JSR Publications

Available Online

J. Sci. Res. **17** (3), 937-949 (2025)

JOURNAL OF SCIENTIFIC RESEARCH

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Volumetric and Viscometric Studies of Binary Mixtures of Ethyl Acetate with n-Propanol and 2-Propanol at T= (303.15, 308.15, 313.15, and 318.15) K under Atmospheric Pressure

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Received 2 February 2025, accepted in final revised form 5 June 2025

Abstract

In this study, densities and viscosities of binary mixtures formed by ethyl acetate with n-propanol and 2-propanol have been measured over the entire range of composition at T = (303.15, 308.15, 313.15, and 318.15) K under atmospheric pressure. Excess molar volume, V^E, deviation in viscosity, η^E and excess Gibb's free energy of activation of viscous flow, $\Delta G^{\ddagger E}$ have been calculated from experimental density and viscosity data. The computed excess functions have been fitted to Redlich-Kister polynomial equation. The observed values of excess properties for both the systems have been interpreted in terms of molecular interaction in the mixtures. Results show that for both mixtures, the chemical or specific interactions between ethyl acetate and alcohol molecules are absent, and dispersion type forces are predominant.

Keywords: Binary liquid mixture; Excess molar volume; Viscosity; Dispersion forces.

doi: https://dx.doi.org/10.3329/jsr.v17i3.79608 J. Sci. Res. **17** (3), 937-949 (2025)

1. Introduction

Organic solvents are widely used in chemistry and chemical engineering. In industrial and chemical processes, liquid mixtures are profusely used more than individual pure liquids as they produce a wide range of solvents with variable physical properties. On mixing two different solvents, the unique behavior of a binary mixture, compared to its constituent components, is believed to arise from the nature of solute-solvent interactions. Because of diverse applications, investigating molecular interactions in binary solvent mixtures is of significant implication and interest to both chemists and chemical engineers. A considerable amount of theoretical and experimental studies has been done on pure liquid and liquid

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mixtures at different temperatures to improve our understanding of intermolecular interactions between the component molecules of liquids and their state of disorder.

The investigation of the changes in thermodynamic properties of liquid mixtures and their extent of deviation from ideal behavior has established a solid qualitative and quantitative way to obtain information about intermolecular interactions in liquid mixtures. The volumetric and viscometric properties obtained from measurements of densities, ρ and viscosities, η for the binary and ternary mixtures are useful to elucidate the nature and type of intermolecular interactions present between the component molecules [1-4]. The nature of molecular interactions in binary liquid mixtures can be well understood in terms of excess thermodynamic functions such as excess molar volume, deviation in viscosity, and excess free energy of activation of viscous flow [5-7]. These thermodynamic functions measure the contribution of interactions between two components in a binary mixture. Thus, the changes of these excess functions with composition and temperature can be used to explain the nature of molecular interactions between the component molecules of the mixtures.

The present studies deal with the densities and viscosities of mixtures of ethyl acetate with n-propanol and 2-propanol over whole composition range at T = (303.15, 308.15, 313.15, and 318.15) K under atmospheric pressure. The mixtures of alcohol and ester are of prime interest from a theoretical aspect because in the mixing process, the breaking of hydrogen-bonded structures of the alcohol is likely to occur, and the formation of new H-bonded molecular species may occur between the alcohol and the ester [8]. We report here the excess molar volume, V^E, deviation in viscosity, η^E, and excess Gibb's free energy of activation, $\Delta G^{\ddagger E}$ of viscous flow over the whole range of composition at T = (303.15, 308.15, 313.15, and 318.15) K. The excess thermodynamic functions have been fitted to Redlich-Kister polynomial equation to find fitting coefficients and standard deviation.

2. Experimental

Solvents used in this work were of analytical grade and obtained from BDH Limited with quoted purity, ethyl acetate (EtOAc) 99.5 %, n-propanol (n-PrOH) 99.5 %, and 2-propanol (2-PrOH) 99.8 %. All these solvents were used without further purification. The purity was ascertained by comparing the measured values of densities and viscosities of pure solvents with literature values [8,9-14] which shows reasonable agreement (Table 1). The binary mixtures of liquids of different compositions were prepared by mass using an analytical balance (METTLER PM 200) with an accuracy of ± 0.0001g. Precautions were taken to minimize the evaporation losses, and the error in the mole fraction is estimated to be ± 0.001.

