SEBHA UNIVERSITY JOURNAL OF PURE & APPLIED SCIENCES VOL.21 NO. 1 2022
DOI: 10.51984/JOPAS.V21I1.1788

مجلة جامعة سبها للعلوم البحتة والتطبيقية
Sebha University Journal of Pure & Applied Sciences

Journal homepage: www.sebhau.edu.ly/journal/index.php/jopas

Thermodynamic Excess Properties of Binary Mixtures of Acetyl acetone and Ethyl Acetate

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Keywords:
Binary mixtures
Molecular interactions
Excess properties
Redlich-Kister equation

ABSTRACT

The density (ρ), viscosity (η), surface tension (σ), and refractive index (R) of binary mixtures of acetylacetone (acac) with ethyl acetate (Etac) were determined at atmospheric pressure over the entire composition range of mixtures. The values of mixtures and pure liquids have been used to calculate the excess volume (VE), deviation in viscosity (Δη), and deviation in surface tension. The computed results were fitted to the Redlich–Kister polynomial equation. The excess molar volume (VE) for the binary system investigated exhibits a positive deviation at 298.15 K, and the positive deviation at 303.15 K becomes too negative as the mole fraction Xacac increases. The deviation in viscosity (Δη) and deviation in surface tension (Δσ) show negative values from the ideality at 303.15 The negative magnitude suggests the presence of strong intermolecular interactions between unlike molecules in the binary mixtures.

الخواص الثرموديناميكية الفائضة للمخاليط ثنائية المكونة من أسيتيل استون وخلات الإيثايل

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الكلمات المفتاحية:
المخاليط الثنائية
التجاذبات الجزيئية
الخواص الفائضة
معادلة ردليش-كاستر

الملخص

أثر تم تعيين الكثافة (ρ) ، واللزوجة (η) ، والتوتر السطحي (σ) ، ومعامل الانكسار (R) للمخاليط الثنائية المكونة من الأسيتيل أسيتون (acac) مع أسيتات الإيثيل (Etac) عند الضغط الجوي على مدى التركيب الكامل للمخاليط . تم استخدام قيم المخاليط والسوائل النقية لحساب الحجم الفائض (VE) والانحراف في اللزوجة (Δη) والانحراف في التوتر السطحي. تم مطابقة النتائج المحسوبة مع معادلة Redlich-Kister متعددة الحدود. يُظهر الحجم المولي الفائض (VE) للنظام الثنائي الذي تم فحصه انحرافًا إيجابيًا عند 298.15 كلفن ، ويصبح الانحراف الإيجابي عند 303.15 كلفن سالبًا مع زيادة الكسر المولي Xacac. يظهر الانحراف في اللزوجة (Δη) والانحراف في التوتر السطحي (Δσ) قيمًا سالبة من المثالية عند 303.15 ويشير الحجم السالب إلى وجود تجاذبات قوية بين الجزيئات المتماثلة وبين الجزيئات المختلفة في المخاليط الثنائية.

Introduction

The nature of physical interactions and physicochemical properties in mixtures has been well understood using thermodynamic and kinetic measurements. Along with this, they are essential for the scheming and enhancing of industrial equipment.

The thermodynamic behaviour of binary mixtures along with the physicochemical properties of liquid-liquid mixtures, such as density, viscosity, refractive index, and surface tension, have been extensively studied [1-3]. These studies were conducted to better understand the nature of interactions between molecules in a mixture, particularly those involving excess mixing properties such as excess molar volume and viscosity, as well as deviations in surface tension and refractivity [3-7]. Such data are extensively employed in solution theory and molecular dynamics for both vital research and technical applications in various chemical processes, engineering disciplines, and other relevant areas [3- 7- 8]. Furthermore, concern about surface tension and viscosity has risen rapidly, as these qualities play a critical role in the design of contacting apparatuses used in several chemical processes. They become increasingly important since these qualities are crucial in the design of contacting apparatuses used in several chemical processes, such as extraction and gas absorption distillation [3-9]. Many studies measured the thermo-physical properties of binary mixtures of liquids [10-14]. This study intends to provide a set of volumetric and transport data to assess the influence of molecular structure on the behaviour of mixtures of ethyl acetate and acetylacetone. Using the Redlich-Kister equation [15], the corresponding derived characteristics (V^E, Δη , and Δσ) were computed and correlated from the experimental results. To our

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Article History : Received 24 February 2022 - Received in revised form 23 May 2022 - Accepted 28 May 2022

knowledge, there are no complete density viscosity data for this system in the literature.

