

# Volumetric and viscometric studies of binary mixtures of methanol and some alkyl acetates at varying temperatures

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## ABSTRACT

The degree of molecular interactions between mixed solvent molecules and thus ideal behavior results from the molecular architecture and chemical nature of component solvents. This understanding is essential in the design and applications of both pure and mixed solvent systems. Density and viscosity measurements of pure and binary mixtures of methanol and n-methyl acetate, n-butyl acetate, and n-pentyl acetate were carried out at different compositions of methanol and temperatures of 25, 30, 35, 40 °C. The experimental data obtained were correlated to the Redlich-Kister equation from where the excess functions; excess molar volumes, excess viscosities, excess Gibbs free energies of activation for viscous flow, fitting coefficients and standard deviations were obtained. The viscosity values were correlated with Hind et al, Kendral and Monroe, Grunberg and Nissan and Frenkel semi empirical models to ascertain the best fit for the systems. The results obtained have been discussed in terms of the structural differences and nature of the interactions between molecules of the mixed solvents.

## KEYWORDS

density, excess functions, semi-empirical models, viscosity

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## INTRODUCTION

Thermodynamic properties of liquid mixtures have attracted considerable interest from scholars due to the vast applications in industries and chemical laboratories.<sup>1</sup> The thermodynamics of organic solvents and non-electrolyte liquids is particularly important in the areas of heat transfer, mass transfer as well as chemical separations.<sup>2</sup> Experimental determination and study of the physical properties such as density, electric conductivity, and viscosity of substances are very important in the field of chemistry, engineering, petroleum exploration, agriculture, and in the designing of instruments.<sup>3,4,5</sup>

The study of changes in thermodynamic properties of mixtures and the degree of deviation from ideality gives excellent information on the molecular structure and intermolecular interactions in solvent mixtures.<sup>6</sup> Such intermolecular interactions between solvent mixtures are a reflection of the degree of deviation from ideality which gives rise to excess properties. These deviations are associated with synergy between mixture components and are attributed to differences in the chemistry of the individual solvents, experimental conditions, such as temperature differences, and mixing ratios of mixture components.<sup>7, 8</sup>

Alcohols are polar solvents with high boiling points attributed to self-association arising from hydrogen bonding present in the molecule.<sup>9</sup> Polarity and size of molecules are reported to be the predominant factors that determine the magnitude of deviations of mixed solvents from ideal behavior and thus the excess thermodynamic properties of such mixtures.<sup>10</sup> Specific interactions arise from structural differences and charge transfers.<sup>11</sup>

Methanol is the simplest known alcohol. In the laboratory, it is majorly used as an analytical solvent for extractions.<sup>12</sup> In the industry, methanol is used as basic stock in the production of plastics, enamels<sup>13</sup> antifreeze, fuel additives, etc.<sup>14,15</sup>

Alkyl acetates (esters) are polar aprotic compounds with dipole interactions present as the predominant intermolecular interactions.<sup>16</sup> They have medical, biological, biochemical, chemical, and industrial applications.<sup>17, 18</sup>

Although alcohols and esters have variety of applications in industries, laboratories, pharmaceuticals, and medicine, they may have been studied

individually or as mixed solvents with other organic or electrolytic solvents, but to the best of our knowledge, data for the binary mixtures of the chosen solvents in this study appear to be scarce in the literature. Some literature on binary mixtures reviewed in the course of carrying out this research is presented in Table 1.

Thus, the need for an extensive study of the thermodynamic properties as well as theoretical behavior of these binary mixtures. In this research work, we measured the density and viscosity of the pure and binary mixtures of the solvents at vary compositions and temperature. The excess functions were calculated and correlated using the Redlich-Kister equation and semi empirical equations used to analyze the experimental data to theoretical results.

