pm S_v$$

$$\sqrt{\left(\frac{\pm S_n}{W - W_e}\right)^2 + \left(\frac{\pm S_v}{V_{\mathrm{pyk}}}\right)^2} = \frac{\Delta\rho}{\rho}$$

where V_{pyk} is pyknometer volume calculated from $(W_0 - W_e)/\rho_0$ and V_ϕ data are computed with ρ from following equation:

$$V_\phi = \frac{M}{\rho} + \frac{1000}{(\rho_0 - \rho)/\rho_0 \rho m}$$

where M is molar mass of solute, and uncertainty in V_ϕ is computed from the following equation:

$$V_\phi = \left(\frac{1000}{m}\right)\frac{\Delta\rho}{\rho}$$

where $\Delta\rho = \rho - \rho_0$, viscosity η is calculated from relation.

$$\eta = \frac{\eta_0(\rho t)}{\rho_0 t_0}$$

where t and t_0 are flow times and η and η_0 are viscosities of solution and solvent, respectively, η_{rel} (relative viscosity) is calculated from η/η_0 relation. Like ρ, the errors in η data were obtained.

3. Results

The ρ, V_ϕ and η data are least-square fitted against m for values at infinite dilution referred to as limiting values from the following equation:

$$\rho = \rho^0 + S_{\mathrm{d}} m$$

where ρ^0 is the limiting density at $m \to 0$ and S_{d} slope, V_ϕ is fitted in equation.

$$V_\phi = V_\phi^0 + S_{\mathrm{v}} m + S_{\mathrm{v}}^* m^2$$

where V_ϕ^0 is limiting constant, S_{v} and S_{v}^* are slopes. The V_ϕ^0 focuses the solute–solvent and S_{v} and S_{v}^* focuses the solute–solute and charge–charge interactions, respectively. The η_{rel} is fitted to extended Jones–Dole equation [3] given below.

$$\frac{\eta_{\mathrm{rel}} - 1}{m} = B + Dm + Cm^2$$

where B ($\mathrm{kg\,mm^{-1}}$) is Jones–Dole coefficient, D $(\mathrm{kg\,mm^{-1}})^2$ and C $(\mathrm{kg\,mm^{-1}})^3$ are slopes measuring heteromolecular interactions. Table 1 contains primary data and tables 2 and 3 the regression constants of aqueous systems.

4. Discussion

The ρ^0 values for binary systems are noted as aqueous nicotine > water, at each K, respectively and depicts stronger structural interactions of nicotine with water due to functional groups than those of water while weaker for the nicotine. Thus nicotine asserts much internal pressure on water structure with comparatively stronger structure-breaking action, and infers that the hydrogen bonding in water is due to

Table 1. Primary data of aqueous nicotine and in ethanol systems.