2. Materials and Methods

The analytical grade ethyl acetate and acetylacetone were obtained at their highest purity of 99% as claimed by the manufacturer (from Merck), and thus, no further purification was performed. Chemical purity was determined by comparing their densities and refractive index values to published data [3-16-18]. (**Table** 1).

Table 1. Experimental and literature values of densities and viscosities of pure liquids at 303.15 K

Parameter	Acetyl acetone		Ethyl acetate	
	Exp.	Lit.	Exp.	Lit.
ρ (g/cm^3)	0.961	0.966[17]	0.890	0.894[16]
η (mPa. s)	0.686	0.702[17]	0.444	0.424[16]
Reactive index	1.452	1.45[3]	1.3715	1.372[18]

To reduce losses due to evaporation during manipulation and after preparation, precautions were taken, such as cooling the chemicals before preparing the samples. The mixtures were moved to the pycnometer, viscometer, or stalagmometer with particular caution to avoid external contamination during the experiments. In glass stoppered bottles, mixtures were made by mass. On the same day, a group of eleven compositions was made, and their physical properties were determined. A pycnometer with a bulb volume of 25 cm^3 and a diameter of 1 mm was used to evaluate the densities of the liquids and their mixes. On a single-pan digital balance, mass measurements were taken with a precision of 0.0001 g. The viscosity of mixes and pure liquids was measured using an Ostwald viscometer. The surface tension was determined by the Stallagmometer method– drop weight method. A sodium D line refractometer was used to determine the refractive indices. The refractive index was calculated using an average of three readings. The measurements were taken three times, at different temperatures of 298.15, 303.15, and 308.15 K, and the average of the three readings was utilized. A thermostat was utilized in all physical properties.

3. Theoretical

The effective molar mass of the binary mixture was computed by:

$$M = X_{acac}M_{acac} + (1 - X_{acac})M_{Etac} \quad (1)$$

where M_{acac} and M_{Etac} refer to the molar mass of acetylacetone (acac) and ethyl acetate, respectively. Where as, X_{acac} refers to the mole fraction of acetylacetone (acac).

The excess molar volume of mixing, V^E, representing the nonideal behaviour was derived from eq.

$$V^E = V_m - \sum_1^2 V_i X_i \quad (2)$$

where V_m refers to the molar volume of the mixture, which was calculated from the mixture density, ρ_m, and the mixture molecular weights as $V_m=M_m/\rho_m$ for each temperature, in cm^3.mol^{-1} [19].

The viscosity deviations (excess viscosity, $\Delta\eta$) were calculated by the following formula:

$$\Delta\eta = \eta_m - x_{acac}\eta_{acac} - x_{Etac}\eta_{Etac} \quad (3)$$

where η_m is the mixture viscosity and x_{acac}, x_{Etac} and η_{acac}, η_{Etac} are the mole fraction and the viscosities of pure liquids acac and Etac, respectively. Furthermore, deviation in surface tension can be calculated using the following equation:

$$\Delta\sigma = \sigma_m - x_{acac}\sigma_{acac} - x_{Etac}\sigma_{Etac} \quad (4)$$

where σ_m is the surface tension of every mixture and x_{acac}, x_{Etac} and σ_{acac}, σ_{Etac} are the mole fraction and the surface tension of pure components acac and Etac, respectively. All the deviations ((V^E, $\Delta\eta$, and $\Delta\sigma$ have been fitted to the Redlich-Kister [15] equation (5) polynomial regression of the type

$$Y_m^E = x_{acac}(1 - x_{acac}) \sum_{i=0}^{n} a_i (2x_{acac} - 1)^i \quad (5)$$

Where Y_m^E denotes V^E, $\Delta\eta$, and $\Delta\sigma$, and n is the optimal number of parameters (n = 3).