## MATERIALS and METHODS

Methyl acetate (MA), butyl acetate (BA), and methanol (M) with 99% minimum assay were products of Loba chemie PVT Ltd, India. Pentyl acetate (PA), with 95% minimum assay was from Kermel Chemicals, Turkey. Purities of the pure solvents were further assessed by measuring the densities at 30 °C and the values were comparable with those of the literature at the same temperature. Mixtures were prepared by mass in the range of 0 to 1 mole fraction of methanol at interval of 0.1 and store in an air tight glass bottle before use to avoid contamination. All solvents and solvent mixtures were weighed using AE 223 electronic balance with a precision of  $\pm 0.1$  mg. The uncertainty in mole fraction was approximated to  $\pm 0.0001$ . Densities of pure and binary mixtures were measured using a 10 ml borosilicate glass pycnometer with a uniform capillary stopper. Calibration of the pycnometer was done using distilled water at 25 °C. Temperatures were controlled using electronical thermostatic water bath and monitored with mercury levels in glass thermometer. Viscosities of the pure solvents and binary mixtures were measured using a 20 ml capillary Oswald viscometer with a known viscometer constant (k) of 0.03. The viscometer was calibrated with distilled water at 25 °C to validate the value of k. An electronic stop watch with uncertainty of  $\pm 0.01$  seconds was used to obtain the flow time. Triplicate measurements of all experiments were done and an average of the readings taken.

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**Table 1:** Some earlier research works on thermodynamic properties of binary mixtures and excess functions

Authors and year	Title	Excess parameters and theoretical models
Pikkarainen L. (1983) <sup>22</sup>	Densities and viscosities of binary mixtures of N, N dimethylacetamide with aliphatic alcohols	Excess molar volume, excess viscosity and excess Gibbs free energy of activation of viscous flow
Altuwaim MS, Alkhalidi KHAE, Al-Jimaz AS, Mohammad AA. (2013) <sup>7</sup>	Comparative study of physico-chemical properties of binary mixtures of N, N. dimethylformamide with 1-octanol, 1-nonanol and 1-decanol at different temperatures	Excess molar volume, Isentropic and excess Isentropic Compressibility, excess refractive indices and deviations in speed of sound
Shaik J, Sankar MG, Ramachandran D, Rambabu C. (2014) <sup>21</sup>	Orientation effect on sign and magnitude of excess thermodynamic functions of non electrolyte solutions at different temperatures (303.15 K, 308.15 K, and 313.15 K)	Excess molar volume, excess viscosity, excess Gibbs free energy of activation of viscous flow, Grunberg–Nissan, Katti-Chaudhri, and Hind et al.
Dikio ED. (2014) <sup>25</sup>	Derived thermodynamic properties of binary mixtures of M-xylene, O-xylene, and P-xylene, with N, N-dimethylformamide at T = (293.15, 303.15, 313.15 and 323.15 K)	Excess volume, excess viscosity, excess Gibbs free energy of activation of viscous flow, Grunberg–Nissan interaction constant, Hind, Frenkel and a modified Kendall–Monroe
Rajalakshmi R, Ravikumar S, Gaba R, Pandiyan V. (2019) <sup>20</sup>	Thermodynamic properties and IR studies of binary mixtures of benzyl amine with alkyl esters at different temperatures	Excess molar volume, excess isentropic compressibility, excess inter molecular free lengths, excess speeds of sound, Prigogine–Flory–Patterson (PFP) theory, intermolecular free length theory (FLT) and collision frequency theory (CFT)
Raju R, Ravikumar S, Arokiaraj RG, Karlapudi S, Sivakumar K, Pandiyan V. (2020) <sup>19</sup>	Excess thermodynamic properties and FTIR studies of binary of 1, 3-dichlorobenzene with alkyl acetates (C1–C5) at Different temperatures	Excess molar volume, excess isentropic compressibility, Prigogine–Flory–Patterson (PFP), collision factor theory (CFT) and free length theory (FLT)
Kemeakegha AJ, Jumbo BA. (2020) <sup>26</sup>	Thermodynamic study on density and viscosity of binary mixtures of ethyl acetoacetate with (C4–C9) aliphatic ketones at (303.15 and 308.15.) K	Excess molar volume, excess viscosity, excess Gibbs free energy of activation of viscous flow, Frenkel, Hind, Grunberg–Nissan and modified Kendall–Monroe

## RESULTS and DISCUSSION

### Experimental result analysis

The excess molar volumes were calculated from the experimental density values with the equation;

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

where  $V^E$  is the excess molar volume,  $\rho_m$  is density of the solvent mixtures,  $X_1$  and  $X_2$ ,  $M_1$  and  $M_2$ ,  $\rho_1$  and  $\rho_2$  are the mole fractions, molar masses and densities of solvents 1 and 2 respectively.