Densities of the pure components and their mixtures were measured using a 25 cm^3 specific gravity bottle. The specific gravity bottle was calibrated with redistilled water. An Ostwald viscometer with a sufficiently long efflux time was used in viscosity measurements. The viscometer was calibrated with double distilled water using density and viscosity values from the literature [14]. An electronic digital stopwatch accurate up to ± 0.01 s was used for the measurement of flow time. The same analytical balance (METTLER PM 200) was used in the density measurements. A thermostatic water bath of accuracy ±

0.05 °C was used to control the temperature for every measurement. All the measurements were conducted in triplicate and averaged for calculations. The overall uncertainty in density and viscosity measurements was found to be ± 0.001 g cm^{-3} and ±0.003 cP, respectively.

The experimental data on densities have been used to estimate the excess molar volume, V^E for the mixtures of different mole fractions using the following equation [15],

$$V^E = (x_1M_1 + x_2M_2)/\rho - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (1)$$

Where ρ is the density of the mixture, x_1, x_2, M_1, M_2, ρ_1, and ρ_2 are mole fractions, molecular weights, and densities of the pure components 1 and 2, respectively.

The deviation in viscosity, η^E of the binary liquid mixture was calculated from the experimental viscosity of the mixture and that of its pure component using the following relation [16],

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

Where η is the measured viscosity of the binary mixture, η_1 and η_2 are the viscosities of pure components 1 and 2 having mole fractions x_1 and x_2, respectively.

The excess Gibb's free energy of activation of viscous flow, $\Delta G^{\ddagger E}$ for the binary liquid mixture was computed from the Eyring equation [17],

$$\Delta G^{\ddagger E} = RT[ln(\eta V) - x_1 ln\eta_1 V_1 - x_2 ln\eta_2 V_2] \quad (3)$$

Where V is the molar volume of the binary liquid mixture, V_1 is the molar volume of the pure component 1, and V_2 is the molar volume of the pure component 2 present in the mixture having mole fractions x_1 and x_2, respectively. The molar volumes, V of the binary liquid mixture were calculated from the measured densities, ρ of the mixture using the following equation,

$$V=(x_1M_1+x_2M_2)/\rho \quad (4)$$

All the excess functions, V^E, η^E and $\Delta G^{\ddagger E}$ were fitted to the Redlich-Kister (R. K) polynomial equation [18],

$$Y^E = x_1x_2\sum_i^n A_i(x_2 - x_1)^i \quad (5)$$

Where Y^E refers to excess parameters V^E or, η^E or $\Delta G^{\#E}$ and x_1 and x_2 are the mole fractions of the components in the mixture, n is the degree of polynomial, A_i is the fitting coefficients of the polynomial equation. The values of coefficient A_i were determined by a multiple regression analysis based on the least-square method along with the standard deviation. The corresponding standard deviation (σ) has been calculated using the following relation,

$$\sigma(Y^E) = [\sum(Y^E_{obs} - Y^E_{cal})^2/(n-m)]^{1/2} \quad (6)$$

Where n is the total number of experimental points, m is the number of coefficients, Y_{obs} and Y_{cal} are the observed and calculated parameters, respectively.

Table 1. Comparison of experimental densities and viscosities of pure liquids with literature values.

Compounds	T/K	10^{-3}. ρ/kgm^{-3}		η/mPa.s	
		Experimental	Literature	Experimental	Literature
Ethyl Acetate	303.15	0.8883	0.8885[20]	0.3936	0.403[20]
	308.15	0.8825	0.8822[21]	0.3733	0.3853[21]
	313.15	0.8760	0.8759[21]	0.3533	0.3664[21]
	318.15	0.8698	0.8699[22]	0.3345	0.346[3]
n-Propanol	303.15	0.7963	0.7962[23]	1.7026	1.7352[21]

	308.15	0.7921	0.7922[23]	1.5116	1.5473[21]
	313.15	0.7879	0.7879[23]	1.3541	1.3848[21]
	318.15	0.7837	0.7842[23]	1.2166	1.2413[21]
2 -Propanol	303.15	0.7778	0.7768[24]	1.7196	1.7240[25]
	308.15	0.7749	0.7724[24]	1.5398	1.5404[24]
	313.15	0.7680	0.7679[24]	1.3454	1.3474[24]
	318.15	0.7651	0.7634[24]	1.1758	1.1784[24]

3. Results and Discussion

Experimental data on densities, viscosities, and the calculated values of excess molar volume, V^E, deviation in viscosity, η^E, and excess free energy of activation of viscous flow, $\Delta G^{\ddagger E}$ for the binary EtOAc + n-PrOH and EtOAc + 2-PrOH liquid systems at T = (303.15, 308.15, 313.15 and 318.15) K as a function of the composition of binary mixtures are shown in Tables 2, 3 and 4. Excess thermodynamic functions provide the extent of deviation of a liquid mixture from its ideal behavior and are found to be completely sensitive to the molecular interactions between the component molecules of liquid mixtures. The strength of interaction between component molecules depends on the sign and magnitude of these excess functions.