	ρ (10^{-2} kg m^{-1})	V_ϕ (10^{-6} m^3 mm^{-1})	η_r	η_{red} (10^{-2} kg mm^{-1})
Aqueous nicotine (mmol kg^{-1})				
298.15 K				
0.02	0.99707	−1.02527	0.9927	−366.9790
0.04	0.99714	−2.17925	0.9937	−158.5500
0.08	0.99717	−1.31648	0.9958	−52.9561
0.16	0.99719	−0.72265	0.9967	−20.3303
0.32	0.99722	−0.35571	0.9990	−3.0860
0.64	0.99724	−0.13864	1.0000	−0.0003
303.15 K				
0.02	0.99568	−1.25281	0.9916	−419.3870
0.04	0.99579	−3.27462	0.9928	−180.2530
0.08	0.99588	−2.78010	0.9952	−60.3834
0.16	0.99594	−1.69050	0.9968	−20.0045
0.32	0.99603	−1.03899	0.9990	−3.1522
0.64	0.99605	−0.46063	0.9998	−0.3275
308.15 K				
0.02	0.99405	−0.28762	0.9893	−533.7540
0.04	0.99406	−0.38899	0.9909	−228.5380
0.08	0.99408	−0.40025	0.9912	−110.5740
0.16	0.99411	−0.25944	0.9937	−39.5505
0.32	0.99413	−0.11723	0.9946	−16.9044
0.64	0.99415	−0.00952	0.9958	−6.5922
Aqueous nicotine in 0.02 mmol kg^{-1} aqueous ethanol				
298.15 K				
0.0202	1.04548	−51.00000	1.9757	48301.3200
0.0203	1.00546	−54.00000	1.9246	45545.4800
0.0204	0.98582	−55.00000	1.8977	44003.6300
0.0205	0.94977	−71.00000	2.2637	61642.0500
0.0206	0.90867	−75.00000	2.1842	57484.5700
0.0207	0.86016	−77.00000	2.0145	49007.7200
0.0208	0.81601	−65.00000	1.5586	26855.5900
303.15 K				
0.0202	1.07672	−3.74821	1.9873	48877.0500
0.0203	1.03672	−1.96215	1.9386	46237.2100
0.0204	0.99267	0.14824	1.8692	42607.0700
0.0205	0.94522	2.61746	2.3036	63592.4100
0.0206	0.90116	−7.99599	2.2223	59333.2000
0.0207	0.85331	−4.94651	2.0458	50523.0000
0.0208	0.80926	−1.85126	1.5502	26452.3200
308.15 K				
0.0202	1.03699	−2.06521	1.8087	40033.5800
0.0203	0.99418	−0.00689	1.7514	37012.8300
0.0204	0.99406	−0.00078	1.7905	38749.4700
0.0205	0.94170	−2.73109	2.1711	57128.8100
0.0206	0.89888	−8.21439	2.2730	61793.7700
0.0207	0.85055	−5.11612	2.0032	48465.6100
0.0208	0.80774	−2.09091	1.5777	27775.5900

higher polarity than that of aqueous nicotine, hence the former may show comparatively larger activities in the biochemical systems.

The higher ρ^0 values than those of water at each K, conclude the stronger hydrogen-bond formation with water. Firstly the nicotine breaks down the hydrogen bonded

Table 2. Density constants $\Delta\rho = \rho^0 - \rho_w$, ρ_w is density of water [6]. $\rho_w = 0.99705$, 0.99565 and $0.99404 \times 10^3\,\mathrm{kg\,m^{-3}}$ at 298.15, 303.15, and 308.15 K, respectively.

T (K)	ρ^0 ($10^{-4}\,\mathrm{kg\,mm^{-1}}$)	S_d ($\mathrm{kg^2\,m^{-3}\,mm^{-1}}$)	$\Delta\rho$ ($10^{-4}\,\mathrm{kg\,mm^{-1}}$)
Aqueous nicotine			
298.15	0.99710	2.05400	0.00005
303.15	0.99580	4.91600	0.00015
308.15	0.99410	1.49500	0.00006
Aqueous nicotine in 0.02 mmol kg^{-1} aqueous ethanol			
298.15	1.00520	−42.30000	0.00815
303.15	1.04730	−30.00000	0.05160
308.15	1.01340	−28.00000	0.01936

Table 3. Limiting apparent molal volume and intrinsic viscosity constants.

T (K)	$\Phi_{v^0} \times 10^{-1}$ ($\mathrm{m^3\,mm^{-1}}$)	$S_v \times 10^7$ ($\mathrm{m^3\,mm^{-2}}$)	S_v^* ($\mathrm{m^3\,mm^{-3}}$)	B ($\mathrm{kg\,mm^{-1}}$)	D ($\mathrm{kg^2\,mol^{-2}}$)	D^* ($\mathrm{kg^3\,mol^{-3}}$)
298.15	−1.73070	6.00	-6.00×10^9	−27.11	2.00×10^4	-2.00×10^9
303.15	−2.54360	5.00	-2.00×10^9	−30.95	2.00×10^4	-2.00×10^9
308.15	−0.39189	−5.00	9.09×10^5	−39.94	2.00×10^4	-3.00×10^9
298.15	-4.00×10^3	-1.00×10^8	1.00×10^6	−2878.9.00	151.21	−2086.30
303.15	-7.00×10^5	7.00×10^{15}	-2.00×10^{19}	-9.00×10^6	9.00×10^{10}	-2.00×10^{17}
308.15	8.00×10^5	-7.00×10^{15}	2.00×10^{19}	-1.00×10^7	9.00×10^{10}	-2.00×10^{17}