Excess viscosities of the binary mixtures were calculated using equation 2;

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

where  $\eta_1$  and  $\eta_2$  are viscosities of the individual solvents and  $\eta_m$  is viscosity of the binary mixtures.

Excess Gibbs free energy of activation for viscous flow of the binary systems was calculated using equation 3;

$$\Delta G^{*E} = RT[\ln\eta_m v_m - (x_1\ln\eta_1 v_1 + x_2\ln\eta_2 v_2)] \quad (3)$$

where R is the universal gas constant and T, the absolute temperature.

The values of the excess molar volumes, viscosities and Gibbs free energies of activation for viscous flow were fitted to the Redlich–Kister polynomial type equation by least-squares fitting (Eq. 4).

$$Y^E = X_1X_2 \sum_{i=1}^n A_i (2X_1 - 1)^{(i-1)} \quad (4)$$

n is the number of coefficients and  $A_i$ , the optimum number of coefficient determined from the examination of the variation of standard deviation as calculated using equation 5

$$\sigma(Y^E) = \left[ \frac{\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{m - n} \right]^{1/2} \quad (5)$$

where m is the number of experimental data points and n is the number of coefficients. The subscripts exp. and cal. represent the experimental and calculated values of any of the excess parameters.

Values of Redlich–Kister coefficients ( $A_n$ ) and standard deviation ( $\sigma$ ) for all binary systems studied are presented in Tables 2, 3 and 4. Methanol + methyl acetate system gave lower standard deviation ( $\sigma$ ) than methanol + butyl acetate and methanol + pentyl acetate systems.

Plots of excess molar volumes ( $V^E$ ) against mole fractions of methanol ( $X_1$ ) for methanol and methyl acetate (M+MA), butyl acetate (M+BA) and pentyl acetate (M+PA) systems at varying temperatures (25, 30, 35 and 40 °C) are presented in Figure 1.

From the results obtained,  $V^E$  were found to be positive in methanol + methyl acetate mixtures but negative in methanol + butyl acetate and methanol + pentyl acetate mixtures at the different mole fractions of methanol and temperatures studied. Positive deviations observed in the methanol + methyl acetate mixtures suggest volume expansion in the binary system. Positive  $V^E$  values are usually attributed to weak intermolecular interaction or repulsive forces between unlike molecules. On mixing, methyl acetate appears to disrupt the self-association of methanol hydrogen bonds leading to rupturing of the bonds and hence, the observed positive deviation. Positive deviation may also be attributed to weak dipole-dipole interaction dominant in the mixed system. The negative  $V^E$  values in methanol + butyl acetate and pentyl acetate suggest volume contraction in the binary systems. It is possible that on mixing, methanol formed new hydrogen bonds with the dipolar oxygen of the esters. This behavior may be attributed

**Table 2:** Redlich–Kister Coefficients ( $A_n$ ) and Standard Deviations ( $\sigma$ ) of the excess functions obtained for the Binary Mixtures of Methanol + Methyl Acetate at temperatures of 25, 30, 35 and 40 °C