4. Results and discussion

Table 2 and **Figure** 1 show the density, viscosity, surface tension, and refractive index of the binary mixtures and pure solvents[20]. The densities and refractive indices increased with the mole fraction of acac in all mixtures over the examined temperature.

Table 2. Experimental values of densities, viscosities, surface tension and reactive index of pure liquids of acac and Etac and their mixtures

Mole fraction	Density g/ml			Viscosity (mPa.s)	surface tension (Dyne/cm)	Reactive Index
X_{acac}	298.15 K	303.15 K	308.15 K	303.15 K	303.15 K	303.15 K
0	0.885	0.890221	0.903	0.444	22.97926	1.3715
0.088	0.888	0.899	0.907677	0.316274	23.83924	1.385
0.187	0.8953	0.90501	0.911326	0.326994	26.13182	1.39
0.290	0.901	0.9143	0.919149	0.334697	27.00007	1.3925
0.389	0.9101	0.922825	0.928	0.346592	27.88558	1.4045
0.491	0.916	0.929297	0.9326	0.366695	28.41152	1.412
0.617	0.925	0.937345	0.9418	0.378784	28.99874	1.421
0.691	0.9315	0.945024	0.9479	0.390872	29.58855	1.435
0.792	0.93855	0.951231	0.9554	0.420573	30.14608	1.434
0.8996	0.949	0.957077	0.9629	0.441358	31.08966	1.4415
1	0.959	0.96205	0.967354	0.6864	31.2	1.452

