

Surface Tension of the 4-Methyl-2-Pentanone/Ethyl Benzoate Binary System in the Temperature Range from 278.15 to 308.15 K

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Surface tensions (σ) and densities (ρ) of 4-methyl-2-pentanone/ethyl benzoate binary mixtures have been measured over the entire composition range at 278.15, 288.15, 298.15, and 308.15 K. Values of the excess surface tensions (σ^E) and excess molar volumes (V^E) have been calculated. The σ^E and V^E values were fitted by the Redlich–Kister polynomial equation and the A_k coefficients have been derived. The standard deviations between the calculated and the experimental excess properties have also been derived. The surface tension values have been further used to calculate the surface entropies (S^S) and surface enthalpies (H^S) per unit surface area. The lyophobicity (β) and the surface mole fractions (x_1^S) of the surfactant 4-methyl-2-pentanone have been derived using the extended Langmuir model. The obtained results are discussed from the viewpoint of the existence of specific interactions between unlike molecules in the bulk region and the surface.

KEY WORDS: Excess thermodynamic properties; surface tension; surface entropy; surface enthalpy; surface mole fraction; lyophobicity; molecular interactions.

1. INTRODUCTION

The surface tension is a fundamental thermodynamic property that characterizes the Gibbs energy per unit surface area required for the formation of a liquid–air interface. It can be considered to be the result of specific molecular interactions that occur not only in the surface but also in the bulk region of the liquid. Among other physical and thermodynamic properties of liquids, surface tension is a basis for practical and theoretical modeling of the liquid state of substances.^(1,2)

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In recent years, surface tension has become increasingly important in numerous scientific and technological areas. Many engineering problems require quantitative data on the surface tension of liquids. For example, in chemical engineering the surface tension not only determines the quality of many industrial products, but also affects the hydrodynamics and mass-transfer rates of some processes where a gas–liquid interface exists, such as gas absorption.^(3,4) A critical review of the literature reveals that systematic investigations of the surface properties of pure liquids and binary liquid mixtures over wide temperature and concentration ranges have been previously reported.^(5–10) Although there is a large databank on the thermodynamic properties of binary systems containing 4-methyl-2-pentanone^(11–13) or ethyl benzoate,^(14–17) data for their binary mixtures are still very scarce.

In a previous paper we reported the densities, viscosities, refractive indices and surface tensions of 4-methyl-2-pentanone/ethyl benzoate binary mixtures in the temperature range from 283.15 to 303.15 K.⁽¹⁸⁾ However, in that paper our attention was focused on the study of the excess thermodynamic properties such as excess molar volumes, deviations in viscosity and deviations in molar refraction. In continuation of our previous work, in this paper we report experimental values of density (ρ) and surface tension (σ) of 4-methyl-2-pentanone + ethyl benzoate binary mixtures over the entire concentration range at four different temperatures, 278.15, 288.15, 298.15 and 308.15 K. From the experimental data, the excess molar volumes (V^E) and the excess surface tensions (σ^E) have been calculated and fitted by the Redlich–Kister-type polynomial relation. The surface entropies (S^S) and the surface enthalpies per unit surface area (H^S) have been obtained as well. The surface mole fractions (x_1^S) and the lyophobicity (β) of the surfactant 4-methyl-2-pentanone have been also derived using the extended Langmuir model. The results provide information on the molecular interactions occurring between the unlike molecules that take place in the bulk region and at the surface. These results, together with our previously published results,⁽¹⁸⁾ should provide a comprehensive database for this binary-liquid system. This work is a continuation of our ongoing studies on the excess thermodynamic properties of binary-liquid mixtures.^(19–22)

2. EXPERIMENTAL SECTION

2.1. Materials

The reagents 4-methyl-2-pentanone (Merck *p.a.* > 99.0%) and ethyl benzoate (Fluka > 99.0%) were dried over 4 Å molecule sieves (Riedel-deHaen) and used directly without further purification. The gas chromatographic analysis of the solvents showed that all chemical impurities were less than 1.0%. The purity of the liquids was assessed by comparing the experimental densities and refractive indices with the literature values at 298.15 K, see Table I. The agreement was

Table I. Comparison of the Experimental Densities (ρ) and Refractive Indices (n_D) of 4-Methyl-2-pentanone and Ethyl Benzoate with Literature Values at 298.15 K

Liquid		ρ (g·cm ⁻³)	n_D
4-Methyl-2-pentanone	expl.	0.79661	1.3935
	lit.	0.79630 ^a /0.79630 ^b	1.3936 ^a /1.39362 ^b
Ethyl benzoate	expl.	1.04255	1.5027
	lit.	1.04210 ^c /1.04250 ^d	1.5027 ^d
		1.0413 ^e	

^aRef. 23.