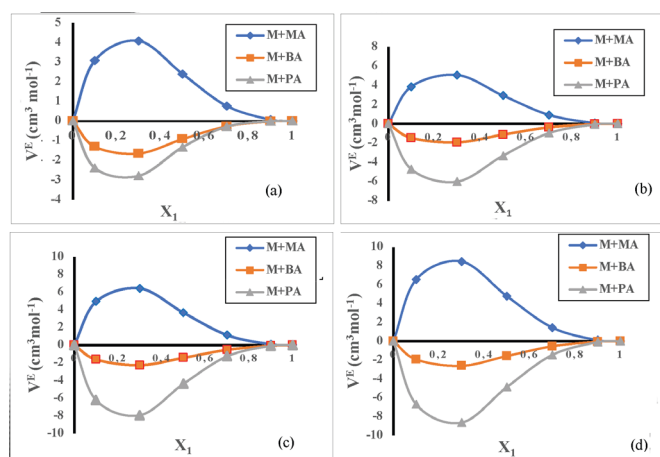
Parameter	Temp. (°C)	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
$V^E$	25	0.0651	1.8881	4.8841	3.5511	6.2041
	30	0.6749	2.1327	5.9795	4.6646	7.5921
	35	0.0512	2.4509	7.5288	6.2287	9.5405
	40	0.0381	2.9234	9.8161	8666.5553	12.4050
$\eta^E$	25	-0.0033	0.0172	-0.3091	-0.6566	0.4434
	30	-0.0048	0.0199	-0.2319	-0.3496	0.2344
	35	-0.0032	0.0172	-0.3091	-0.4443	0.3209
	40	-0.0037	-0.0559	-0.4377	-0.5036	0.5075
$\Delta G^{*E}$	25	-344.4291	-3123.2402	-6843.0701	-4574.2901	8606.5651
	30	-410.8221	-3720.3701	8119.7201	5616.4601	10337.5701
	35	-683.2731	-5882.9401	-13111.5001	-9306.7501	16597.2601
	40	-771.5451	-6698.6001	-14966.7001	-10636.0001	18950.2201

**Table 3:** Redlich–Kister coefficients ( $A_n$ ) and standard deviations ( $\sigma$ ) of the excess functions obtained for the binary mixtures of methanol + butyl acetate at temperatures of 25, 30, 35 and 40 °C

Parameter	Temp. (°C)	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
$V^E$	25	-0.1981	-1.6031	-2.7010	-1.4533	3.6424
	30	-0.1537	-1.4164	-3.0174	-2.1519	4.0342
	35	-0.0996	-0.8550	-2.1463	-1.8403	2.8542
	40	-0.0353	-0.4755	-1.7668	-1.9098	2.5175
$\eta^E$	25	-0.0005	0.1309	0.6459	0.6677	0.8039
	30	-0.0249	0.1032	0.5224	0.5066	0.6953
	35	-0.0023	0.1265	0.4505	0.4079	0.5863
	40	-0.0023	0.0332	0.3803	0.4619	0.4551
$\Delta G^{*E}$	25	-624.8441	-5231.7501	11481.3001	8062.6801	14529.4601
	30	-750.5331	-6223.7002	-13594.6001	9515.6301	17199.7601
	35	-856.6301	-7186.5010	-15644.0001	-10900.1001	19818.4801
	40	-966.3651	-8164.0801	-17775.9001	-12377.4001	22531.9501

**Table 4:** Redlich–Kister coefficients ( $A_n$ ) and standard deviations ( $\sigma$ ) of the excess functions obtained for the binary mixtures of methanol + pentyl acetate at temperatures of 25, 30, 35 and 40 °C

