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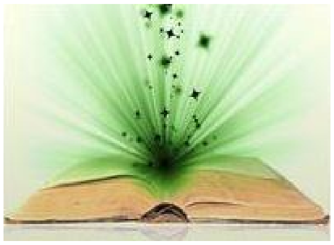

Viscosity, Density and Excess Molar Volume of Binary Mixtures of Methanol and Ethanol with p-anisaldehyde

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ABSTRACT

The density and viscosity of binary mixtures of methanol and ethanol with p—anisaldehyde were measured at 303.15 K and 313.15 K, using this data excess molar volume V^E*, Viscosition deviation* $\Delta\eta$ *and activation parameters* ΔG^*, ΔH^* *and* ΔS^* *have been calculated. The results were fitted by Redlich—Kister equation. All mixtures show negative values of* V^E *due to interactions between unlike molecules or very large difference in the molar volumes of pure components at relatively low temperature.*

Keywords: Density; Viscosity; Redlich—Kister; Excess parameters.

INTRODUCTION

The density (ρ) and viscosity (η) measurements find wide applications in characterising the physico—chemical behaviour of liquid mixtures[1] and in the study of molecular interactions. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters and their excess values with compositions gives an insight into the molecular process.[2] The investigations regarding the molecular association in organic binary mixtures having 1—alkanol group as one of the components is of the particular interest, since 1—alkanol group is highly polar and can associates with any other group having some degree of polar attractions. P—anisaldehyde is aprotic, strongly associated due to highly polar C=0 group in the molecule and large dipole moment (B).

In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixture of methanol and ethanol with p—anisaldehyde respectively at 303.15 K and 303.15 K. Further the excess functions are used to explain intermolecular interactions in these binary mixtures.

MATERIALS AND METHODS

Source and purity of sample: All the chemicals used in the present research work are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9 % obtained from Himedia and Spectrochem which are used as such without further purification The purities of the above chemicals were checked by density determination at 303.15 K and 303.15 K.

Method: The uncertainty is less than ± 1 x 10^{-4} g cm^{-3}. The binary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density and viscosity were measured as a function of composition of the binary liquid mixtures of methanol and ethanol with p—anisaldehyde respectively at 303.15 K and 303.15 K.

The density was determined using a Bicapillary Pycnometer. All measurement of mass was performed on an electronic digital balance with an accuracy of ± 0.1 mg. The Pycnometer was calibrated with triple distilled water. Measurement of the dynamic viscosity (η) were obtained with a modified suspended level Ubbelohde viscometer. The viscometer was submerged in a thermostatic bath at 303.15 K and 303.15 K with equilibrium for the content of viscometer was 3 min. The flow time was measured with stopwatch to an accuracy of ± 0.01 s. The viscometer was calibrated separately with water, benzene and toluene[3,4]. The reproducibility in the viscosity measurements was 0.004 mPaS. Four—five sets of readings for the flow times were taken for each pure liquid or liquid mixtures and arithmetic mean was considered for the calculations.

Theory and Calculations: Excess molar volume V^E were calculated from the density measurement by the relationships as follows:

$$V^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho} - (x_1 V_1 + x_2 V_2) \quad \text{--- (1)}$$

Dynamic viscosities (η) of methanol and ethanol with p—anisaldehyde mixtures at different temperatures were calculated by the measuring density and flow time of the mixture (Table 1 and Table 2).

Table 1: Values of density, viscosity and excess properties of binary liquid mixture of methanol and p-anisaldehyde at 303.15 and 313.15 K.

