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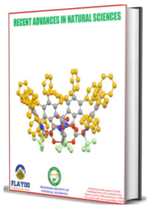

Thermodynamic properties of binary mixtures of methyl acetate and some selected ketones at varying compositions and temperatures

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ABSTRACT

Density and viscosity measurements of binary mixtures of methyl acetate with propanone, butan-2-one and pentan-2-one were carried out at varying compositions (0 to 1) of methyl acetate and temperatures of 25, 30, 35 and 40°C. The experimental data obtained were correlated with the Redlich-Kister polynomial equation from where excess molar volumes (V^E), excess viscosities (η^E), excess Gibbs free energies of activation for viscous flow (ΔG^{*E}), fitting coefficients and standard deviations of the mixtures were calculated. The η^E values were positive for mixtures of butan-2-one and pentan-2-one at all compositions and temperatures but gradually decrease with increasing composition and temperature. The mixtures of methyl acetate with propanone showed negative values of excess viscosity at all compositions of methyl acetate. The negative values are observed to be directly proportional to temperature. The values of V^E for mixtures of methyl acetate + propanone system display positive deviations at lower compositions (0-0.4) and negative for higher mole fractions. The excess molar volumes of mixtures of butan-2-one and pentan-2-one are negative at the studied compositions and temperatures with a minimum at 0.3 composition and subsequent gradual decrease in negativity with increasing composition. The excess Gibbs free energy of activation for viscous flow (ΔG^{*E}) are positive at all compositions and temperatures and reaches a maximum at 0.3 composition above which it decreases. These results have been interpreted on the basis of the type and nature of interactions as well as differences in molecular architecture between the solvent mixtures.

1. INTRODUCTION

Overtime, researchers have shown great interest in the study of the thermodynamic properties of liquids and liquid mixtures for better understanding of the nature and strength of interactions between molecules of mixed solvents [1–5]. The effects of these interactions manifest in the excess properties of the mixed system. This knowledge is very important in the design and handling of chemical, engineering and industrial processes.

Esters and ketones are polar solvents but do not self- associate as they do not undergo hydrogen bonding. Ketones are very important intermediates in the production of organic materials. For instance, propanone is used as a solvent in the manufacturing of

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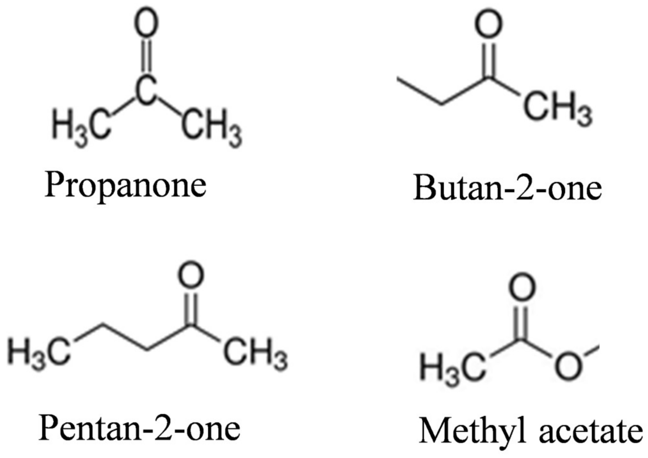

Figure 1. Schematic diagram describing the synthesis of these composites.

fat, rubber, vanishes, explosives and photographic films. Butan-2-one has important applications in solvent coatings and cleaning fluids. Pentan-2-one is commonly used in producing flavours, pesticides and pharmaceutical products [6]. Esters are good solvents for polymers as well as plasticizing agents. The unique aroma of esters also makes them very useful in food and cosmetic industries [1, 7].

In this study, the measurements of densities and viscosities of binary mixtures of methyl acetate with propanone, butan-2-one and pentan-2-one have been carried out at varying temperatures and solvent compositions of methyl acetate and the experimental excess functions correlated with theoretical Redlich-Kister equation.