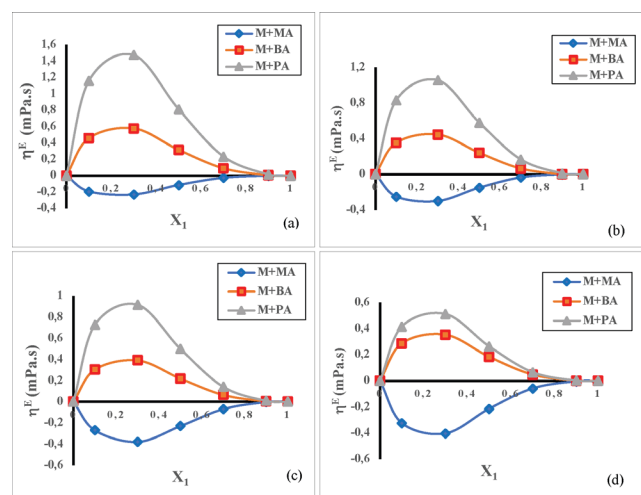
Parameter	Temp. (°C)	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
$V^E$	25	-0.1509	0.6739	-2.7040	-4.6329	1.8667
	30	-0.1507	-1.5179	-6.7626	-6.6759	7.7301
	35	-0.0280	-2.0936	-9.1232	-8.7051	10.8482
	40	-0.0478	-2.8556	-10.0678	-8.8253	12.3496
$\eta^E$	25	-0.0073	0.3924	1.6885	1.6155	2.0810
	30	0.0019	0.2637	1.2032	1.2752	1.4595
	35	0.0026	0.2031	1.0313	1.0547	1.2351
	40	0.0001	0.0061	0.6374	0.6278	0.6539
$\Delta G^{*E}$	25	-675.1981	-5542.3401	-11969.6601	-6831.8001	15168.1301
	30	-797.5471	-6606.4601	14309.1001	-9952.5401	18140.7401
	35	-918.3401	-7649.8301	-16557.6001	-11497.3001	20997.7001
	40	-1033.8601	-8679.3501	-18896.0001	-13182.4001	23962.8601

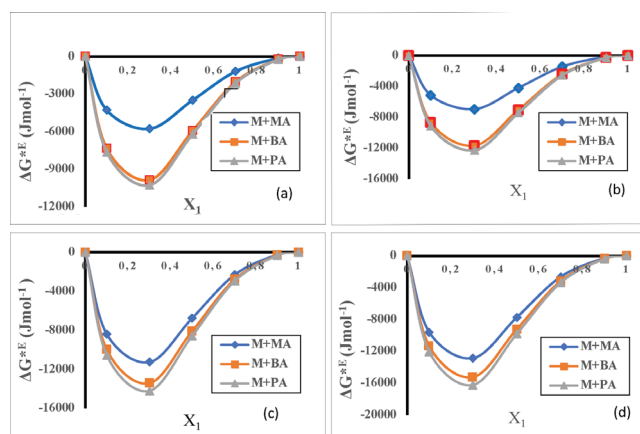
**Figure 1:** Plots of excess molar volumes ( $V^E$ ) against mole fractions of methanol ( $X_1$ ) for methanol and methyl acetate (M+MA), butyl acetate (M+BA) and pentyl acetate (M+PA) systems at varying temperatures of (a), 25 (b) 30, (c) 35 and (d) 40 °C.

to inductive effect which increased the electron density and thus, the proton accepting ability of the alkyl acetate. Increase in alkyl chain length of acetates increase the inductive effect. Hence, the observed trend in  $-V^E$  values methanol + pentyl acetate > methanol + butyl acetate > methanol + methyl acetate. Raju et al., reported similar results.<sup>19</sup> The degree of deviation increased with increase in temperature as seen in the plots. This observation is due to the increase in entropy and dominance of packing effect. This is in line with Rajalakshmi et al. observation.<sup>20</sup>

Plots of deviation in excess viscosity ( $\eta^E$ ) against mole fraction at 25, 30, 35 and 40 °C for methanol + methyl acetate, methanol + butyl acetate and methanol + pentyl acetate are presented in Figure 2 (a–d).  $\eta^E$  values were found to be negative for methanol + methyl acetate and positive for methanol + butyl acetate and methanol + pentyl acetate systems. Negative  $\eta^E$  suggest that the binary system is less viscous than the pure solvents. Weak intermolecular interactions have been reported by Shaik et al. to be responsible for negative excess molar volume.<sup>21</sup> Negative  $\eta^E$  may be attributed to dissociation of dipolar acetates and rupturing of associated hydrogen bonds of the methanol. Negative  $\eta^E$  may also be due to the presence of weak dipole-dipole interaction contributed by methyl acetate. The positive deviations observed for methanol + butyl acetate and pentyl acetate suggest that the binary system were more viscous than the pure solvents. Positive deviations also suggest that there was strong intermolecular interaction arising from hydrogen bonding between unlike molecules of methanol and the esters. Similar reports were presented by Pikkaraine,<sup>22</sup> Furthermore, the deviation in viscosity may also be accounted for in terms of difference in molar volume of the individual solvents which favoured the accommodation of smaller molecules by the larger ones. At 25 °C, pentyl acetate and butyl acetate with molar volumes of 150.64 mol dm<sup>-3</sup> and 133.49 mol dm<sup>-3</sup> respectively tend to accommodate methanol (with molar volume = 40.71 mol dm<sup>-3</sup>) better than methyl acetate whose molar volume is 80 mol dm<sup>-3</sup>. The magnitude of deviation in viscosities decreased as temperature increased. The observed decrease in  $\eta^E$  may be attributed to increase in thermal energy which may oppose attractive force binding the molecules together. Seeton, made similar observation.<sup>23</sup>