^bRefs. 24 and 25.

^cRef. 15.

^dRef. 14.

^eRefs. 17 and 26.

satisfactory. The binary mixtures were prepared by mass using an analytical balance (Sartorius, AG 204) with a precision of ± 0.0001 g. A set of ten compositions was prepared with an increment of 0.1 mole fraction. For the conversion of the masses to mole fractions, the relative atomic masses issued by IUPAC were used. The possible error in the mole fraction was estimated to be ± 0.0001 in all cases.

2.2. Apparatus and Procedure

The surface tensions were measured using the ring method with a Du Nouy Tensiometer (A. Krüss, model K8600, Germany) equipped with a platinum-iridium ring of wire, diameter 0.37 mm. The platinum-iridium ring was cleaned with chromosulfuric acid and distilled water. The sample was introduced into a double-walled glass cell connected to a water-bath thermostat. A precision digital thermometer was used to read the cell temperature with an accuracy of ± 0.01 K. The tensiometer was calibrated with distilled water at the experimental temperatures and a correction factor was employed. The probable error of the surface tension values is less than ± 0.1 mN·m⁻¹.

Densities were measured with an Anton Paar (DMA 58, Austria) micro-computer-controlled precision densimeter with a built-in solid-state thermostat controlled to ± 0.01 K. The sample size was *ca.* 0.7 cm³. The densimeter was calibrated with dry air and distilled water at the experimental temperatures. The densities of water and air at different temperatures were selected from the literature. The estimated uncertainty of the measured densities was (1×10^{-5}) g·cm⁻³. All the measurements were performed three times at each temperature and composition.

3. CALCULATIONS AND RESULTS

The experimental values of surface tension (σ) and density (ρ) of 4-methyl-2-pentanone + ethyl benzoate binary mixtures in the temperature range from 278.15 to 308.15 K are listed in Table II.

The excess molar volumes ($V^E/\text{cm}^3\cdot\text{mol}^{-1}$) and excess surface tensions ($\sigma^E/\text{mN}\cdot\text{m}^{-1}$) were calculated from the general equation:

$$\Delta Y = Y_m - \sum_{i=1}^2 x_i Y_i \quad (1)$$

where ΔY is the excess molar volume or the excess surface tension, Y_m and Y_i are the mixture property and the property of the i th pure component, respectively, and x_i is the mole fraction of the i th component. The molar volumes of the pure

Table II. Experimental Surface Tensions (σ) and Densities (ρ) of 4-Methyl-2-Pentanone (1) + Ethyl Benzoate (2) Binary Mixtures in the Temperature Range 278.15–308.15 K

x_1	ρ (g·cm ⁻³)	σ (mN·m ⁻¹)	x_1	ρ (g·cm ⁻³)	σ (mN·m ⁻¹)
$T = 278.15$ K			$T = 288.15$ K		
0.0000	1.06052	36.3	0.0000	1.05171	35.3
0.1121	1.05317	34.9	0.1121	1.04417	33.9
0.2100	1.03530	33.6	0.2100	1.02630	32.7
0.3010	1.01691	32.4	0.3010	1.00791	31.5
0.4050	0.99381	31.1	0.4050	0.98481	30.1
0.5020	0.97024	29.7	0.5020	0.96124	28.8
0.6020	0.94392	28.3	0.6020	0.93492	27.4
0.7220	0.90961	26.6	0.7220	0.90061	25.7
0.8110	0.88224	25.4	0.8110	0.87324	24.4
0.9050	0.85156	24.0	0.9050	0.84256	23.1
0.9520	0.83639	23.3	0.9520	0.82699	22.4
1.0000	0.81652	22.6	1.0000	0.80652	21.7
$T = 298.15$ K			$T = 308.15$ K		
0.0000	1.04255	34.3	0.0000	1.03355	33.4
0.1121	1.03517	32.9	0.1121	1.02617	32.0
0.2100	1.01730	31.7	0.2100	1.00830	30.7
0.3010	0.99891	30.5	0.3010	0.98991	29.6
0.4050	0.97581	29.1	0.4050	0.96681	28.2
0.5020	0.95224	27.8	0.5020	0.94324	26.9
0.6020	0.92592	26.4	0.6020	0.91692	25.5
0.7220	0.89161	24.7	0.7220	0.88261	23.8
0.8110	0.86424	23.4	0.8110	0.85524	22.5
0.9050	0.83356	22.1	0.9050	0.82456	21.2
0.9520	0.81808	21.4	0.9520	0.80898	20.5
1.0000	0.79661	20.7	1.0000	0.78770	19.8