Temp (K)	X_1	ρ (gm/cm^3)	η (mPaS)	V^E (m^3 mol^{-1})	Δη (mPaS)
303.15	0.0000	1.1111	3.6307	0.0000	0.0000
	0.1227	1.1024	3.0673	-0.6207	-0.1804
	0.2453	1.0921	2.5722	-1.2508	-0.2928
	0.3312	1.0814	2.2440	-1.5163	-0.3529
	0.4171	1.0669	1.9614	-1.6168	-0.3674
	0.5090	1.0463	1.6882	-1.5535	-0.3538
	0.6600	1.0008	1.2905	-1.3403	-0.2801
	0.7481	0.9654	1.0732	-1.1865	-0.2225
	0.8101	0.9348	0.9190	-1.0551	-0.1831
	0.9185	0.8614	0.6546	-0.5961	-0.1092
	0.9625	0.8221	0.5633	-0.3312	-0.0631
	1.0000	0.7815	0.5094	0.0000	0.0000

Temp (K)	X_1	ρ (gm/cm^3)	η (mPaS)	V^E (m^3 mol^{-1})	Δη (mPaS)
313.15	0.0000	1.1024	2.8504	0.0000	0.0000
	0.1227	1.0934	2.3974	-0.6057	-0.1571
	0.2453	1.0828	2.0015	-1.2328	-0.2574
	0.3312	1.0719	1.7430	-1.4953	-0.3088

	0.4171	1.0571	1.5263	-1.5868	-0.3184
	0.5090	1.0363	1.3133	-1.5235	-0.3098
	0.6600	0.9907	1.0131	-1.3173	-0.2459
	0.7481	0.9553	0.8541	-1.1684	-0.1925
	0.8101	0.9243	0.7397	-1.0263	-0.1574
	0.9185	0.8512	0.5448	-0.5814	-0.0909
	0.9625	0.8121	0.4805	-0.3212	-0.0491
	1.0000	0.7719	0.4392	0.0000	0.0000

Table 2: Values of density, viscosity and excess properties of binary liquid mixture of ethanol and p-anisaldehyde at 303.15 and 313.15 K

Temp (K)	**X_1**	**ρ (gm/cm^3)**	**η (mPaS)**	**V^E (m^3 mol^{-1})**	**Δη (mPaS)**
303.15	0.0000	1.1111	3.6307	0.0000	0.000
	0.0935	1.0884	2.9224	-0.3067	-0.1232
	0.1869	1.0774	2.6763	-0.6305	-0.2144
	0.3322	1.0652	2.4323	-1.0222	-0.3205
	0.4630	1.0365	2.0694	-1.1234	-0.3377
	0.5799	1.0034	1.7791	-1.0743	-0.3191
	0.6569	0.9765	1.6227	-0.9602	-0.2720
	0.7464	0.9394	1.4477	-0.7859	-0.2105
	0.8324	0.8965	1.2719	-0.5882	-0.1590
	0.8877	0.8641	1.1836	-0.4357	-0.1022
	0.9454	0.8239	1.0752	-0.1991	-0.0571
	1.000	0.7809	0.9880	0.0000	0.0000

The viscosity deviation was calculated [10—11] by

$$\Delta\eta = \eta - \{x_1 \eta_1 + x_2 h_2\} \qquad \text{--- (2)}$$

The activation parameters ΔG^*, ΔH^* and ΔS^* were determined. Using Erying and John's equation —

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right) \qquad \text{--- (3)}$$

where η — is viscosity of mixture, h, N and V are Planck's Constant, Avogadros number and molar volume respectively.

When ln(ηv/hN) is plotted against 1/J, the slope is equal to $\Delta H^*/R$ and intercept is equal to — $\Delta S^*/R$. Using both graphical and least squares method, the activation parameters ΔH^* and ΔS^* were obtained and ΔG^* was obtained. Using the equation $\Delta G^* = \Delta H^* - T\Delta S^*$ values obtained are presented in Table 3 and Table 4.