Plots of deviation in excess Gibbs Free Energy of activation for viscous flow ( $\Delta G^{*E}$ ) against mole fraction at 25, 30, 35 and 40 °C for methanol + methyl acetate, methanol + butyl acetate and methanol + pentyl acetate are presented in Figure 3 (a–d).  $\Delta G^{*E}$  were found to be negative in all studied binary systems. Negative  $\Delta G^{*E}$  values suggest spontaneous mixing and presence of weak intermolecular interaction between unlike molecules. As temperature increased, the magnitude

**Figure 2:** Plots of excess viscosities ( $\eta^E$ ) against mole fractions of methanol ( $X_1$ ) for methanol and methyl acetate (M+MA), butyl acetate (M+BA) and pentyl acetate (M+PA) systems at varying temperatures of (a) 25, (b) 30, (c) 35 and (d) 40 °C



**Figure 3:** Plots of excess Gibbs free energy of activation ( $\Delta G^{*E}$ ) against mole fractions of methanol ( $X_1$ ) for methanol and methyl acetate (M+MA), butyl acetate (M+BA) and pentyl acetate (M+PA) at varying temperatures of (a), 25 (b) 30 (c) 35 and (d) 40 °C

of negative  $\Delta G^{*E}$  increased and this could be attributed to increase in entropy that accompanies increase in temperature and thus increased spontaneity. This is in line with results published by Tuck.<sup>24</sup>

### Theoretical analysis

Experimental viscosity data were further correlated with semi-empirical models (Frenkel, Hind, Grunberg–Nissan and Kendral–Monroe; equations 6, 8, 9 and 11, respectively).

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \quad (6)$$

where  $\eta$  is expressed as follows:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 \eta_{12} \quad (7)$$

where  $\ln \eta_{12}$  is the Frenkel correlation parameter and  $\eta_{12}$  is the Hind correlation parameter

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \quad (8)$$

The dynamic viscosities were also tested by the Grunberg–Nissan equation;

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + 2x_1 x_2 d' \quad (9)$$

where  $d'$  is an interaction parameter proportional to energy interchange which is also a function of temperature of the binary mixtures.

$$\eta_m = (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad (10)$$

Equation 10 is referred to as the Kendall–Monroe cube-root equation. The right-hand side of equation 10 has been multiplied by the product of the mole fractions to obtain equation 11.

$$E\eta_m = x_1 x_2 (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^3 \quad (11)$$

where  $E\eta_m$  is the Kendral–Monroe correlation parameter

The correlating ability of equation 6, 8, 9 and 11 were tested by calculating the Average Percentage Deviations (APD) between the experimental and the calculated viscosities using equation.

$$APD = \frac{100}{N} \sum_{i=1}^N \left[ \frac{|\eta_{\text{exp,tal}} - \eta_{\text{calc}}|}{\eta_{\text{exp,tal}}} \right] \quad (12)$$

where  $\eta_{\text{exp,tal}}$  and  $\eta_{\text{calc}}$  represent the experimental and calculated viscosities respectively,  $N$  is the number of experimental data points.