Table 2. Densities, ρ and viscosities, η of ethyl acetate (x_1) + n-propanol (x_2) and ethyl acetate (x_1) + 2-propanol (x_2) at different temperatures under atmospheric pressure.

	10^{-3}. ρ/kgm^{-3} at T/K				η/mPa.s at T/K			
ethyl acetate + n-propanol								
x_2	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0000	0.8883	0.8825	0.8760	0.8698	0.3936	0.3733	0.3533	0.3345
0.1160	0.8788	0.8729	0.8665	0.8602	0.4212	0.3967	0.3730	0.3584
0.2079	0.8710	0.8652	0.8589	0.8527	0.4375	0.4192	0.3958	0.3802
0.2825	0.8647	0.8590	0.8528	0.8468	0.4650	0.4375	0.4155	0.3943
0.3962	0.8549	0.8494	0.8434	0.8376	0.5111	0.4783	0.4479	0.4230
0.4961	0.8460	0.8407	0.8349	0.8293	0.5636	0.5245	0.4878	0.4576
0.5938	0.8375	0.8323	0.8263	0.8209	0.6548	0.6089	0.5666	0.5284
0.6808	0.8288	0.8237	0.8184	0.8132	0.7554	0.7061	0.6411	0.5931
0.7778	0.8193	0.8144	0.8092	0.8043	0.8819	0.8202	0.7447	0.6850
0.9131	0.8054	0.8007	0.7960	0.7915	1.2536	1.1415	1.0332	0.9404
1.0000	0.7963	0.7921	0.7879	0.7837	1.7026	1.5116	1.3541	1.2166
ethyl acetate + 2-propanol								
x_2	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0000	0.8883	0.8825	0.8760	0.8698	0.3936	0.3733	0.3533	0.3345
0.1139	0.8769	0.8710	0.8637	0.8569	0.4288	0.4060	0.3822	0.3603
0.2044	0.8675	0.8617	0.8540	0.8475	0.4669	0.4404	0.4196	0.3837
0.3102	0.8562	0.8503	0.8428	0.8369	0.4857	0.4549	0.4253	0.4003
0.3911	0.8475	0.8418	0.8345	0.8280	0.4913	0.4588	0.4300	0.4042
0.4907	0.8368	0.8318	0.8241	0.8188	0.5376	0.4998	0.4644	0.4357
0.5623	0.8295	0.8247	0.8170	0.8116	0.6008	0.5504	0.5168	0.4799
0.6921	0.8169	0.8122	0.8043	0.7991	0.7429	0.6754	0.6279	0.5770
0.7825	0.8080	0.8043	0.7969	0.7930	0.8695	0.7840	0.7386	0.6699
0.8999	0.7939	0.7903	0.7830	0.7794	1.1716	1.0899	0.9698	0.8715

1.0000	0.7773	0.7749	0.7680	0.7651	1.7196	1.5398	1.3454	1.1758

Table 3. Excess molar volume, V^E and deviation in viscosities, η^E of ethyl acetate (x_1) + n-propanol (x_2) and ethyl acetate (x_1) + 2-propanol (x_2) at different temperatures under atmospheric pressure.