Table 3: The activation parameters ΔG*, ΔH* and ΔS* of Methanol + p-anisaldehyde mixture at 303.15 K and 313.15 K

X_1	**$\Delta H^* \times 10^{-3}$ (J mol^{-1})**	**— ΔS (JK^{-1} mol^{-1})**	**$\Delta G^* \times 10^{-3}$ (J mol^{-1})**	
			303.15 K	**(J mol^{-1})**
0.0000	20097.045	163.352	0.0000	0.0000
0.1227	21358.186	157.974	69248.215	70827.962
0.2453	23435.987	148.664	68503.681	69990.328
0.3312	24668.206	142.797	67957.285	69385.261
0.4171	25417.669	138.550	67419.352	68804.860
0.5090	26638.961	132.469	66797.228	68121.928
0.6600	27272.537	126.669	65672.290	66938.982

0.7481	26509.921	126.666	64908.929	66175.596
0.8101	24382.822	131.984	94393.486	65713.326
0.9185	18660.100	146.777	63155.724	64623.499
0.9625	14917.914	156.598	62390.830	63956.817
1.0000	3762.457	190.744	61586.562	63494004

Table 4: The activation parameters ΔG^*, ΔH^* and ΔS^* of Ethanol + p-anisaldehyde mixture at 303.15 K and 313.15 K

X_1	**ΔH^* x 10^{-3} ($J\ mol^{-1}$)**	**— ΔS ($JK^{-1}\ mol^{-1}$)**	**ΔG^* x 10^{-3} ($J\ mol^{-1}$)**	
			303.15 K	**($J\ mol^{-1}$)**
0.0000	0.000	0.0000	0.0000	0.0000
0.1869	16955.928	171.695	69005.357	70722.309
0.2596	15985.615	173.663	68631.852	70368.492
0.3322	14523.955	173.908	68243.444	69982.525
0.4630	14527.955	174.920	67555.180	69304.388
0.5799	14670.656	172.387	66930.065	68653.944
0.6569	14467.666	171.652	66504.219	68220.747
0.7464	14636.355	169.370	65981.101	67674.808
0.8324	15023.703	166.115	65381.702	67042.859
0.8877	14394.121	166.828	64968.240	66636.527
0.9454	13945.904	166.463	64409.463	66074.103
1.000	13986.142	164.371	63815.489	65459.208

The excess molar volume V^E were correlated by Redlich—Kister[14] as

$$V^E = x_1 x_2 \sum A_i \left(x_1 - x_2\right)^i \qquad \text{--- (4)}$$

In each case the optimum number of coefficients A_i was determined from an examination of the variation of standard deviation as calculated by:

$$\sigma\,(V^E) = \left[\sum \frac{\left(V^E_{obs} - V^E_{cal}\right)}{(n-m)}\right]^{1/2} \qquad \text{--- (5)}$$

where n represents the number of experimental points and
m represents the number of coefficients in fitting the data.

RESULTS AND DISCUSSION

In their pure state, the self association of alkanols decreases with increasing chain length, when alkanols are mixed with p-anisaldehyde then there is interaction between their individual functional groups (- OH and - CHO). The presence of electron withdrawing group on benzene ring decreases its electron densities. The polarity of alkanol is less hence there degree of self association is less as compared to p-anisaldehyde. The experimental values of density, viscosity, excess volume and viscosity deviation are presented in Table 1 and Table 2. The graphical variation of excess molar volume (V^E) for the binary mixture of methanol and ethanol with p-anisaldehyde at 303.15 K and 313.15 K is shown in the Fig. 1 and Fig. 2. The sign and magnitude of V^E gives a good estimate to the strength of unlike molecular interactions in the solution phase. Positive V^E indicates the weak interactions, whereas, large negative values of V^E are found, when these interactions are strong.[5,6] In the present investigation, the values of excess molar volumes are found to be negative indicating strong hydrogen bonding interaction for the entire mole fraction of methanol and ethanol. Maximum deviation in excess molar volume occurs at 0.4 - 0.5 mole fraction. The increase in V^E with increasing chain length of alkanol implies that dipole-dipole interactions are weak.

