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## Excess volumes of binary mixtures of ethyl acetoacetate and C<sub>4</sub>-C<sub>7</sub> aliphatic esters at 298.15K.

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**Abstract** The density data of binary mixtures of ethyl acetoacetate (EAA) with aliphatic esters (methyl acetate, n-propyl acetate, iso-propyl acetate and amyl acetate) have been obtained with a single capillary pycnometer at 298.15K over the entire range of solvent compositions. Excess molar volumes of the binary mixtures,  $V^E$  over the entire mole fractions of EAA have been calculated from the density data. The excess molar volumes of the binary mixtures of EAA with methyl acetate and n-propylacetate are negative at lower compositions of EAA but positive at higher compositions. In the case of binary mixtures of EAA and iso-propyl acetate,  $V^E$  values are positive at lower compositions but negative at higher compositions. For EAA mixtures with amyl acetate, the excess molar volumes are positive at all compositions except at 0.9. The observed positive and negative excess molar volumes of the mixtures have been explained in terms of differences in size and intermolecular interactions between like and unlike molecules of ethyl acetoacetate and the esters studied. A comparison of the results obtained for the four binary mixtures shows that  $V^E$  values generally increase with increase in chain length of the esters. This behaviour may suggest that the interactions between EAA and the esters are primarily influenced by dipole-dipole interactions, dispersion forces as well as geometric effects. The computed  $V^E$  values of the binary mixtures were fitted to Redlich-Kister polynomial equation to derive the fitting coefficients and standard deviations of the excess molar volumes.

**Keywords** Thermodynamics, Intermolecular interactions, Ketoesters, Esters, Excess molar volumes

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### Introduction

We have been investigating in our laboratories, the types of intermolecular interactions which take place between a ketoester and some organicsolvents. Arising from the studies, we have published our findings on the intermolecular interactions in binary mixtures of ethyl acetoacetate and some straight and branched chain aliphatic ketones [1]. The results of the investigation showed that the excess volumes of the binary mixtures were influenced by chemical and geometric factors. The chemical factor identified was that of dipole-dipole interactions between molecules of each of the single solvents and unlike molecules of the binary systems. Interstitial fitting of smaller ketone molecules into large molecules of ethyl acetoacetate accounted for the geometric contributions to the excess molar volumes. The carbonyl carbon of an ester has an additional electron-withdrawing group (oxygen) when compared with that of ketone. In order to investigate the effect of this additional oxygen attached to the carbonylcarbon atom of an ester on

the volumetric behaviour of binary mixtures of ethyl acetoacetate and carbonyl compounds, we report here our findings on the excess volumes of binary mixtures of ethyl acetoacetate and some aliphatic esters, viz: methylacetate, n-propylacetate, iso-propylacetate and amylacetate. EAA has been chosen as the common solvent since it is the least volatile of the esters and so errors that could arise due to evaporation of the solvents during the measurements would be minimized. The magnitude and signs of the excess volumes have been used to interpret the nature and type of interactions between the binary mixed solvents.

Generally, ketoesters are highly polar and known to self-associate through dipole-dipole interactions [2-3]. Ethyl acetoacetate (EAA) is a unique polar and highly ionizable ketoester exhibiting 93% keto and 7% enol forms with two  $\alpha$ -hydrogens located alpha to two carbonyl groups. Thus, EAA ionizes to yield particularly stable carbonion in which the two carbonyl groups help to accommodate the charge, thereby making EAA a much stronger acid than any other compound containing a single carbonyl group. EAA is widely used as a solvent and chemical intermediate in the production of a large number of compounds such as amino acids, analgesics, antimalarial agents, antipyrine and aminopyrine. In industries, EAA is an essential solvent in the manufacture of dyes, inks, lacquers, perfumes, plastics and yellow paint pigments [4].