	$10^6.V_m^E$/ m^3mol^{-1} at T/K				η^E/mPa.sat T/K			
ethyl acetate + n-propanol								
x_2	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0000
0.1160	0.126	0.156	0.171	0.208	-0.124	-0.109	-0.096	-0.078
0.2079	0.215	0.249	0.275	0.319	-0.228	-0.191	-0.166	-0.138
0.2825	0.256	0.290	0.323	0.360	-0.298	-0.257	-0.221	-0.189
0.3962	0.290	0.321	0.359	0.396	-0.401	-0.346	-0.302	-0.261
0.4961	0.299	0.325	0.365	0.401	-0.479	-0.414	-0.362	-0.315
0.5938	0.285	0.316	0.352	0.388	-0.516	-0.440	-0.380	-0.329
0.6808	0.258	0.293	0.324	0.357	-0.529	-0.442	-0.394	-0.342
0.7778	0.208	0.239	0.283	0.305	-0.530	-0.439	-0.387	-0.336
0.9131	0.109	0.142	0.170	0.181	-0.335	-0.271	-0.234	-0.199
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0000
ethyl acetate + 2-propanol								
x_2	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000
0.1139	0.143	0.194	0.281	0.392	-0.116	-0.100	-0.084	-0.070
0.2044	0.249	0.321	0.451	0.559	-0.198	-0.171	-0.137	-0.123
0.3102	0.355	0.475	0.579	0.656	-0.319	-0.280	-0.236	-0.195
0.3911	0.403	0.529	0.607	0.689	-0.421	-0.371	-0.311	-0.259
0.4907	0.411	0.510	0.622	0.685	-0.507	-0.444	-0.376	-0.312
0.5623	0.342	0.429	0.540	0.649	-0.538	-0.479	-0.394	-0.336
0.6921	0.075	0.196	0.316	0.446	-0.568	-0.505	-0.412	-0.346
0.7825	-0.155	-0.107	-0.049	-0.031	-0.562	-0.502	-0.391	-0.327
0.8999	-0.274	-0.194	-0.153	-0.121	-0.415	-0.333	-0.276	-0.222
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4. Excess Gibb's free energy of activation of viscous flow, ΔG^{*E} of ethyl acetate (x_1) + n-propanol (x_2) and ethyl acetate (x_1) + 2-propanol (x_2) at different temperatures under atmospheric pressure.

ΔG^{*E} /kJ mol^{-1} at T/K				
ethyl acetate + n-propanol				
x_2	303.15	308.15	313.15	318.15
0.0000	0.000	0.000	0.000	0.000
0.1160	-0.2449	-0.2464	-0.2504	-0.1993
0.2079	-0.4803	-0.4261	-0.4083	-0.3467
0.2825	-0.5976	-0.5787	-0.5377	-0.5000
0.3962	-0.8251	-0.7527	-0.7345	-0.6969
0.4961	-0.8942	-0.8739	-0.8599	-0.8280
0.5938	-0.8788	-0.8424	-0.8123	-0.7819
0.6808	-0.8408	-0.7758	-0.7977	-0.7761
0.7778	-0.8141	-0.7450	-0.7522	-0.7320
0.9131	-0.4393	-0.4191	-0.3972	-0.3695
1.0000	0.0000	0.0000	0.0000	0.0000
ethyl acetate + 2-propanol				
x_2	303.15	308.15	313.15	318.15

0.0000	0.000	0.000	0.000	0.000
0.1139	-0.1963	-0.1855	-0.1766	-0.1638
0.2044	-0.3104	-0.2399	-0.2388	-0.2882
0.3102	-0.5968	-0.5895	-0.5640	-0.5203
0.3911	-0.8651	-0.8576	-0.8136	-0.7580
0.4907	-1.0066	-0.9992	-0.9583	-0.8912
0.5623	-0.9944	-0.9676	-0.9309	-0.8745
0.6921	-0.9517	-0.9796	-0.8846	-0.8265
0.7825	-0.9013	-0.9288	-0.7911	-0.7504
0.8999	-0.5962	-0.5204	-0.5008	-0.4497
1.0000	0.000	0.000	0.000	0.000

3.1. *Excess molar volume*

Variation of excess molar volumes, V^E of EtOAc + *n*-PrOH and EtOAc + 2-PrOH systems as a function of mole fraction of alcohols at different experimental temperatures are shown in Figs. 1 and 2. An inspection of the figures reveals that V^E of the binary mixture of EtOAc + n-PrOH are positive over the whole range of composition. The V^E values increase with the increase in the mole fraction of n-propanol and show a maximum at around $x_2 = 0.5$ (Fig. 1). For the EtOAc +2-PrOH system, the V^E values are positive up to the mole fraction of 2-propanol, $x_2 \approx 0.7$ beyond that the values become negative for the system (Fig. 2). The data in Table 3 show that V^E for EtOAc + n-PrOH is higher than that of EtOAc + 2-PrOH system in the ethyl acetate-rich region. The effect of temperature for both these systems is almost the same, and V^E values become more positive with the increase of temperature i.e., $\partial V^E/\partial T$ is positive over the whole range of concentration.