Data on these binary mixtures of ester and ketones under the same experimental conditions as applied in this work appear not to be in literature. Moreover, correlating experimental and theoretical excess functions of the mixtures helps to give insight on the magnitude of deviations from ideality of the interactions of the mixing solvents. This understanding is of great value in the areas of applications of these solvents and their binary mixtures. The molecular structures of the solvents are shown in Figure 1

2. MATERIALS AND METHOD

The reagents, methyl acetate and propanone were products of JHD, China, butan-2-one was a product of LOBA CHEMIE, India. Pentan-2-one was from CDH, China and all reagents were used without further purification. The purities of the solvents were confirmed by comparing their densities with data from literature at 25°C. There was good agreement between the experimental and literature values as shown in Table 1. The solvent mixtures were prepared by mass in the range of 0 to 1 mole fraction of methyl acetate at an interval of 0.1 and stored in an air tight glass bottle before use to avoid contamination.

2.1. DENSITY AND VISCOSITY MEASUREMENTS

Densities of pure and binary mixtures were obtained using a 10ml capillary pycnometer with internal diameter of 1 mm. Calibration of the pycnometer was done using distilled water at 25°C. All weighings were done with an electronic weighing balance, model AE223 with a precision of ±0.1 mg. Viscosities were performed with a 10ml capillary Oswald Ubbelohde viscometer which was calibrated with doubly distilled water at 25°C. The measurements were done at varying compositions and temperatures. An electronic stop watch with uncertainty of ±0.01 seconds was used to obtain the flow time. Triplicate measurements of all the mixtures were done at each composition and the average of these values used in all calculations.

Table 1. Experimental and literature density values of methyl acetate and the selected ketones at 25°C.

	Density (g/cm^3)	
Solvent	Expt.	Lit.
Propanone	0.7841	0.7843 [8]
		0.7840 [9]
Butanone	0.7992	0.8034 [9]
		0.7995[10]
Pentan-2-one	0.8013	0.8017[8]
		0.8019[11]
Methyl acetate	0.9265	0.9271[12]
		0.9278[7]

2.2. THE EXCESS VISCOSITY (η^E)

The excess viscosities (η^E) of the binary systems were obtained using equation 1;

$$\eta^E = \eta_m - (x_1\eta_1 + x_2\eta_2), \tag{1}$$

where η_m, η_1 and η_2 are viscosities of the mixtures, solvents 1 and 2 respectively while x_1 and x_2 are mole fractions of solvents 1 and 2. Solvent 1 is methyl acetate while 2 is the corresponding ketone in the mixture.

2.3. THE EXCESS MOLAR VOLUME (V^E)

The excess molar volumes (V^E) of the binary systems were calculated from the measured density data using the equation;

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho_m} - \left[\frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2}\right], \tag{2}$$

where x_1, x_2, M_1, M_2, ρ_1, ρ_2 are mole fractions, molar volumes and densities of solvents 1 and 2 respectively, ρ_m is the density of the mixtures.

2.4. THE EXCESS GIBBS FREE ENERGY OF ACTIVATION FOR VISCOUS FLOW (ΔG^{*E})

ΔG^{*E} values were calculated from the experimental viscosities of pure and binary mixtures with the relation;

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

where R is the universal gas constant, T is temperature, V_m, V_1 and V_2 are molar volumes of solvent mixtures, solvents 1 and 2 respectively. Other parameters are as defined earlier.

The experimented data obtained were correlated with the Redlich-Kister polynomial equation using the least-square method;

$$Y^E = X_1\, X_2 \sum_{i=1}^{n} A_i\, (2X_1 - 1)^{i-1}, \tag{4}$$

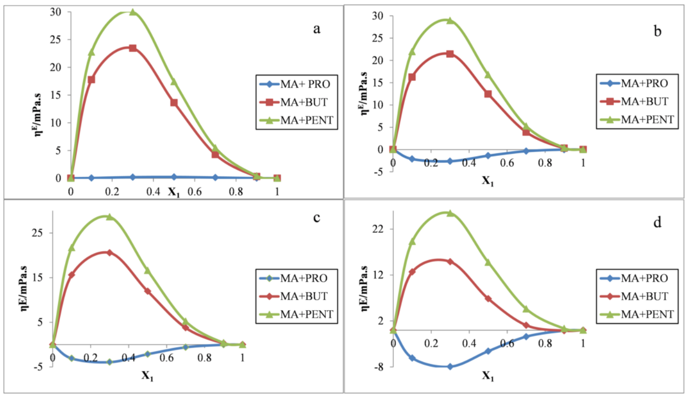

Figure 2. Plots of excess viscosity (η^E) against mole fractions of methyl acetate for the binary mixed systems at (a) 25, (b) 30, (c) 35 and (d) 40 °C.