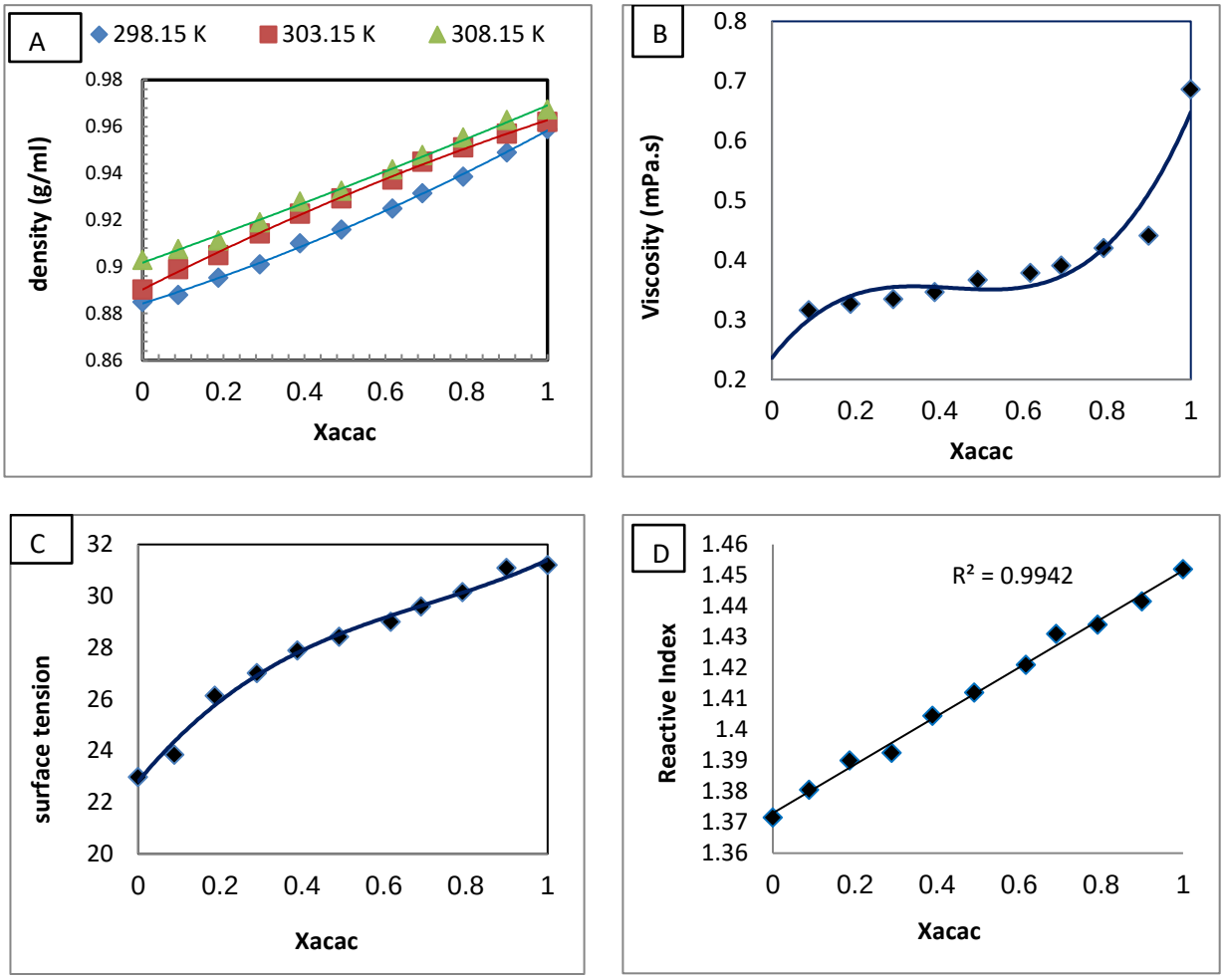

Fig. 1: Change in physicochemical properties of the binary mixture of acac and etac: A) density, B) viscosity, C) surface tension, and D) refractive index.

Tables 3 and 4 provide the experimental data for excess molar volumes and deviation in viscosities and surface tension of all binary mixes as a function of mole fraction and temperature. The sign of excess volume and deviation in viscosities and surface tension of a system depends on the relative magnitude of expansion/contraction in the mixing of two liquids.

Table 3. Experimental excess molar volume (V^E) at T = (298.15, 303.15 and 308.15) K

X_{acac}	Excess molar volume		
	298.15 K	303.15 K	308.15 K
0.088	1.951755	0.72308	-0.22506
0.187	1.84047	0.757616	0.065673
0.290	1.925341	0.446617	-0.08191
0.389	1.594286	0.188571	-0.37208
0.491	1.637635	0.169156	-0.18913
0.617	1.483925	0.123885	-0.35813
0.691	1.251874	-0.22923	-0.53874
0.792	1.134668	-0.25191	-0.69977
0.8996	0.676467	-0.2032	-0.82815

Table 3 and **Figure 2** show that at 298.15 K, the excess molar volumes (V^E) exhibit a positive deviation from ideality. However, at 303.15 K, the table reveals that raising the mole fraction X_{acac} causes a deviation to become too negative. This can be described in terms of dipole-induced dipole and dipole-dipole interactions, along with donor-acceptor interactions (hydrogen bonding) between different molecules, which generate volume reduction.