Esters like ketones are carbonyl compounds which are polar and associated. However, esters do have two electron-withdrawing groups (alkoxy and carbonyl) and so are known to be more polar than ketones. They are biodegradable and thus used as important constituents of numerous products such as cosmetics, printing, marine engine oils, drugs, hydraulic fluids, compressors, automotive oils etc [5]. For example, the high volatility and low toxicity of methylacetate have been utilised in glues, paints and nail polish remover as well as in the production of acetic anhydride by carbonylation of methyl acetate. Primary amylacetate is useful in coatings, extraction of solvents for pharmaceuticals, cleaning fluids and leather polishes. N-propyl acetate finds application in printing inks, coatings, aerosol sprays, nail care, cosmetics etc. Iso-propyl acetate is a commercial solvent specifically utilized in printing processes for rotogravure inks for books, magazines, newspapers etc. and for flexographic inks for cardboard and plastic-packaging materials. The potential use of esters in industries has necessitated numerous studies on binary mixtures of esters with other organic solvents [6-10]. Rathnam et al [11] investigated the densities, viscosities and speeds of sound of binary liquid mixtures of hexyl acetate with chlorobenzene, bromobenzene, fluorobenzene and nitrobenzene at different temperatures. Comelli et al [12] have studied the excess enthalpies and excess molar volumes of diethyl carbonate with alkyl acetates at 298.15K. El-Banna [13] reported the densities and viscosities of binary mixtures of pentyl acetate and hexyl acetate with normal alkanols. Ismadji et al [14-15] determined the densities and viscosities of binary mixtures of ethyl valerate and hexyl acetate with 1-pentanol and 1-hexanol. Veeraswamy Nallani [16] have reported the thermodynamic and transport properties of binary liquid mixtures of n-methylacetamide with alkyl (methyl, ethyl, n-propyl and n-butyl) acetates at 308.15 K. Several other authors have studied the volumetric and viscometric properties of binary solvent mixtures of esters and other organic solvents [17-18]. The focus has been to relate the thermodynamic properties such as density and viscosity to the molecular interactions between single components of solvent mixtures. Such understanding is of great help in many industrial applications involving transport phenomena of single solvents and solvent mixtures such as design calculation, mass and heat transfer [19] etc.

## Experimental

The reagents, methylacetate (98%) and amylacetate (98%) were products of BDH, UK. N-propylacetate (99%) and iso-propylacetate (99%) of purified grade were products of Merck, Germany. Ethyl acetoacetate (99.5%) was a product of Riedel-De Haenag Seelze Hannover, Germany. The solvents were dried using molecular sieves and the pure solvents recovered via distillation. The purity of the solvents after recovery was confirmed by comparing their densities with those reported for the same solvents in the literature at 298.15K [20]. There was good agreement between the experimental and literature density values. Binary mixtures of ethyl acetoacetate and the esters ranging in composition from 0.00 to 1.00mole fraction of ethyl acetoacetate were prepared by mass. The densities of the



pure solvents and the binary mixtures were determined with a single 10 ml stem capillary pycnometer at  $298.15 \pm 0.01$  K. All experimental procedures are as reported in our previous papers.

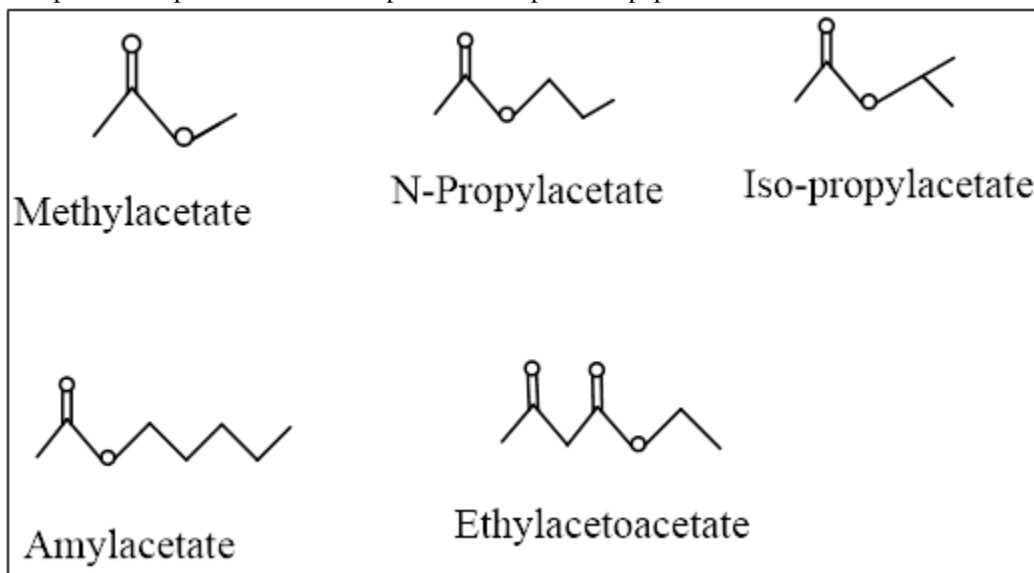


Figure 1: Structures of the solvents used in this study

## Results and Discussion

The experimental density values of the pure solvents and the corresponding literature values are shown in Table 1.

