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Interactions of ethyl acetoacetate with some (C_4–C_9) aliphatic ketones at 298.15 K: Insight from volumetric studies

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ABSTRACT

Density of binary mixtures of ethyl acetoacetate (EAA) with straight chain aliphatic ketones butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one were measured at varying compositions of the ethyl acetoacetate at 298.15 K. The derived properties such as excess molar volumes, V_m^E, of the binary mixtures were calculated from the experimental density data of the mixtures. The calculated excess molar volumes were fitted into the Redlich-Kister polynomial to obtain the fitting parameters and standard deviations. The excess molar volumes of the binary mixtures investigated were negative over the entire range of composition. The negative values were attributed to dipole–dipole interactions between the unlike molecules of mixtures than those between the like molecules of the pure solvents. The observed negative values of the excess molar volumes for the studied binary mixtures were discussed in terms of intermolecular interactions which were present in the mixtures.

1. Introduction

The thermodynamic properties derived are used to understand different kinds of association, the nature and various types of intermolecular interactions and their strength influenced by the size of the pure components in binary liquid mixtures [1]. These properties are generally convenient parameters for interpreting the interactions in solution. The ultimate goal of the thermodynamics is to explain the excess properties using different interaction parameters. The excess thermodynamic properties of the mixtures correspond to the difference between the actual property and the property if the system behaves ideally. The mixing of two solvents has been reported to result in specific interactions such as hydrogen bonding, dipole–dipole, and charge transfer reactions [2]. Strong and weak interactions between unlike molecules in mixtures lead to deviations from ideality. Deviations from ideality in binary liquid mixtures are associated with synergy and are usually attributed to differences in the chemistry and molecular arrangement of the mixing solvents [3–7] as well as the experimental conditions such as temperature and the mixing ratios of the binary solvents. The theoretical values of excess functions depend critically on the assumption about the extent of their interactions [8].

Ketones, Scheme 1, are produced on massive scales in industry as a solvents, polymer precursors, and pharmaceuticals, especially for the solvating properties associated with its own character as an aprotic and protophilic medium. It is used in the industry as paints, varnishes, and printing inks. They are also used as a solvent for insecticides, fungicides and as an intermediate in the synthesis of pharmaceutical products.

Thermodynamic data of solvent mixtures, such as excess molar volumes, V_m^E, of non-aqueous binary mixed organic solvents are replete in literature. However, investigations of the physical properties of 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone and 2-nonanone in a binary mixture with ethyl acetoacetate, over a temperature range and compositions are still scarce in the literature. Therefore, this study aimed to obtain reliable density data for binary mixtures of these ketones at 298.15 K. Excess molar volumes of alcohol solutions containing 3-pentanone and butanone solvents have been reported [9,10]. Holgado et al. [11] have reported the densities and viscosities of 2-methoxyethanol and butanone mixtures at different temperatures. Liang-sun Lee et al. [12] reported the excess molar volumes for cyclohexane with 2-propanone, 2-butanone, 3-pentanone, 4-methyl-2-pentanone at (298.15 and 303.15) K. Comelli et al. [13] have published excess molar volumes of diethyl carbonate + linear or cyclic ketones at 298.15 K. Izonfuo and Kemeakegha [14] have reported the excess molar volumes of ethyl acetoacetate with (C_4–C_6) aliphatic ketones at 298.15 K. Gowrisankar et al. [15,16] reported the molecular interactions in binary mixtures of N-methyl aniline with methyl

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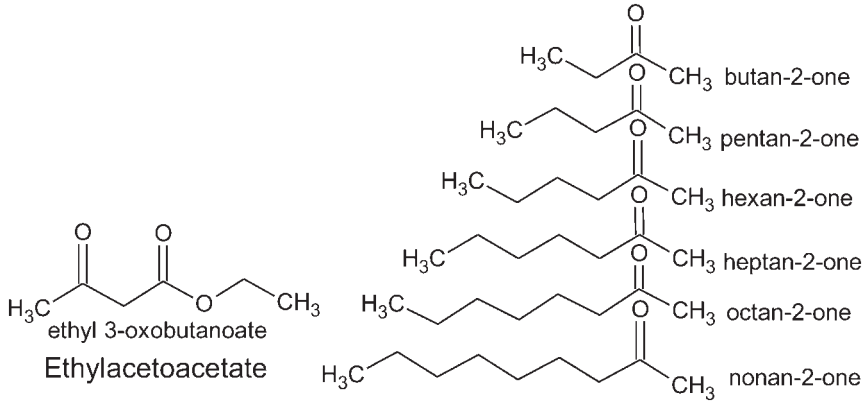


Scheme 1. Structure of ethyl acetoacetate and aliphatic (C_4–C_9) ketones.

isobutylketone, 3-pentanone and cycloalkanones at 303.15 K. The nature of excess molar volumes changes from negative deviation to positive deviation as carbon chain increases in linear ketone. Several other workers [17–30] have investigated other thermodynamic parameters to explain the types and strengths of intermolecular interactions in various binary mixed organic solvent systems. Such studies have shown that the type and strength of intermolecular interactions depend largely on the structures and chemistry of the molecules in the binary mixtures.