water structure whereby the broken water structure is accessible for stronger interactions with nicotine, thereby the nicotine behave as water-structure breaker. It reveals stronger nicotine structural interactions, due to functional groups. Order of S_d values at each K, comparatively show a larger activity of water predicting water–water intermolecular interactions. The S_d values of water signify larger reorientation structure followed by destabilization with composition and conformational states. Such arrangement in their structures favors stronger water–water hydrophobic intermolecular interactions generating much of the internal pressure on the solutions.

Secondly such electrostatic changes could favor a cage formation around itself, applying larger internal pressure facilitating stronger hydrophobic interaction. The lower S_d values for nicotine prove weaker effect of compositions on nicotine–nicotine interactions at each K, it concludes that the hydrated nicotine molecules may not further destabilize the water inferring stabilization of water structure breaking action. The V_ϕ^0 and S_v^* values for binary aqueous nicotine are negative and value of V_ϕ^0 provides evidence of electrostriction [4]. Again, since V_ϕ^0 is a measure of ion–solvent interaction, the negative value indicates weaker ion–solvent interaction. As observed, S_v values are high and positive at 298.15 and 303.15 K except at 308.15 K and decrease with temperature. Since, S_v is a measure of ion–ion interaction, the result indicates the presence of ion–ion interaction in the system at every temperature and the nicotine ionizes to a greater extent with increase in temperature.

The B values of nicotine show larger decrease with K, respectively. It shows larger dependence of the stability of hydrodynamic size of their hydrated complex on thermal energy. And its values are lower than those of water at three temperatures. It proves weaker Newtonian force on viscous flow due to weakly stable water–nicotine hydrogen bonding. It is evident from table 3 that S_v is positive for nicotine in water at

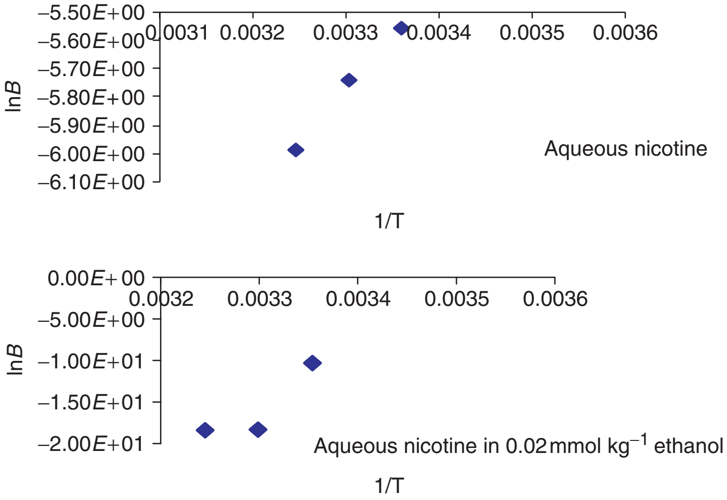

Figure 1. Plots of lnB *vs.* $1/T$ (i) aqueous nicotine and (ii) aqueous nicotine in ethanol.

298.15 and 303.15 K. A comparison of results obtained in nicotine + water with those obtained in ethyl alcohol suggests a possible explanation for the presence of negative S_v values (i.e. negative slopes). The B values so obtained decreased with increasing temperature. When we (figure 1) plotted $\ln B$ against $1/T$, approximately straight lines resulted for water, but concave curves for the lower alcohols were obtained and observed by Douheret *et al.* [5].

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