**Table 1:** The experimental and literature densities ( $\text{g cm}^{-3}$ ) of the pure solvents at 298.15 K

Pure solvent	Experimental Values	Literature Values
Ethylacetoacetate	1.0210	1.0213
methylacetate	0.9278	0.9279
n-propylacetate	0.8860	0.8830
iso-propylacetate	0.8660	0.8668
amylacetate	0.8700	0.8707

The densities of the pure solvents were highly reproducible to  $\pm 0.002 \text{ g cm}^{-3}$  with very good agreement between the experimental and literature values. The density data of the single solvents (Table 1) and those of the binary mixtures (Table 2) were used to calculate the excess molar volumes,  $V^E$  of the binary systems using equation 1

$$V^E = V - [X_1V_1 + X_2V_2] \quad (1)$$

Where  $V$ ,  $V_1$  and  $V_2$  are the molar volumes of the mixtures, ethyl acetoacetate and the esters respectively.  $X_1$  and  $X_2$  are the respective mole fractions of ethyl acetoacetate and the esters. The molar volumes of the mixtures were obtained using equation 2

$$V = \frac{M}{\rho} \quad (2)$$

Here,  $\rho$  is the density of the mixture calculated from the experimental density data and  $M$ , is the molar mass of the mixture calculated from equation 3.

$$M = X_1M_1 + X_2M_2 \quad (3)$$

$M_1$  and  $M_2$  are the molar masses of pure mixture components, EAA and the ester.  $X_1$  and  $X_2$  are as defined earlier. Values of the excess volumes of the binary mixtures of EAA and the named esters over the entire solvent compositions calculated using equation 1 are shown in Table 3. The calculated values of the excess molar volumes were correlated to the Redlich-Kister polynomial equation (Eq. 4) [21-26] and the fitting coefficients,  $a_i$  obtained.

$$V^E = X(1 - X) \sum_{i=0}^n a_i (2X - 1)^i \quad (4)$$

In equation 4,  $X$  is the mole fraction of EAA,  $n$ , the number of fitting coefficients and  $a_i$  is the fitting coefficients obtained by the method of least squares. The standard deviations of the excess molar volumes were calculated from the total number of data points,  $m$  and the number of fitting coefficients using equation 5.

$$\sigma(V^E) = \sqrt{\frac{\sum(V_{expt}^E - V_{cal}^E)^2}{m - n}} \quad (5)$$

The values of the fitting coefficients and the corresponding standard deviations of the excess molar volumes for the binary mixtures of the solvent systems studied are shown in Table 4.

**Table 2:** Densities,  $\rho$ , ( $\text{g cm}^{-3}$ ) of binary mixtures of ethylacetoacetate (EAA) and named aliphatic esters at 298.15 K

$X_{(\text{EAA})}$	Methylacetate	n-propylacetate	iso-propylacetate	Amylacetate
0.10	0.9484	0.8969	0.8866	0.8763
0.20	0.9588	0.9072	0.9072	0.8969
0.30	0.9691	0.9278	0.9278	0.9072
0.40	0.9794	0.9484	0.9381	0.9272
0.50	0.9897	0.9588	0.9484	0.9381
0.60	0.9948	0.9691	0.9588	0.9588
0.70	1.0000	0.9794	0.9691	0.9794
0.80	1.0103	0.9897	0.9897	0.9897
0.90	1.0155	1.0000	1.0103	1.0000

**Table 3:** Excess molar volumes,  $V^E$ , ( $\text{cm}^3 \text{mol}^{-1}$ ) of the binary mixtures of ethylacetoacetate (EAA) and named aliphatic esters at 298.15 K

$X_{(\text{EAA})}$	Methylacetate	n-propylacetate	iso-propylacetate	Amylacetate
0.00	-0.00240	-0.00021	0.00180	0.00170
0.10	-0.07934	-0.83176	0.60538	0.55522
0.20	-0.10706	-1.24530	0.84956	0.90412
0.30	-0.10424	-1.32996	0.73689	0.104280
0.40	-0.07540	-1.12349	0.40800	0.99809
0.50	-0.03614	-0.79461	-0.06310	0.83457
0.60	0.00662	-0.39933	-0.45684	0.60534
0.70	0.045220	0.01421	-0.84237	0.36032
0.80	0.06121	0.28646	-0.96418	0.13193
0.90	0.04961	0.32422	-0.77660	-0.00900
1.00	0.00060	0.00014	0.00140	-0.00050

