

Derived Properties of Binary Mixtures of n-Propanol and n-Butanol with Pyridine at 303.15 & 313.15 K Temperature

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Abstract:

Densities, viscosities of binary liquid mixtures composed of pyridine and primary alcohols n-propanol and n-butanol were determined at 303.15 & 313.15 K. From the experimental results obtained, deviation in viscosity ($\Delta\eta$), excess molar volume (V^E), excess Gibbs free energy of activation of viscous flow (ΔG^{*E}), were determined. The deviations in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow were correlated with Redlich-Kister polynomial equation.

Keywords: Density, Viscosity, Binary mixtures, Pyridine, Alcohols

1. INTRODUCTION

The mixing of different solvents results in the formation of a solution that is different from ideal. The thermodynamic properties of multicomponent liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject. The characterization of mixtures through their thermodynamic and transport properties is important from the fundamental viewpoint of understanding their mixing behavior. A thorough knowledge of transport properties of non-aqueous solutions is essential in many chemical and industrial applications.

The studies of excess properties such as deviation in viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow and Grunberg-Nissan interaction constant of binary mixtures are useful in understanding the nature of intermolecular interactions between two liquids. Properties such as density and viscosity at several temperatures both for pure chemicals and their binary liquid mixtures over the whole composition range are useful for understanding of the thermodynamic and transport properties associated with heat and fluid flow. Binary liquid mixtures due to their unusual behavior have attracted considerable attention due to their importance from both theoretical and practical point of view because these mixtures are used in titration, calorimetry and reaction calorimetry, among other uses.

Alcohols serve as simple examples of biological and industrially important amphiphilic materials that exist in the liquid state which may be due to hydrogen bonding of their O-H group. They are polar and self-associated liquids. The dipolar association of alcohols decreases when they are mixed with aromatic hydrocarbons due to some specific intermolecular interactions between the alcohol and an aromatic hydrocarbon. Primary alcohols have both a proton donor and a proton acceptor group. It is expected that there will be a significant degree of H-bonding leading to self-association in the pure state in addition to mutual association in their binaries.

In this study, experimental viscosity and density are reported at two temperatures 303.15 & 313.15 K for binary mixtures of pyridine and alcohols namely n-propanol and n-butanol. Deviation in viscosity ($\Delta\eta$), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the density (ρ), and viscosity (η), data. Calculated deviation in viscosity and excess functions were fitted to the Redlich-Kister polynomial equation.

2. EXPERIMENTAL

Mixture preparation

Materials Reagent grade propanol, butanol and pyridine were purchased from Sigma-Aldrich, South Africa and used without further purification.

Binary mixtures were prepared by weighing appropriate amounts of pyridine and alcohol on an electronic balance. An AE Adam balance (Adam Equipment Inc. USA) model PW124 with a maximum capacity of 120 g,

a readability range 0.0001 g and repeatability (S.D.) of 0.00015 g, linearity 0.0002 g, operating temperature +10°C to 40°C was used in all measurements.

Density measurement

Density measurement of binary mixtures was carried out with an Anton Paar DMA-4500 M digital densitometer thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers were provided for good precision in temperature control internally ($T \pm 0.01$ K). The densimeter protocol includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1.0×10^{-5} g/cm³, and the uncertainty of the measurements was estimated to be better than $\pm 1.0 \times 10^{-4}$ g/cm³. Calibration of the densimeter was performed at atmospheric pressure using doubly distilled and degassed water.

Viscosity measurement

Viscosity measurements were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of 0.2 to 20 000 mPa.s, a kinematic viscosity range of 0.2 to 20 000 mm²/s and a density range of 0.65 to 3 g/cm³. The instrument is equipped with a maximum temperature range of +105°C and a minimum of 20°C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility of 0.0005 g/cm³.