The results of viscosity semi empirical calculations and average percentage deviations are presented in Table 5. The use of semi empirical models in multicomponent mixtures has been reported Dikio,<sup>25</sup> to provide the following information:

1. They identify some models as convenient reference for the interpretation of observed deviations.

**Table 5:** Fitting parameters and average percentage deviation values of the binary mixtures of methanol and acetate at temperatures of 25, 30, 35 and 40 °C

T/°C	Frenkel		Hind		Grunberg–Nissan		Kendal–Monroe	
	$\ln \eta_{12}$	APD	$\eta_{12}$	APD	$d'$	APD	$E\eta_m$	APD
Methanol + Methyl Acetate								
25	-5.064	37.153	3.420	-1.159	-3.407	29.671	0.413	12.421
30	-5.334	39.118	3.286	-1.009	-3.072	28.585	0.397	12.436
35	-5.597	29.857	3.163	5.488	-1.876	19.506	0.383	13.221
40	-5.877	43.496	3.041	-0.841	-2.562	27.032	0.368	12.455
Methanol + Butyl Acetate								
25	-3.479	26.075	4.271	-1.111	-0.444	15.781	0.518	12.541
30	-3.835	27.769	4.061	0.008	-0.067	14.521	0.492	12.556
35	-4.122	25.753	3.898	3.442	0.491	12.919	0.472	12.972
40	-4.477	21.171	3.703	0.320	0.893	10.919	0.449	12.593
Methanol + Pentyl Acetate								
25	-2.648	21.934	4.871	0.217	1.331	10.442	0.585	12.595
30	-5.334	30.323	3.286	4.408	13.319	-25.761	0.397	13.091
35	-5.597	29.857	3.163	5.488	14.658	-26.49	0.383	13.221
40	-5.871	33.827	3.041	4.167	12.999	-28.97	0.368	13.061

2. They help in suggesting models that best describe the characteristics of the systems.

3. They also predict the parameter that should be improved when the models have multiple contributors.

The Grunberg–Nissan interactive parameter ( $d'$ ) has been reported by Shaik et al. to be a good predictive yardstick for the type of interaction in mixed systems.<sup>21</sup> Positive  $d'$  values are ascribed to specific interaction and negative  $d'$  values are described in terms of weak intermolecular interactions present in the system. The value of  $d'$  for methanol + methyl acetate was negative at all temperatures and solvent compositions, indicating the presence of weak interaction. As the alkyl chain of the acetate group increased the value of  $d'$  appreciated to positive values. The  $d'$  parameter for methanol + butyl acetate and methanol was positive at all temperatures and solvent composition, indicating formation of new hydrogen bonds between unlike moles and interstitial fitting of molecules as the predominant factors in the systems. The APD values for Kendral–Monroe model have a minimal uniform positive variation at all temperatures and this suggest that the model describes the system better than other models as suggested by Kemeakagha.<sup>26</sup>

### CONCLUSIONS

The excess properties of binary mixtures of methanol + methyl acetate, methanol + butyl acetate and methanol + pentyl acetate have been determined at 25, 30, 35 and 40 °C over the entire range of methanol compositions. Excess molar volumes were found to be positive for methanol + methyl acetate mixtures and negative for methanol + butyl acetate and methanol + pentyl acetate mixtures over the entire compositions and temperatures. Excess viscosities were negative for methanol + methyl acetate mixture but positive for methanol + butyl acetate and methanol + pentyl acetate binary mixtures. Excess molar volumes and excess viscosities were attributed to weak dipole-dipole interaction, rupturing of hydrogen bond associates, formation of hydrogen bonds between unlike molecules and geometrical fitting of molecules. Gibbs Free Energies of activation for viscous flow were found to be negative and deviations were discussed in terms of spontaneity of binary systems. It was observed that the magnitude of interaction increased with increase in carbon chain length of the acetates. Grunberg–Nissan and Kendral–Monroe models were also identified as best semi empirical models for the systems. The properties of the mixed solvent systems studied exhibited better interactive properties than those of the pure solvents for methanol + butyl acetate and pentyl acetate binary mixtures and will give better industrial

applications while the methanol + methyl acetate mixture had a lesser interactive property as compared with the molecules of pure solvents.

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