**Table 4:** Fitting coefficients and standard deviation of the excess molar volumes of binary mixtures of EAA and some aliphatic esters at 298.15 K

$A_i$ coefficients	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
EAA+Methylacetate	-0.003250	-1.00574	2.76725	-1.76103	0.00341
EAA+n-propylacetate	0.02174	-11.27201	27.45436	-16.18170	0.09736
EAA+iso-propylacetate	-0.05123	9.47361	-28.53049	19.07679	0.06870
EAA+Amylacetate	-0.02576	7.54217	-15.75104	8.20511	0.03520

The plots of the calculated excess molar volumes,  $V^E$  of the binary mixtures studied over the entire mole fraction range of ethylacetoacetate at 289.15 K are shown in Figure 2. The values of the excess molar volumes of EAA + methylacetate are slightly negative at lower compositions of EAA and slightly positive at higher compositions. The small negative excess molar volumes may suggest formation of weak molecular complexes due to hydrogen bonding and dipole-dipole interactions. Due to the bulky nature of EAA, the expected dipolar association between the



mixture components may be lost at higher EAA compositions resulting in increased mixture volume and thus positive  $V^E$  values. Similar observation has also been reported by Satyananayana et al, 2008 [27] for excess molar volumes of binary mixtures of n-methylacetamide + ethylchloroacetate. The  $V^E$  values for the mixtures of EAA and n-propylacetate show relatively large negative deviations at lower compositions of EAA with increasing positive values as the composition of EAA increases. Large negative  $V^E$  contributions arise due to strong intermolecular interactions which could be attributed to dipole-dipole interactions and hydrogen bonding between the unlike molecules. In contrast, the mixtures of EAA and iso-propylacetate show positive deviations at lower EAA concentration (higher mole fractions of iso-propylacetate) but negative values at higher compositions. However, the positive and negative excess molar volumes of this curve appear to be nearly symmetrically distributed.

The positive excess molar volumes in this mixed solvents system may be ascribed to steric hindrance [28] due to branching in iso-propylacetate and loss of dipolar association [29].

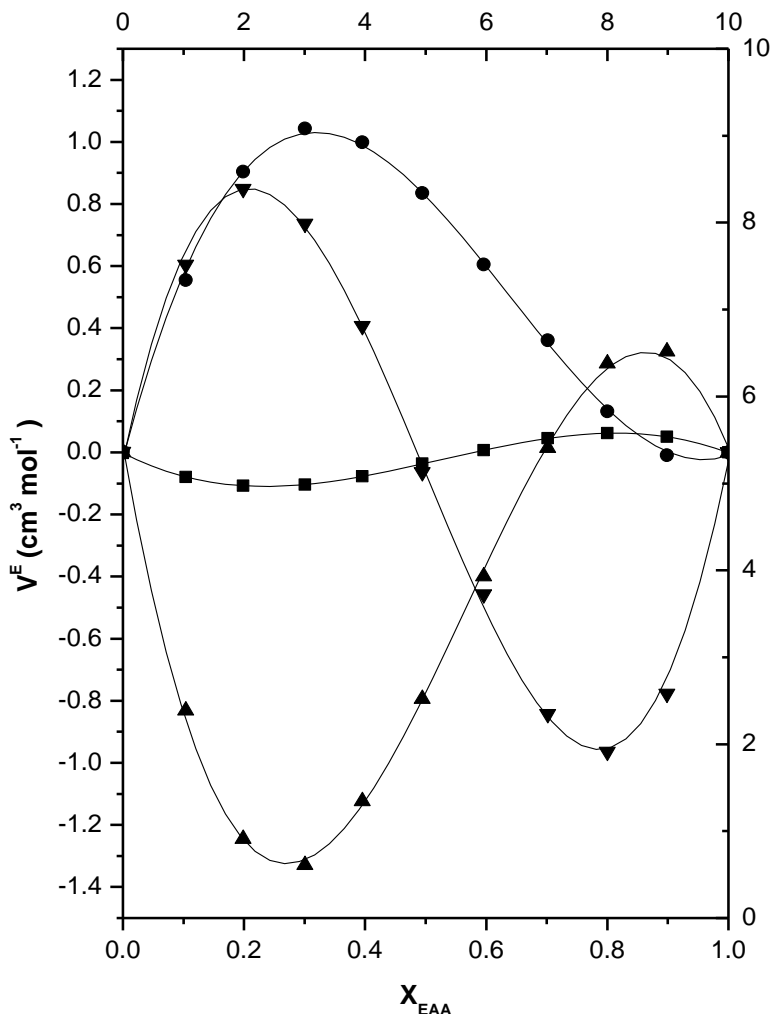


Figure 2: Variation of  $V^E$  as a function of mole fraction of EAA in binary mixtures of EAA and aliphatic esters at 298.15 K