liquids (V_i) and the binary mixtures (V_m) were calculated using the relations:

$$V_i = \frac{M_i}{\rho_i} \quad (2)$$

$$V_m = \frac{\sum_{i=1}^2 x_i M_i}{\rho_m} \quad (3)$$

where ρ_m is the density of the binary mixture, and M_i and ρ_i are the molar mass and the density of the i th pure component, respectively. The derived excess molar volumes and excess surface tensions are accurate to $\pm 0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$, respectively. The obtained values of V^E and σ^E are listed in Table III. The values of V^E and σ^E were fitted by the Redlich–Kister⁽²⁷⁾ polynomial

Table III. Excess Surface Tensions (σ^E) and Excess Molar Volumes (V^E) of 4-Methyl-2-pentanone (1) + Ethyl Benzoate (2) Binary Mixtures in the Temperature Range 278.15–308.15 K

x_1	$V^E (\text{cm}^3 \cdot \text{mol}^{-1})$	$\sigma^E (\text{mN} \cdot \text{m}^{-1})$	x_1	$V^E (\text{cm}^3 \cdot \text{mol}^{-1})$	$\sigma^E (\text{mN} \cdot \text{m}^{-1})$
$T = 278.15 \text{ K}$			$T = 288.15 \text{ K}$		
0.0000	0.000	0.00	0.0000	0.000	0.00
0.1121	-2.212	0.13	0.1121	-2.252	0.12
0.2100	-2.718	0.21	0.2100	-2.791	0.21
0.3010	-3.031	0.27	0.3010	-3.132	0.27
0.4050	-3.207	0.31	0.4050	-3.333	0.31
0.5020	-3.194	0.32	0.5020	-3.342	0.32
0.6020	-3.005	0.29	0.6020	-3.168	0.29
0.7220	-2.533	0.22	0.7220	-2.707	0.22
0.8110	-2.002	0.17	0.8110	-2.180	0.17
0.9050	-1.267	0.10	0.9050	-1.440	0.10
0.9520	-0.953	0.04	0.9520	-1.064	0.05
1.0000	0.000	0.00	1.0000	0.000	0.00
$T = 298.15 \text{ K}$			$T = 308.15 \text{ K}$		
0.0000	0.000	0.00	0.0000	0.000	0.00
0.1121	-2.336	0.12	0.1121	-2.384	0.10
0.2100	-2.903	0.22	0.2100	-2.967	0.19
0.3010	-3.266	0.27	0.3010	-3.341	0.25
0.4050	-3.489	0.31	0.4050	-3.572	0.30
0.5020	-3.513	0.32	0.5020	-3.598	0.32
0.6020	-3.349	0.29	0.6020	-3.432	0.29
0.7220	-2.893	0.22	0.7220	-2.964	0.21
0.8110	-2.362	0.17	0.8110	-2.418	0.14
0.9050	-1.613	0.11	0.9050	-1.645	0.08
0.9520	-1.244	0.05	0.9520	-1.248	0.05
1.0000	0.000	0.00	1.0000	0.000	0.00

Table IV. Parameters A_k of the Redlich–Kister Equation [Eq. (4)] and Standard Deviations d [Eq. (5)] of 4-Methyl-2-Pentanone + Ethyl Benzoate Binary Mixtures in the Temperature Range 278.15–308.15 K