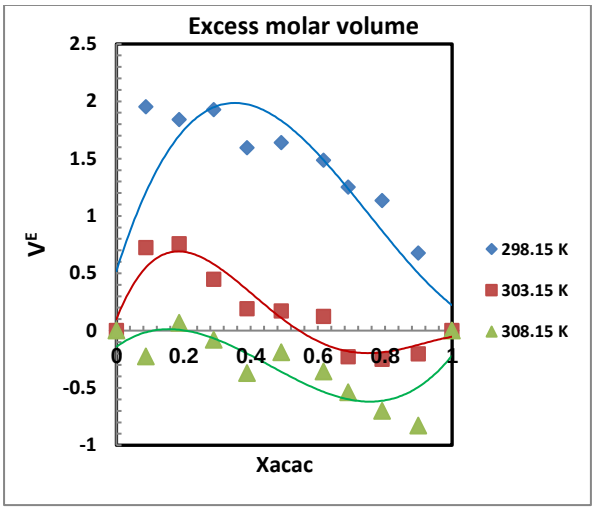

Fig. 2: Excess molar volume (V^E) at 298.15, 303.15, and 308.15 K

Table 4. Experimental deviations in viscosity and surface tension at 303.15 K

X_{acac}	Δη	Δσ
0.088	-0.14911	0.134923
0.187	-0.1624	1.613194
0.290	-0.17954	1.638839
0.389	-0.19164	1.710633
0.491	-0.19635	1.395186
0.617	-0.21477	0.947591
0.691	-0.22057	0.930825
0.792	-0.2154	0.656458

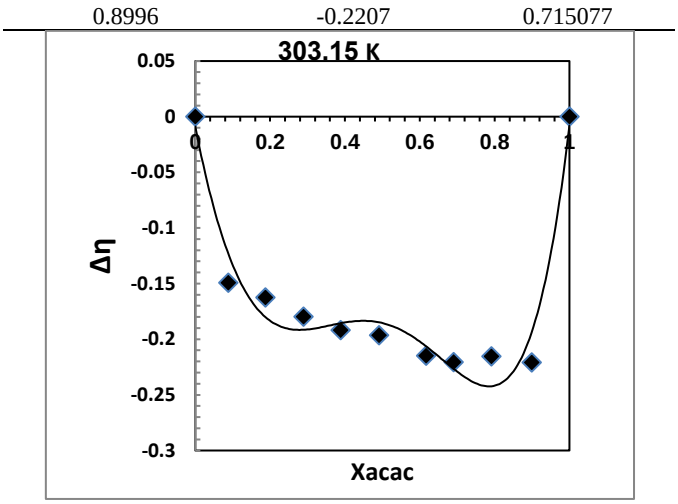

Fig. 3: Experimental excess properties of viscosity deviations (Δη) at 303.15 K

Figures 3 and **4** show plots of deviation in viscosity (Δη), and s deviation in surface tension (Δσ) against mole fraction of acetylacetone, respectively. In the whole range of acac concentrations investigated, the solutions demonstrate a negative deviation of viscosity and surface tension. **Figure 3**. A negative excess of viscosity in a mixture indicates that its flow resistance is lower than that of the pure components. A mixing process partially destroys the intermolecular structures that exist in pure liquids, allowing the flow easier than in pure liquids.

Using equation 4, the surface tension deviations were computed from the experimental readings. **Table** 4 shows the dependence of $\Delta\sigma$ on the mole fraction of acac at 303.15. The data obtained are graphically shown in **Figure 4**. The surface tension deviation for the entire mole fraction is negative, and the curve (**Figure** 4) is not symmetric, with minima at x_{acac} = 0.8. The electronic disturbance of individual molecules during mixing causes these negative values, which are highly dependent on the composition of the mixing molecules [21].

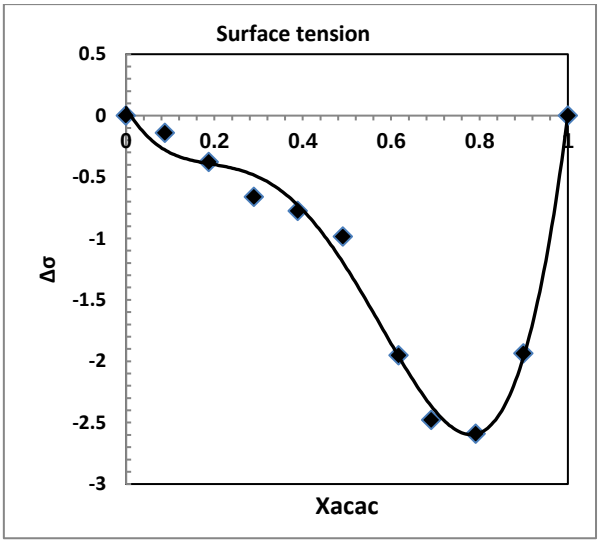

Fig. 4*:* Experimental excess properties surface tension deviations Δσ at 303.15 K