As far as we are aware no experimental excess molar volume data for the present systems under investigation have been reported in the literature, hence, the present work was undertaken to study the nature of interactions between unlike molecules in terms of dipole–dipole interactions and dispersion forces.

Ethyl acetoacetate, Scheme 1, is a non-aqueous bifunctional polar solvent and a ketoester with two hydrogen atoms located at alpha to the two carbonyl groups. Thus, ionization yields a stable carbonium ion in which the two carbonyl groups accommodate the charge, Scheme 2. Ethyl acetoacetate is therefore a much stronger acid than other compounds containing a single carbonyl group.

Ketoesters are highly polar and are known to be self-associated through dipole–dipole interactions [31]. The properties of mixtures of a ketoester and other solvents are dependent on the nature and types of intermolecular interactions between the component molecules. Such interactions can be evaluated in terms of the mixing parameters of the binary mixtures.

The present paper is devoted to study the physical properties of ethyl acetoacetate with some (C_4–C_9) aliphatic ketones. This is interesting due to the presence of double bounded carbonyl group (C═O) in ketones. In other words the functional group of ketone is polarized so that the carbon is electrophilic. The ketones are aprotic and protophilic, having carbonyl group (C═O) producing dipole. So it is interesting to study intermolecular interactions between the ketones and the ketoester having the same functional group.

The present work reported the experimental measurements of density, ρ, for the binary mixtures of ethyl acetoacetate with the (C_4–C_9) aliphatic ketones (butan-2-one, pentan-2-one, hexan-2-one, heptan-2-one, octan-2-one and nonan-2-one) at 298.15 K. The experimental values of density, ρ were used to calculate the excess molar volumes. The results have been used to discuss the nature of interactions between unlike molecules in terms of dipole–dipole interactions and dispersion forces.

2. Experimental

2.1. Materials

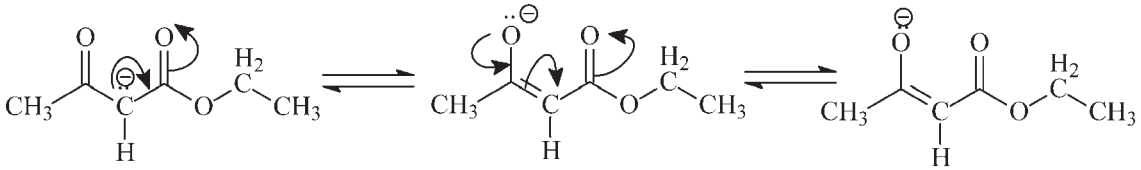
All reagents were supplied by Acros Organics Belgium and used without any further purification. The purity of these materials is (99%) for ethyl acetoacetate, (99.9%) for butan-2-one, pentan-2-one, hexan-2-one, and (99.95%) for heptan-2-one, octan-2-one and nonan-2-one. The chemicals were degassed by ultrasound, kept out of light over Fluka 0.3 nm molecular sieves for several days before the experiments were performed. The mass percent water content was determined using a Metrohm 702 SM Titrino Metter before the experiments, and was found to be ≤0.05% in all chemicals. The densities of the pure solvents are shown in Table 1. The purity of the pure liquids was ascertained by comparing their measured densities (ρ), with those reported in the literature and our results agree closely with the published values (Table 1) [19–25].

2.2. Mixture preparation

Binary mixtures were prepared by mass in airtight stoppered glass bottles. The mass were recorded on a digital electronic balance. An AE Adam balance (Adam Equipment Inc. USA) model PW124 with a maximum capacity of 120 g, a readability range 0.0001 g and repeatability (S.D.) of 0.00015 g, linearity 0.0002 g, was used. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into stoppered bottles. The uncertainty in mole fraction was thus estimated to be less than ±0.0001. A set of nine binary mixtures was prepared for each system, and their physical properties were measured at the respective composition of the mole fraction varying from 0.0000 to 1.0000 in interval of 0.1.

2.3. Density measurement

The densities of the pure liquids and their binary mixtures were measured with an Anton Paar DMA-4500 M digital densitometer at 298.15 K. Two integrated Pt 100 platinum thermometers were provided for good precision in temperature control internally (T = ±0.01 K). The



Scheme 2. Keto-enol tautomerism of ethylacetoacetate.