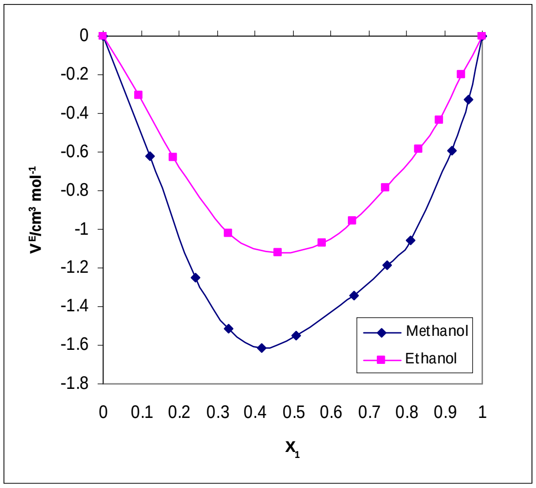

Fig. 1 : Excess molar volume verses mole fraction for binary system of methanol (1) and ethanol (1) with p-anisaldehyde at 303.15 K

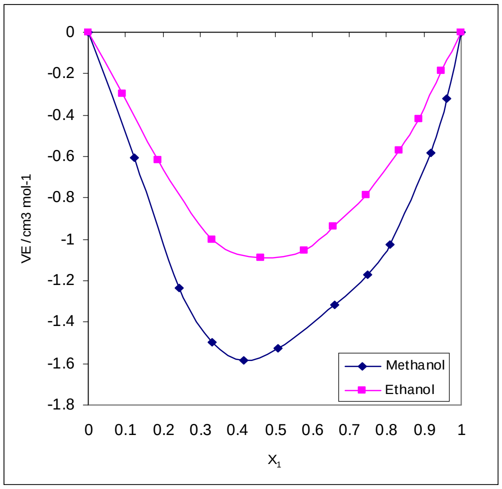

Fig. 2 : Excess molar volume verses mole fraction for binary system of methanol (1) and ethanol (1) with p-anilaldehyde at 313.15 K

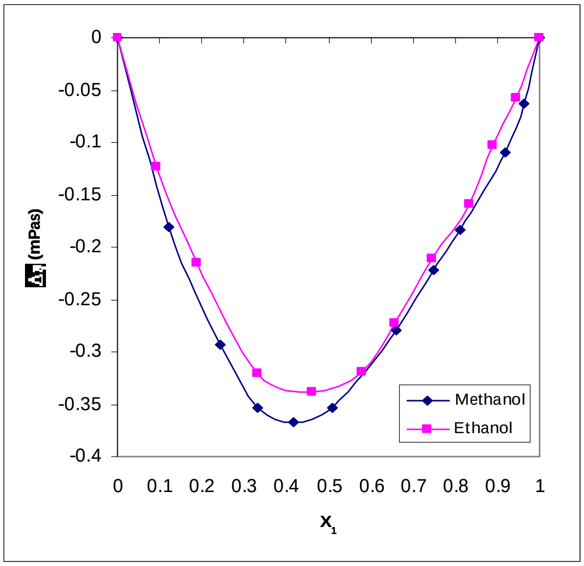

Fig 3 : Viscosity deviation vs mole fractions for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 303.15 K

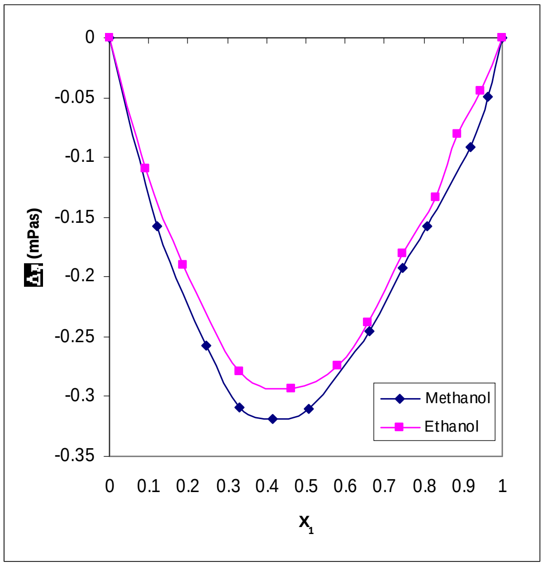

Fig 4 : Viscosity deviation vs mole fractions for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 313.15 K

It is seen from Fig. 3 and Fig. 4 that, the curves for Δη values are negative over the entire mole fraction of methanol and ethanol at 303.15 and 313.15 K temperatures these curves are 'U' - shaped with minimum at X1 = 0.4 - 0.5 mole fraction. These excess parameters at a particular mole fraction of methanol and ethanol becomes less negative with increase of temperature. The negative Δη may be attribute to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the molecules[7]. Increase of temperature disturb hereto and homo-association of the molecules which increases fluidity of the liquid. Values of Δη are more at higher temperature provide additional evidence for the existence of interactions of weak magnitude like dipole-induced dipole type between components of liquid mixtures. [8.9].