The observed values of V^E can be explained by physical, chemical, and geometrical contributions of component molecules in the mixtures. Chemical or specific interactions induce the volume reduction leading to negative V^E and these interactions comprise the formation of hydrogen bonds and other complex-forming interactions. Physical interactions involve predominantly dispersion forces that make a positive contribution to V^E. Structural contribution arising from the geometrical fitting of one component into others because of differences in the molar volume of component molecules, and free volume between them leads to a negative contribution to V^E. Alcohols are strongly associated through hydrogen bonding and tend to dissociate from aggregates in the presence of organic molecules or form H-bonds with them in the mixtures. Ethyl acetate is also a polar compound, and it acts as hydrogen bond acceptor. Consequently, there is a possibility of intermolecular interactions of ethyl acetate with alcohols in the mixtures. A positive or negative deviation from the ideal behavior of a mixture may thus be observed for a system containing alcohol, depending on the predominance of these two types of interactions.

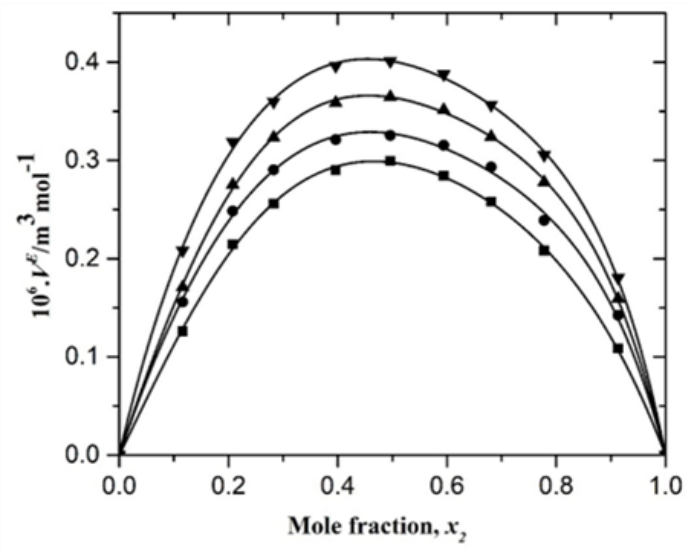

Fig. 1. V^E of binary system of ethyl acetate + n-propanol as a function of mole fraction of n-propanol at T= (■, 303.15; ●, 308.15; ▲, 313.15; and ▼, 318.15) K. The solid lines represent fitting to R.K. equation.

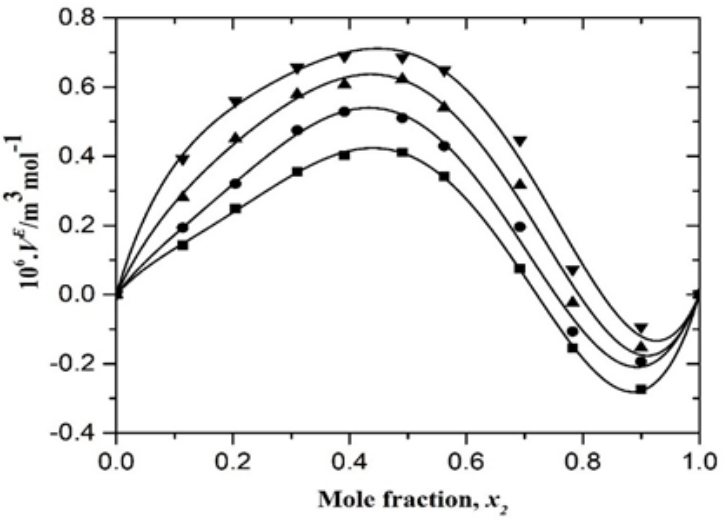

Fig. 2. V^E of binary system of ethyl acetate + 2-propanol as a function of mole fraction of 2-propanol at T= (■, 303.15; ●, 308.15; ▲, 313.15; and ▼, 318.15) K. The solid lines represent fitting to R.K. equation.

In the present work, for EtOAc + n-propanol binary system, the presence of chemical or specific interactions is found to be absent at all temperatures, and dispersion type of forces are predominant in these mixtures as indicated by the observed positive values of V^E. The