3. RESULTS AND DISCUSSION

A comparison of experimentally determined values of density (ρ), and viscosity (η) measured for all pure liquids at 303.15 & 313.15 K, with literature values are presented in table 1

Table 1. Comparison of experimental densities (ρ) and viscosities (η) with literature values

component	Comparative values	T = 303.15 K		T = 313.15 K	
		$\rho(\text{g/cm}^3)$	$\eta(\text{mPa.s})$	$\rho(\text{g/cm}^3)$	$\eta(\text{mPa.s})$
n-propanol	Experimental	0.7967	1.7153	0.7820	1.4339
	Literature	0.79574	1.72	0.78746	1.405
n-butanol	Experimental	0.8037	2.2662	0.7958	1.7680
	Literature	0.8022	2.2243	0.79396	1.7734
Pyridine	Experimental	0.9780	1.2054	0.9680	1.0098
	Literature	0.9737			

Table 2. Experimental values of density $\rho(\text{g/cm}^3)$, viscosity $\eta(\text{mPa.s})$, deviation in viscosity $\Delta\eta(\text{mPa.s})$, excess molar volumes $V^E(\text{cm}^3/\text{mol})$, molar volume of mixture $V_m(\text{cm}^3/\text{mol})$, excess Gibbs free energy of activation of viscous flow $\Delta G^{*E}(\text{J/mol})$ and modified Kendall and Monroe viscosity correlation $E\eta_m$ (mPa.s) with pyridine (x_1) at 303.15 & 313.15 K.

Pyridine (1)+ n-Propanol (2) at 303.15 K

X1	ρ	η	$\Delta\eta$	v^E	v_M	ΔG^{*E}	$E\eta_m(\text{mPas})$
1.0000	0.9747	0.9691	0.0000	0.0000	81.1532	0.0000	0.0000
0.9003	0.9526	0.9840	-0.0732	0.3100	81.0473	703.2704	0.1489
0.8008	0.9747	1.1677	0.0223	-3.0537	77.2763	1304.8547	0.2560

0.7003	0.9005	1.1918	-0.0422	1.6135	81.5166	1621.8207	0.3253
0.6006	0.8874	1.4231	0.1010	1.0980	80.5853	2046.9496	0.3591
0.4760	0.8744	1.2571	-0.1752	0.1084	79.0759	1548.1616	0.3575
0.4013	0.8557	1.5283	0.0300	0.4894	79.1454	1884.0999	0.3353
0.2997	0.8432	1.6233	0.0352	-0.2029	78.0293	1689.2286	0.2824
0.2032	0.8232	1.6496	-0.0238	-0.1320	77.6978	1307.5202	0.2104
0.1028	0.8027	1.8072	0.0451	-0.1054	77.3056	936.4934	0.1155
0.0000	0.7807	1.8530	0.0000	0.0000	76.9822	0.0000	0.0000

at 313.15 K.

X1	ρ	η	$\Delta\eta$	v^E	v_M	ΔG^{*E}	$E\eta_m(\text{mPas})$
1.0000	0.9643	0.9638	0.0000	0.0000	82.0284	0.0000	0.0000
0.9003	0.9426	0.8368	-0.1738	0.2954	81.9072	383.4332	0.1240
0.8008	0.9645	0.9663	-0.0913	-3.1103	78.0935	998.7747	0.2123
0.7003	0.8908	0.9949	-0.1098	1.6282	82.4042	1415.0639	0.2686
0.6006	0.8778	1.1437	-0.0079	1.1072	81.4666	1820.5142	0.2953
0.4760	0.8649	1.0381	-0.1720	0.1057	79.9445	1457.3345	0.2923
0.4013	0.8463	1.2196	-0.0256	0.4978	80.0245	1764.2923	0.2733
0.2997	0.8339	1.2573	-0.0357	-0.2026	78.8995	1551.6114	0.2291
0.2032	0.8142	1.3061	-0.0323	-0.1422	78.5566	1277.2762	0.1699
0.1028	0.7937	1.3768	-0.0088	-0.0971	78.1822	859.8977	0.0928
0.0000	0.7720	1.4339	0.0000	0.0000	77.8497	0.0000	0.0000