The magnitude of Δη, the sign and extent of deviation of this property from ideality depends on the strength of interaction between unlike molecules. According to Fort et al, the excess viscosity gives the strength of the molecular interaction between interacting molecules, the large negative values of excess viscosity for all the systems can be attributed to the presence of the dispersion, induction and dipolar forces between the components [10,11]. It is found that, for the solution of the fifth degree, polynomial, the agreement between the experimental values and calculated ones is satisfactory. The derived parameters A0, A1, A2, A3, A4 and σ are presented in Table 5 and 6[12].

Table 5: The binary coefficient of Redlich-Kister equation and the corresponding standard deviations (σ) for the binary mixtures at 303.15 K

Binary System	**Function**	**Binary Coefficient**					
		A_0	**A_1**	**A_2**	**A_3**	**A_4**	**σ**
Methanol + p— Anisaldehyde	**V^E**	**-5.9720**	**-0.47165**	**-4.11584**	**-0.16034**	**0.179424**	**0.100052**
	$\Delta\eta$	-217.33	-69.7508	51.79812	0.040929	-0.956	1.746143
Ethanol + p— Anisaldehyde	V^E	-8.0484	2.380502	-1.25647	0.0452994	-8.04848	2.380502
	$\Delta\eta$	-131.37	-24.4081	3.245355	-2.28418	3.694108	1.208577

Table 6: The binary coefficient of Redlich-Kister equation and the corresponding standard deviations (s) for the binary mixtures at 313.15 K

Binary System	**Function**	**Binary Coefficient**					
		A_0	**A_1**	**A_2**	**A_3**	**A_4**	**σ**
Methanol + p-Anisaldehyde	V^E	-5.9095	-0.5042	-3.88304	-0.14941	0.166098	0.092894
	$\Delta\eta$	-204.43	-65.3429	81.16991	2.728758	-3.52865	2.494518
Ethanol + p-Anisaldehyde	V^E	-8.1971	2.425324	-1.2068	-0.02361	0.10384	0.060086
	$\Delta\eta$	-115.40	-26.4202	10.99061	-1.02258	1.680671	0.719638

A good agreement was found in between Redlich—Kister parameters the solution of the fifth degree polynomial obtained with V^E and $\Delta\eta$.The observed values of ΔH^* and ΔG^* for the binary mixture are positive as shown in Table 5 and 6. The ΔG^* and ΔH^* values steadily decreases with increase concentration of methanol and ethanol in p-anisaldehyde. The ΔH^* values increases steadily to mole fraction 0.660 of methanol and decreases[13,14].

APPLICATIONS

The results are useful in calculating several thermodynamics excess functions and in the studies to explain the intermolecular interactions between mixing components.

CONCLUSIONS

This paper reports experimental data for density, and viscosity at 303.15 K and 313.15 K for binary mixture of methanol + p-anisaldehyde and ethanol + p-anisaldehyde. From these data, several thermodynamics excess functions have been calculated and studied to explain the intermolecular interactions between mixing components. Very large negative deviations are observed for both the investigated binary systems. This reveals that the existence of molecular interactions in the binary mixtures. The present investigation shows that greater molecular interaction exists in methanol mixtures which may be due to hydrogen bond formation and weak molecular interaction that exists in the ethanol mixtures which may be due to dominance of dispersion forces and dipolar interaction between unlike molecules. The interaction tends to be weaker with rise in temperature which may be due to weak intermolecular forces and thermal dispersion forces. The existence of molecular interaction in the mixture is in the order: methanol > ethanol[13,14].

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