where A_i is the optimum number of coefficients determined from the examination of the variation of standard deviation, n is the number of coefficients, Y^E is the studied excess properties. The standard deviations were calculated using [11]:

$$\sigma(Y^E) = \sqrt{\frac{\sum (Y^E_{expt.} - Y^E_{calc.})^2}{m - n}}, \tag{5}$$

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

3. RESULTS AND DISCUSSIONS

Plots of the excess functions obtained versus mole fractions of methyl acetate for the various mixtures at different temperatures are given below. Figure 2 shows the plots of η^E versus mole fraction of methyl acetate for mixtures of methyl acetate + propanone + butanone + pentanone at varying temperatures. The plots show that η^E values were positive for mixtures of methyl acetate + butanone, + pentanone at all compositions and temperatures while mixtures of methyl acetate and propanone had positive but very small values at 25°C and increasing negative values with temperature.

It has been reported [13, 14] that positive values of excess viscosity indicate dominance of strong specific attractive intermolecular interactions while negative values suggest weak interactions between mixing solvents. Esters and ketones are polar solvents by virtue of the carbonyl group common to both molecules. Thus strong interactions leading to positive η^E are expected as observed in the binary mixtures of butanone and pentanone. The predominant negative excess viscosity for mixtures of methyl acetate and propanone at the various temperatures may suggest weak dipolar interactions and non-dominance of interstitial fitting of the molecules of the two solvents since the molar volumes are relatively close (molar volumes are 79.49 and 74.08 $cm^3 mol^{-1}$ for methyl acetate and propanone respectively). Temperature effect shows decrease in the magnitude of η^E values in all solvent systems. This could be attributed to bond breakage within molecules due to strong molecular agitation with temperature increase. Such observation and interpretation have also been reported elsewhere [15].

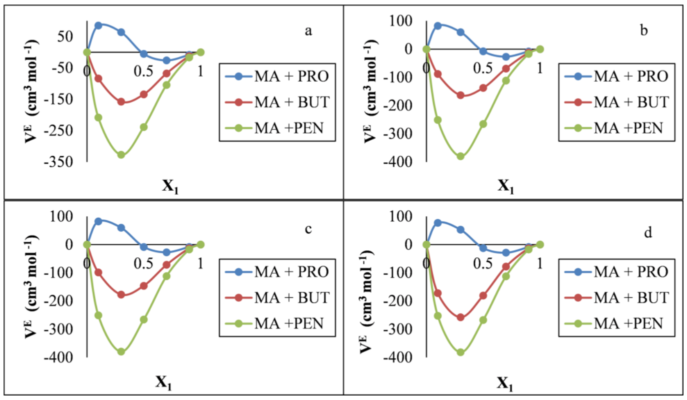

Figure 3. Plots of excess molar volume (V^E) against mole fractions of methyl acetate for the binary mixed systems at (a) 25 (b) 30, (c) 35 and (d) 40°C.

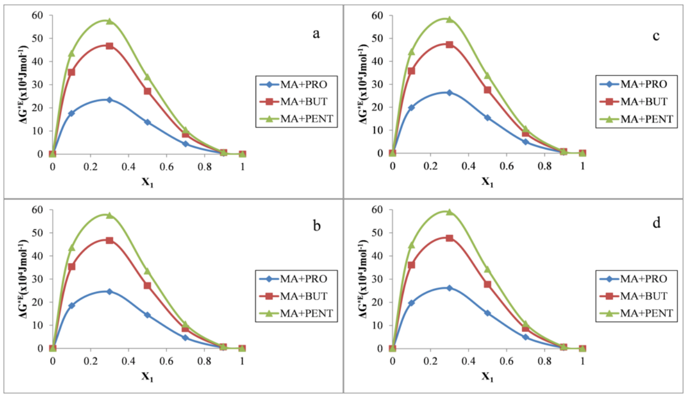

Figure 4. Plots of excess Gibbs free energy (ΔG^{*E}) of activation for viscous flow against mole fractions of methyl acetate for the binary mixed systems at (a) 25 (b) 30, (c) 35 and (d) 40°C.