Pyridine (1)+ n-butanol(2) at 303.15 K

X1	ρ	η	$\Delta\eta$	v^E	v_M	ΔG^{*E}	$E\eta_m(\text{mPas})$
1.0000	0.9752	0.9765	0.0000	0.0000	81.1116	0.0000	0.0000
0.9003	0.9540	1.0421	-0.0630	0.1742	82.3936	777.1638	0.1921
0.8008	0.9166	1.3470	0.1133	1.8887	85.2230	1705.3286	0.3221
0.7003	0.9339	1.1972	-0.1659	-1.3414	83.1004	1380.6199	0.3990
0.6006	0.9024	1.3747	-0.1169	-0.0987	85.4510	1712.2245	0.4291
0.4760	0.8844	1.3657	-0.2866	-0.4456	86.4886	1469.8553	0.4128
0.4013	0.8836	1.7037	-0.0450	-1.6184	86.1459	1788.0016	0.3792
0.2997	0.8656	1.6900	-0.1897	-1.5405	87.3527	1395.6712	0.3101
0.2032	0.8521	1.7216	-0.2825	-1.7929	88.1727	963.2680	0.2244
0.1028	0.8351	1.8864	-0.2472	-1.7123	89.3689	544.5442	0.1194
0.0000	0.8037	2.2662	0.0000	0.0000	92.2235	0.0000	0.0000

At 313.15 K

X1	ρ	η	$\Delta\eta$	v^E	v_M	ΔG^{*E}	$E\eta_m(\text{mPas})$
1.0000	0.9651	0.8188	0.0000	0.0000	81.9604	0.0000	0.0000
0.9003	0.9441	0.8904	-0.0230	0.1827	83.2576	870.9028	0.1507
0.8008	0.9072	1.1079	0.0999	1.9095	86.1060	1749.0260	0.2544
0.7003	0.9243	0.9939	-0.1094	-1.3471	83.9635	1456.7037	0.3171
0.6006	0.8932	1.1123	-0.0856	-0.0940	86.3312	1751.0800	0.3433
0.4760	0.8754	1.1219	-0.1943	-0.4402	87.3777	1563.6854	0.3331
0.4013	0.8747	1.3530	-0.0341	-1.6306	87.0224	1818.0784	0.3076
0.2997	0.8569	1.3092	-0.1743	-1.5492	88.2396	1367.2904	0.2535
0.2032	0.8435	1.3856	-0.1895	-1.7958	89.0716	1038.4001	0.1848
0.1028	0.8268	1.5131	-0.1573	-1.7238	90.2660	615.6071	0.0992
0.0000	0.7958	1.7680	0.0000	0.0000	93.1390	0.0000	0.0000

Experimental density (ρ), dynamic viscosity (η), at temperatures of (303.15 & 313.15 K) are presented in table 2. The table also lists deviation in viscosity, $\Delta\eta$, excess molar volume, V^E and excess Gibbs free energy of activation of viscous flow ΔG^{*E} , for(*n*-propanol + pyridine) and (*n*-butanol + pyridine) as a function of mole fraction of the alcohol.

To investigate the molecular interaction between pyridine and the alcohols, (methanol, ethanol, *n*-propanol and *n*-butanol), viscosity deviation, $\Delta\eta$, excess molar volumes V^E and excess Gibbs free energy of activation of viscous flow, ΔG^{*E} , have been evaluated from experimental density and viscosity using equations 1 and 2 respectively.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \tag{1}$$

$$\Delta\eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \tag{2}$$

where x_1 and x_2 are the mole fractions calculated from mass fractions. M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, η_1 and η_2 are the viscosities of pure components 1 and 2 respectively. ρ_m and η_m are the density and viscosity of the mixture.