As we mentioned early that the measured density, viscosity, and surface tension values of acac and etac binary mixtures were used to calculate the excess molar volumes, viscosity deviations, and deviation in surface tension of this system and then fitted to the Redlich-Kister equation. The Redlich-Kister Model was used to correlate the mole fraction X_{acac} with the excess molar volumes (V^E), deviations in viscosities (Δη), and deviation in surface tension (Δσ) to derive the coefficients (a_0, a_1, a_2, and a_3) of these systems using a least-squares regression method. The coefficients $a_{0\text{-}3}$, listed in Table 5, were estimated by the least-squares method.

Table 5. Coefficients of a_0, a_1, a_2 and a_3 of Equation 5

Temp. (K)	Para.	a_0	a_1	a_2	a_3
298	V^E	7.5837	-17.139	9.2566	0.5201
303	V^E	8.1558	-12.523	4.2104	0.1916
308	V^E	5.8867	-8.0531	2.0894	-0.1401
298	Δη	0.5293	-0.077	-0.4576	-0.0502
298	Δσ	22.385	-28.385	5.958	-0.2911

It can be summarized that (i) certain forces between molecules as hydrogen bonding, charge transfer complexes, and hydrogen bond dissociation, might alter excess values[21-22]. (ii) structural properties of the component resulting from the geometrical adaptation of one component into another structure due to changes in the shape and size of the components and free volume [20-21]. The negative values of V^E imply significant interactions between the dissimilar molecules of the binary liquid systems. When two components of acetylacetone and ethyl acetate are mixed, the strong hydrogen bonding (as in **Figure** 5.) and dipole-dipole interactions between acetylacetone and ethyl acetate are formed.

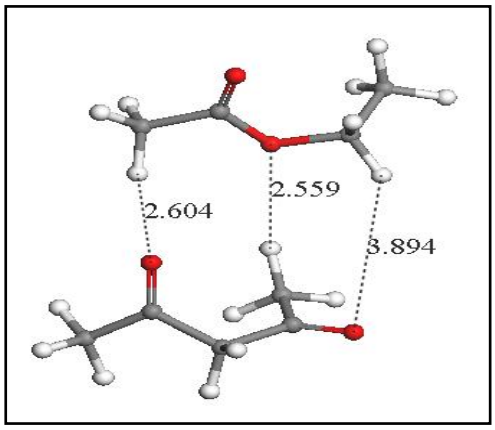

Fig. 5: Intermolecular forces of hydrogen bonds between unlike molecules calculated by $Dmol^3$ software.

Let's remember that in general, we have the three following considerations: (i) The chemical effects, such as the breaking of the molecular association present in the pure liquids results in the positive values, and negative values, on the other attributed to the formation of hydrogen bonds and other complex-forming interactions.

5. Conclusion

In this research, the densities, viscosities, surface tension, and reactive index of binary mixtures of acetylacetone and ethyl acetate were experimentally determined for the whole composition range of the selected liquids. The excess molar volumes (V^E) deviations in viscosity (Δη), and deviations in surface tension (Δσ) have all been estimated using experimental data at the temperatures under consideration. In relation to the molecular interfaces between the mixing liquids, the magnitude and sign of those determined values have been discussed. The positive excess molar volume (V^E) becomes too negative a deviation with an increase in temperature. whoever the result showed a negative Δη and a negative. The excess molar volumes, surface tension deviations, and viscosity deviations were fitted to the Redlich-Kister polynomial equation.

Acknowledgment

We would like to express our gratitude to the chemistry department at Sebha University for providing the required resources for the research.

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