Values of excess molar volumes can also be a measure of the strength of interactions between molecules of mixed solvents that result from the contraction or expansion of the volumes of solvent mixtures in relation to the volumes of the component solvents [13, 16–18]. Figure 3 shows plots of V^E versus mole fraction of the mixtures of methyl acetate and the respective three ketones at varying temperatures. The figure presents positive V^E values at lower compositions and negative values at higher compositions for methyl acetate + propanone mixtures. For methyl acetate + butanone and pentanone mixtures, the values are negative at all temperatures and mole fractions of methyl acetate. The magnitude of the negative V^E values increase with increasing chain length of the ketones. This suggests strong structural hindrance in the interactions between the binary systems and subsequent volume expansion in the binary mixtures. At higher temperatures, structure breaking effect is suspected with the increasing negative V^E values.

Excess Gibbs free energy of viscous flow is the energy of a mixed solvent system that is in excess of what it would be if it were ideal. This could also be referred to as the energy required for the flow of a solvent mixture as compared to that of a pure component solvent [3, 11]. The difference in energy is thought to arise from the nature and strength of intermolecular interactions between mixed solvents [21]. Figure 4 shows positive values of ΔG^{*E} for all mixtures at the studied compositions

Table 2. The adjustable parameters (A_i) of the Redlich-Kister equation and Standard Deviations (σ) of the excess functions of the binary mixtures of Methyl Acetate and Butanone at temperatures of 25, 30, 35 and 40°C.

Excess Function	Temp.°C	A_0	A_1	A_2	A_3	σ
η^E (mPa.s)	25	-0.0620	10.5086	28.16181	20.83225	34.81141
	30	-0.0555	-9.7299	25.98861	19.17238	20.9104
	35	-0.0561	9.6297	25.77387	19.04523	31.86694
	40	-0.0538	9.2336	24.70636	18.25162	30.58344
V^E (cm^3mol^{-1})	25	-58.23	-306.69	-416.357	-71.9977	394.0459
	30	-58.59	-308.98	-420.053	-73.1183	397.6114
	35	-58.8727	-309.247	-416.171	-67.7949	392.8002
	40	-59.0793	-311.126	-418.225	-67.6496	395.4127
ΔG^{*E} ($Jmol^{-1}$)	25	-1061.82	211904.2	561552.3	411580.2	690174.9
	30	-1051.71	212064	561505.8	411258.8	690146.5
	35	-1068.54	214740.6	568770.8	416688.4	698974.5
	40	-1077.38	216462.7	573317.5	420010.9	704726.5

and temperatures. Positive values of excess Gibbs free energy express more free energy of the mixtures than the sum of those of pure individual component solvents. This is usually attributed to stronger intermolecular interactions between unlike molecules than that of like component molecules in the system. Negative ΔG^{*E} indicates weaker interactions among mixture molecules [6, 15, 19–21] as well as spontaneity of the mixing process. The maxima of all mixtures are observed at 0.3 composition of methyl acetate which gradually decreased with increasing composition. Recall that ketones and esters contain carbonyl group with polar $C^{\delta+}$=$O^{\delta-}$. However, the partial positive charge on the carbon atom due to differences in electronegativity between carbon and oxygen makes ketones susceptible to attack by nucleophilic reagents. Alkyl groups are known to be electron donating and so the positive charge on a carbonyl carbon will largely be more as the alkyl chain increases. Thus, the increase in Gibbs free energy of the mixtures from propanone down to pentanone could have emanated from stronger interactions of the component solvents as the number of carbon atoms of the ketones increased.

4. CONCLUSION

The experimental density and viscosity values of the binary mixtures of methyl acetate + propanone, butan-2-one and pentan-2-one respectively have been determined at varying compositions of methyl acetate and temperatures. The data obtained were correlated with the Redlich-Kister polynomial equation to obtain excess viscosity (η^E), excess molar volume (V^E), excess Gibbs' free energy of activation for viscous flow (ΔG^{*E}), binary coefficients and standard deviations of the binary mixtures. The values of the η^E were positive at all temperatures and compositions for methyl acetate + butanone and pentanone mixtures but negative for propanone mixed systems. The V^E values are negative over the entire compositions and temperatures of the binary mixtures studied except for methyl acetate + propanone system that displayed positive deviations at lower compositions. The ΔG^{*E} is positive at all compositions and temperatures and increase with increasing chain length of the ketones. The plots show that the effect of temperature is only significant on the excess viscosities of the mixed systems All other excess properties were not obviously influenced by temperature changes. Overall, the results of the excess functions obtained suggest the existence of strong specific interactions between methyl acetate and the ketones studied.

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