The excess Gibbs free energy of activation of viscous flow was obtained from equation 3.

$$\Delta G^{*E} = RT[\ln\eta_m V_m - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2)] \tag{3}$$

where R is the universal constant of gases, T is the absolute temperature, V_1 and V_2 are the molar volumes of component 1 and 2, x_1 and x_2 represents the mole fraction of component 1 and 2. V_m is obtained from equation 4 below. η_1 , η_2 and η_m are the viscosity of component 1 and 2 and mixture respectively.

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \tag{4}$$

The values of V^E , $\Delta\eta$ and ΔG^{*E} were correlated by a Redlich-Kister type polynomial, equation 5 and 6.

$$\Delta Y = x_1 x_2 \sum_{k=1}^n A_k (2x_1 - 1)^{k-1} \tag{5}$$

$$\Delta Y = x_1 x_2 [A_0 + A_1 (2x_1 - 1)^1 + A_2 (2x_1 - 1)^2 + A_3 (2x_1 - 1)^3 + A_4 (2x_1 - 1)^4] \tag{6}$$

The values of the parameters A_k , are obtained by fitting the equation to the experimental values with the least-squares method. The correlated results for excess molar volume, viscosity deviation and excess Gibbs free energy of activation of viscous flow are presented in table 3. The standard deviation $\sigma(\Delta Y)$ is calculated from equation 7.

$$\sigma(\Delta Y) = \left[\frac{\sum (Y_{\text{expt}} - Y_{\text{calc}})^2}{N - n} \right]^{1/2} \tag{7}$$

where ΔY is the excess volume, V^E , deviation in viscosity $\Delta\eta$, and excess Gibbs free energy of activation of viscous flow, ΔG^{*E} . The subscript *expt* and *calc* represents the experimental and calculated values respectively. N and n are the number of experimental data points and the number of coefficients in the Redlich-Kister polynomial equation.

Kendall and Monroe [23] derived equation 8 for analyzing the viscosity of binary mixtures based on zero adjustable parameter

$$\eta_m = \left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \tag{8}$$

$$E\eta_m = x_1x_2\left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \tag{9}$$

where $E\eta_m$ is a modified Kendall-Monroe equation, 9.

The predictive ability of some selected viscosity models such as the one parameter model of Frenkel equation 10 and Hind equation 11, apply to the studied binary mixtures.

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \tag{10}$$

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2 \eta_{12} \tag{11}$$

where η_{12} is a constant attributed to unlike pair interactions. Its value is obtained from equation 12.