positive values of V^E for this system are expected to arise due to the breaking of hydrogen bonds in the self-associated n-propanol molecules in the presence of ethyl acetate. Dipole-dipole interaction between the component molecules may be another possibility to interact. The dipole moment of ethyl acetate (1.78 D) is higher than n-propanol (1.68 D). It is expected that the interactions between the ethyl acetate molecules are stronger than those with n-propanol molecules. This will exert a positive influence on V^E. Thus, for EtOAc + n-PrOH system, the positive values of V^E indicate that the effect of breaking of H-bonds in alcohol and dipole-dipole interactions between ethyl acetate molecules induce the volume expansion of the mixtures leading to positive values of V^E. In the case of EtOAc + 2-PrOH the main contribution to the volume expansion is due to (i) dissociation of associated alcohol in the solution system, particularly in the ethyl acetate-rich region, and (ii) steric hindrance exhibited by 2-PrOH, which significantly contribute towards volume expansion. The presence of branching in the alcohol molecules affects both hydrogen bonding as well as electron donor-acceptor interactions [19]. The steric effect thus causes a positive contribution to $V.^E$ On the other hand, the factors that are considered responsible for volume reduction in the alcohol-rich region may be due to donor-acceptor interaction between C=O group of ethyl acetate and hydroxyl hydrogen of alcohol. The negative values of V^E may also arise due to structural contribution arising from geometrical fitting (interstitial accommodation) of ethyl acetate, at least partially into the structural network of alcohol.

The positive values of V^E for EtOAc + 2-PrOH system is higher than that of EtOAc +2-PrOH system. The higher V^E values of EtOAc + 2-PrOH system than that of EtOAc + n-PrOH system in ethyl acetate-rich region indicate that dispersion type of interactions in the mixture and the steric hindrance exhibited by bulky isopropyl group, $(CH_3)_2CH$ of 2-PrOH might be predominant and responsible for the observed more positive values of V^E for EtOAc + 2-PrOH mixture i.e. EtOAc + 2-PrOH mixture is more non-ideal than EtOAc + n-PrOH system. The positive values of $\partial V^E/\partial T$ for both the systems are attributed to the rupture of H-bonds in self-associated alcohol and the reduction of dipolar interactions between the molecules of ethyl acetate.

3.2. *Deviation in viscosity*

The variation of deviation in viscosity, η^E of the binary mixtures of EtOAc + n-propanol and EtOAc + 2-propanol systems with mole fraction of n-propanol and 2-propanol at T = (303.15, 308.15, 313.15, and 318.15) K is shown in Figs. 3 and 4. The values of η^E for both systems are negative over the whole range of composition and temperature. η^E becomes more negative with the increase in the mole fraction of both n-propanol and 2-propanol. The ethyl acetate + n-propanol system shows a minimum at around x_2= 0.68 (Fig. 3), and ethyl acetate + 2-propanol system has a minimum almost at the same mole fraction (x_2 = 0.69) of 2-propanol (Fig. 4).

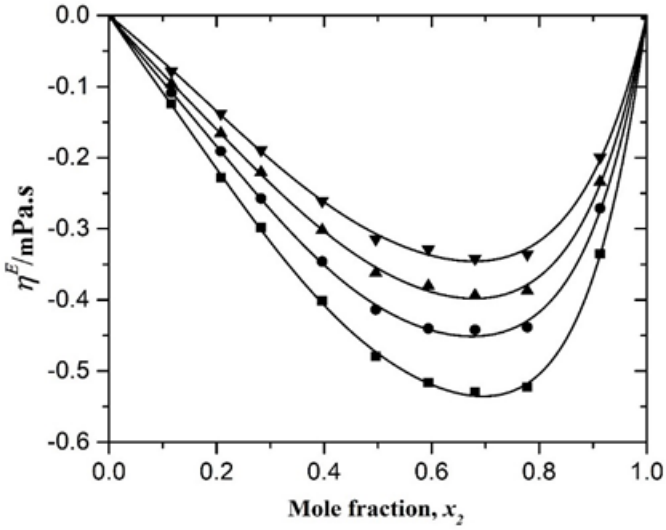

Fig. 3. η^E of the binary system of ethyl acetate + n-propanol as a function of mole fraction of n-propanol at T= (■, 303.15; ●, 308.15; ▲, 313.15; and ▼, 318.15) K. The solid lines represent fitting to R.K. equation.

Negative values of η^E for both binary mixtures of EtOAc + n-PrOH and EtOAc + 2-PrOH systems suggest that the viscosities of the mixtures are lower than the corresponding ideal state. It indicates that no specific interaction or weak interactions occur between the components of the mixtures, and some physical forces of attraction, such as dispersion forces, are predominant in the mixtures [20]. The negative value of η^E results from breaking of hydrogen bonds between the alcohol molecules in the presence of ethyl acetate and the reduction of dipole-dipole interactions between the ethyl acetate molecules upon the addition of increasing amount of alcohols. This quantitatively overcomes the viscosity increase exhibited by probable interstitial accommodation of ethyl acetate molecules into the hydrogen bonded alcohol network and the formation of new bonds. It is observed that the binary mixture of EtOAc with branched chain 2-PrOH has larger negative values of deviation in viscosity, η^E than with straight chain isomer n-PrOH. It implies that EtOAc + 2-PrOH system is more nonideal than EtOAc + n-PrOH system where dispersion forces are more dominant. It is expected that branched-chain alcohol (2-propanol) is less strongly associated than the straight-chain 1-propanol through hydrogen bonding due to steric hindrance and dissociates more easily into smaller units.