■ EAA +methylacetate ● EAA +amylacetate ▲ EAA + n-propylacetate ▼EAA+ iso-propylacetate

It may be tempting to associate the negative  $V^E$  values to the different molecular sizes of EAA and iso-propylacetate mixed solvents. However, interstitial accommodation of iso-propylacetate molecules into the molecules of EAA appears to play negligible role since the molecular volumes of iso-propylacetate ( $1.9566 \times 10^{-22} \text{ cm}^3 \text{ mol}^{-1}$ ) and EAA ( $2.1161 \times 10^{-22} \text{ cm}^3 \text{ mol}^{-1}$ ) are very close. It is thus suspected that the negative  $V^E$  values at higher EAA compositions

are due to the formation of intermolecular association complexes resulting from strong dipole-dipole interactions between the unlike molecules of the component solvents.

The excess molar volumes of EAA and amylacetate solvent system are largely positive with a maximum at about 0.3 composition of EAA. Above this composition,  $V^E$  values gradually decrease. Positive excess molar volumes of binary mixtures of esters with hexane-1-ol have also been reported [24]. In the region of high amylacetate composition, the positive  $V^E$  values could result from steric hindrance due to the bulky nature of amylacetate which leads to volume expansion. As the composition of amylacetate decreases, this effect gradually reduces therefore the magnitude of  $V^E$  values decreases.

Generally, the excess molar volumes of the binary mixtures of ethylacetoacetate and the esters; methylacetate, n-propylacetate, iso-propylacetate and amylacetate show increasing positive values with chain length of the esters. For EAA + methylacetate and n-propylacetate mixtures,  $V^E$  values are generally negative at lower compositions of EAA with slight positive values at higher concentrations. In both cases, the magnitude of  $V^E$  is much larger for EAA + n-propylacetate mixtures than those of EAA + methylacetate. The alkoxy group of methylacetate has smaller +I inductive effect than that of propyl group on the alkoxy of n-propylacetate, making the carbonyl group of n-propylacetate more reactive. Thus, interaction between n-propylacetate and EAA is expected to be stronger resulting in larger values of negative excess molar volume. Iso-propylacetate differs structurally from n-propylacetate from the extra methyl group attached to its terminal carbon. The effect of this extra bulkiness of iso-propylacetate is reflected on the  $V^E$  values of its mixtures with EAA over those of EAA and n-propylacetate. At higher compositions of iso-propylacetate, the excess volumes are positive indicating the prevalence of steric hindrance. At higher EAA concentrations, an opposing effect overrides and  $V^E$  values become negative. For the straight chain n-propylacetate, the values of the excess volumes are in reverse order. At higher concentrations of n-propylacetate, the  $V^E$  values are largely negative as opposed to those observed for EAA + iso-propylacetate mixtures with positive excess molar volumes for same compositions of iso-propylacetate. In the region of high ethylacetoacetate, the excess volumes of binary mixtures of EAA + n-propylacetate are slightly positive. This is contrary to those of iso-propyl acetate where  $V^E$  values are negative in this region of solvent compositions. Therefore, strong dipole-dipole interactions between unlike molecules of the component solvents are expected in the binary mixtures of EAA and iso-propylacetate, thus leading to volume reduction in the binary mixtures. The large positive excess molar volumes of EAA + amylacetate binary mixtures over those of EAA + n-propylacetate and iso-propylacetate mixtures could be an indication of the steric effect of the increased chain length of amylacetate which decreases as its concentration decreases.

## Conclusion

Excess volumes of binary mixtures of solvents usually arise from specific interactions between co-solvents. The resultant effect is often non-ideality in the binary mixtures when compared to the single components. The values of the excess molar volumes of ethyl acetoacetate and the named aliphatic esters at 298.15 K at different compositions of ethyl acetoacetate have been calculated from the density measurements of the pure components and the mixtures. The results show increasing positive values of excess molar volumes as the chain length of the esters increase, indicating weaker molecular interactions with increasing chain length. This observation is suggestive of the effect of steric hindrance on the molecular interactions between EAA and the esters. In conclusion, the thermodynamic study of volume changes in binary mixtures of EAA and aliphatic esters reveal that several effects such as dipole-dipole interactions, dispersion forces and molecular geometry are primarily responsible for the interactions between the molecules of the mixture components.

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