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \tag{12}$$

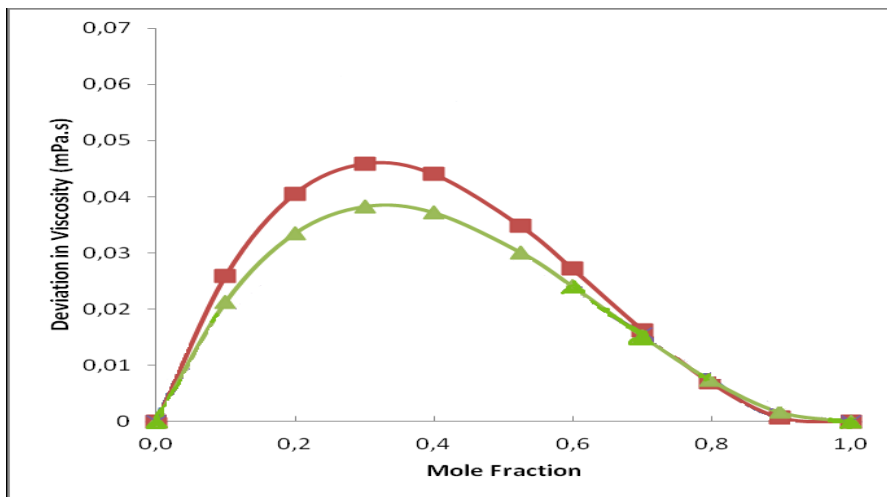
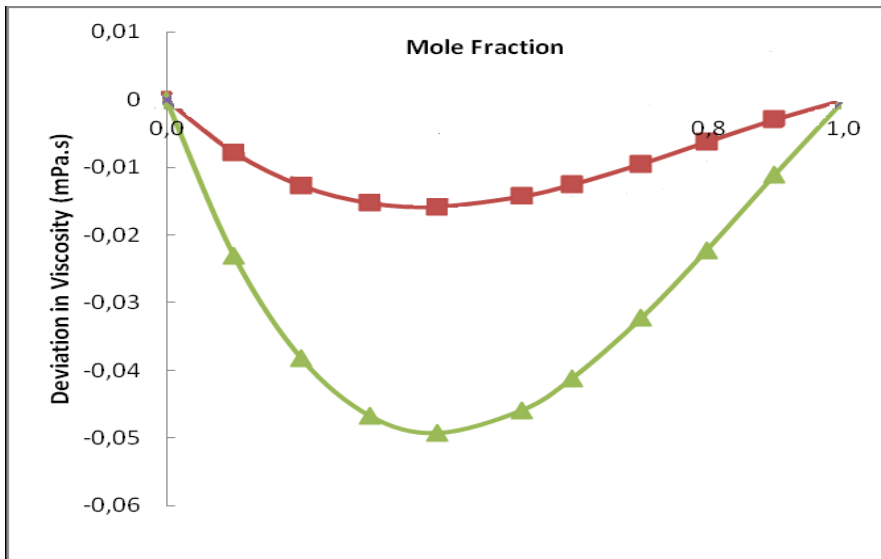
Table 3. Adjustable parameters A_i , with standard deviations $\sigma(\Delta Y)$, for deviation in viscosity ($\Delta\eta$), Excess volume (V^E), and Excess Gibbs free energy (ΔG^{*E}), for binary mixtures at two temperatures

parameter	temperature	A0	A1	A2	A3	σ
Pyridine (1)+ <i>n</i> -Propanol (2)						
$\Delta\eta$ (mPa.s)	303.15	-0.0246	0.0343	-7.0×10^{-15}	3.0×10^{-14}	0.007
	313.15	-0.1026	0.0855	-1.0×10^{-14}	9.0×10^{-15}	0.14
V^E (cm ³ /mol)	303.15	-0.1209	0.2639	4.0×10^{-16}		0.27
	313.15	-0.1341	0.2823	4.0×10^{-16}		0.27
ΔG^{*E} (kJ/mol)	303.15	1.14	0.090			4.9
	313.15	0.91	0.277			3.5

parameter	temperature	A0	A1	A2	A3	σ
Pyridine (1) + <i>n</i> -Butanol (2)						
$\Delta\eta$ (mPa.s)	303.15	-0.0283	-0.1763	7×10^{-13}	-1×10^{-12}	0.63
	313.15	-0.01	-0.1374	9×10^{-13}	-1×10^{-12}	0.44
V^E (cm ³ /mol)	303.15	0.3431	-1.8606	7×10^{-12}	-4×10^{-12}	4.13
	313.15	0.3509	-1.8763	5×10^{-12}	-1×10^{-11}	4.14
ΔG^{*E} (kJ/mol)	303.15	1.20	-0.296	-1×10^{-10}	1×10^{-10}	3.52
	313.15	1.26	-0.288	-7×10^{-12}		3.42

4. CONCLUSION

The deviation in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow for the systems pyridine + *n*-propanol and pyridine + *n*-butanol at $T = 303.15$ & 313.15 K has been reported.



Plots of Excess molar volume (VE) against mole fraction for the system (a) Pyridine (1) + n-Propanol (2) (b) Pyridine (1) + n-Butanol (2) at different temperatures: ■, 303.15 K; ▲, 313.15 K; The solid line represents the corresponding correlation by the Redlich - Kister equation.

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