Further, it is observed that (Figs. 3 and 4) the magnitude of the negative values of excess viscosity, η^E decreases for both the EtOAc + n-PrOH and EtOAc + 2-PrOH systems with the increase of temperature. It indicates that the system tends to be ideal in behavior with the rise in temperature. An increase in temperature here disturbs the association of the component molecules increasing the fluidity of the mixtures.

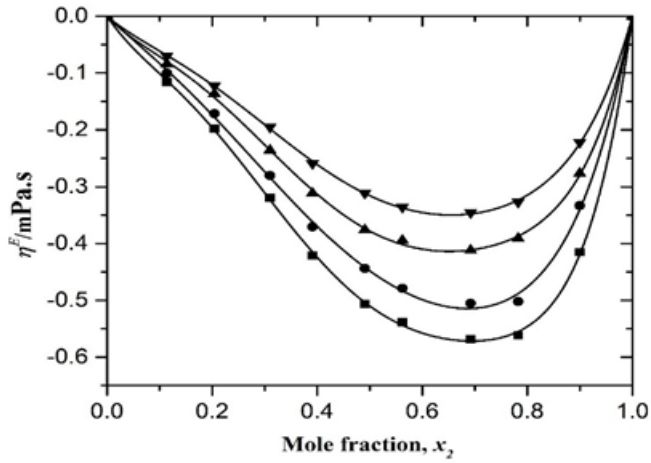

Fig. 4. η^E of binary system of ethyl acetate + 2-propanol as a function of mole fraction of 2-propanol at T= (■, 303.15; ●, 308.15; ▲, 313.15; and ▼, 318.15) K. The solid lines represent fitting to R.K. equation.

3.3. *Excess Gibb's free energy of activation of viscous flow*

The values of $\Delta G^{\ddagger E}$ for the binary systems EtOAc + n-PrOH and EtOAc + 2-PrOH have been plotted against the mole fractions, x_2 of n-propanol and 2-propanol at T = (303.15, 308.15, 313.15, and 318.15) K (Fig. 5). It is observed that $\Delta G^{\ddagger E}$ is negative for both systems for the whole range of composition and at all experimental temperatures. Both the curves show a minimum at around x_2= 0.5. In addition, the values of $\Delta G^{\ddagger E}$ for the EtOAc + 2-PrOH system are significantly larger than those obtained for EtOAc + n-PrOH system, except for $x_2 < 0.2$.

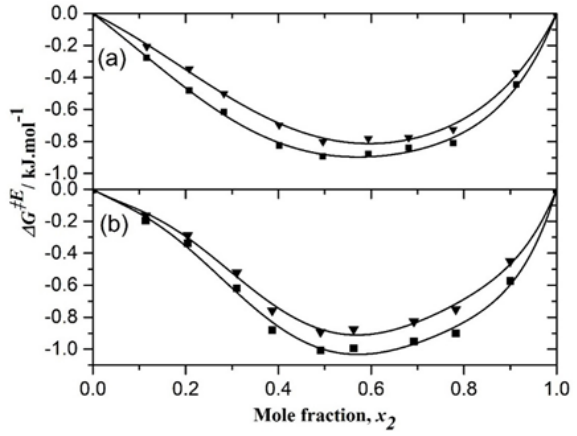

Fig. 5. Variation of $\Delta G^{\ddagger E}$ as a function of mole fraction of (a) n-propanol and (b)2-propanol at T= (■, 303.15; ▼, 318.15) K. To avoid the overlapping among curves, the lines were drawn only at two temperatures. The solid lines represent fitting to R.K. equation.

According to Houkhani *et al*. [21] $\Delta G^{\ddagger E}$ is considered a reliable measure to infer the presence of molecular interaction between the component molecules. Positive values of $\Delta G^{\ddagger E}$ are found in binary mixtures where specific interactions (hydrogen bonding) between the component molecules are prevalent, while the negative values of $\Delta G^{\ddagger E}$ indicate the dominance of dispersion forces. In the present work, the observed negative values of $\Delta G^{\ddagger E}$ for both the systems indicate the presence of weak interactions between the unlike molecules i.e., dispersion forces are dominant in the mixtures. The effect of temperature on the values of $\Delta G^{\ddagger E}$ seems to be significant. It is found that like η^E, the values of $\Delta G^{\ddagger E}$ appear to be less negative with the increase of temperature, indicating that the solutions tend to approach the ideal behavior with the rise of temperature. All the values of V^E, η^E and $\Delta G^{\ddagger E}$ have been fitted to Redlich-Kister type polynomial equation (eq. 6). The values of coefficients A_i of the equation and the corresponding standard deviation (σ) were obtained (eq. 7) using the least square regression method. The calculated values of A_i for V^E, η^E and $\Delta G^{\ddagger E}$ along with standard deviation (σ) are given in Tables 5.

Table 5. The coefficient of A_i of R.K Eq and standard deviation of fit, σ at T = (303.15, 308.15, 313.15 and 318.15) K under atmospheric pressure.

Parameters	Ethyl acetate + n-propanol			Ethyl acetate + 2-propanol		
	$10^6.V^E$/ m^3mol^{-1}	η^E/ mPa.s	$\Delta G^{\ddagger E}$/ $kJmol^{-1}$	$10^6.V^E$/ m^3mol^{-1}	η^E/ mPa.s	$\Delta G^{\ddagger E}$/ $kJmol^{-1}$
T=303.15K						
A_0	1.191	-1.9007	-3.5274	1.6143	-2.0398	-4.0131
A_1	0.1424	1.1205	0.8556	1.3549	1.3346	1.6808
A_2	0.2245	-0.7152	-0.3791	-4.3335	-0.0657	2.2107
A_3	-0.3058	1.0663	1.6287	2.3410	1.3608	2.2273
A_4	-0.1149	-0.7107	-0.8157	0.8584	-1.9656	-3.7774
σ	0.0038	0.0059	0.0282	0.0066	0.0066	0.0467
T=308.15 K						
A_0	1.3088	-1.6351	-3.3843	2.0515	-1.7925	-3.8977
A_1	0.1599	0.9244	1.0545	1.6318	1.3154	1.7981
A_2	0.4101	-0.4363	-0.0576	-4.2606	-0.3968	2.3608
A_3	-0.3876	0.8058	1.2275	1.5945	0.7269	1.6008
A_4	0.1547	-0.669	-1.0199	1.1647	-0.7371	-3.4284
σ	0.0062	0.0075	0.0281	0.0112	0.0112	0.0479
T=313.15 K						
A_0	1.456	-1.4232	-3.2726	2.4577	-1.5118	-3.7707
A_1	0.1754	0.8645	1.1364	1.4203	0.9802	1.652
A_2	0.5667	-0.4608	0.0314	-3.4353	0.1906	2.8548
A_3	-0.5158	0.5913	1.0564	2.5548	0.7253	1.5397
A_4	0.0009	-0.4565	-0.885	0.5955	-1.3532	-4.1364
σ	0.0033	0.0077	0.0301	0.0067	0.0067	0.0385
T=318.15 K						
A_0	1.6032	-1.234	-3.1253	2.7951	-1.2629	-3.5305
A_1	0.1951	0.7632	1.3039	0.9948	0.863	1.6492
A_2	0.6268	-0.3879	0.17	-2.5148	0.0252	2.4949
A_3	-0.3858	0.5256	0.8258	3.8101	0.4123	1.1022
A_4	0.3466	-0.295	-0.658	0.5393	-0.8212	-3.3853
σ	0.0052	0.0074	0.0295	0.0035	0.0035	0.0391

4. Conclusion

The present work describes the volumetric and viscometric properties of EtOAc + n-PrOH and EtOAc + 2-PrOH binary mixtures at various temperatures. Excess molar volume, V^E, deviation in viscosity, η^E, and excess Gibb's free energy of activation of viscous flow, $\Delta G^{\ddagger E}$ are calculated from experimental density and viscosity data. It appears that for both systems excess volumes, V^E is positive while the deviation in viscosity, η^E values are negative. This is attributed to the dissociation of associated alcohols in solution in the presence of ethyl acetate. The observed negative values of $\Delta G^{\ddagger E}$ for both the systems indicate the presence of weak interactions between the unlike molecules and domination of dispersion forces in the binary mixtures. Temperature seems to have a significant effect and both mixtures tend to approach ideal behavior with the rise in temperature.

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