Function	A_0	A_1	A_2	A_3	d
$T = 278.15$ K					
V^E (cm ³ ·mol ⁻¹)	-12.4286	2.1056	-8.6582	2.8469	0.14
σ^E (mN·m ⁻¹)	1.2474	-0.2038	-0.1731	0.1853	0.01
$T = 288.15$ K					
V^E (cm ³ ·mol ⁻¹)	-12.9852	1.8889	-9.4232	1.6851	0.15
σ^E (mN·m ⁻¹)	1.2478	-0.2454	-0.1776	0.2850	0.01
$T = 298.15$ K					
V^E (cm ³ ·mol ⁻¹)	-13.6100	1.9051	-10.5378	0.2344	0.18
σ^E (mN·m ⁻¹)	1.2444	-0.2806	-0.1078	0.3626	0.01
$T = 308.15$ K					
V^E (cm ³ ·mol ⁻¹)	-13.9510	1.8611	-10.6385	0.4723	0.17
σ^E (mN·m ⁻¹)	1.2371	-0.1992	-0.5064	0.2156	0.01

equation:

$$\Delta Y = x_1 x_2 \sum_{k=0}^n A_k (2x_1 - 1)^k \quad (4)$$

where A_k represent the parameters. A nonlinear least-squares method was used to estimate the parameters A_k . The optimum number m of the A_k parameters ($m = n + 1$) was obtained through an examination of the standard deviation (d) between the calculated and the experimental values:

$$d = \left[\frac{\sum (\Delta Y_{\text{Calc}} - \Delta Y_{\text{Exp}})^2}{(p - m)} \right]^{1/2} \quad (5)$$

where p represents the number of experimental data points and m the number of the A_k estimated parameters used for fitting the experimental data with Eq. (4). The values of the polynomial coefficients A_k are presented in Table IV with the corresponding root mean square deviations, d .

The experimental surface tension (σ) values have been further used to calculate the entropies of surface formation per unit surface area ($S^S/\text{J}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$), using the thermodynamic equation of Clapeyron modified for liquid surfaces:^(28–30)

$$S^S = - \left(\frac{\partial \sigma}{\partial T} \right)_P \quad (6)$$

Here S^S represents the variation of the entropy per unit surface area due to interface formation, which, according to Eq. (6), is equal to the negative of the temperature coefficient of the surface tension. Considering that the surface enthalpy ($H^S/\text{J}\cdot\text{m}^{-2}$)

Table V. Surface Entropies (S^S) and Surface Enthalpies per Unit Area (H^S) of 4-Methyl-2-Pentanone + Ethyl Benzoate Binary Mixtures in the Temperature Range 278.15–308.15 K

x_1	S^S (mJ·m ⁻² ·K ⁻¹)	H^S (mJ·m ⁻²)
0.0000	0.097	63.28
0.1121	0.097	61.87
0.2100	0.097	60.58
0.3010	0.097	59.34
0.4050	0.096	57.79
0.5020	0.096	56.30
0.6020	0.095	54.82
0.7220	0.095	53.03
0.8110	0.095	51.73
0.9050	0.095	50.31
0.9520	0.094	49.53
1.0000	0.094	48.75

is the sum of the surface Gibbs energy required to extend the surface (*e.g.*, the surface tension, σ) and the latent heat (q) required to maintain isothermal conditions, $H^S = \sigma + q$, the surface enthalpies per unit surface area of the binary mixtures of 4-methyl-2-pentanone + ethyl benzoate have been calculated according to the following equation:

$$H^S = \sigma - T \left(\frac{\partial \sigma}{\partial T} \right)_p = \sigma + T S^S \quad (7)$$

The calculated surface entropies and enthalpies are listed in Table V. Both the surface enthalpies and entropies per unit surface area appear to be constant and independent of the temperature in the range from 278.15 to 308.15 K, as previously observed.⁽³¹⁾ Equations (6) and (7) have been used by many researchers to study the surface thermodynamics of binary mixtures.^(32–34)

In order to study the influence of the bulk composition on the surface tension of the mixture, the new model of Piñeiro *et al.*⁽³⁵⁾ was applied. This model, called the extended Langmuir model, is based on a generalization of the Langmuir equation. According to this model, the surface of a liquid is considered to be a thin layer of finite depth. At equilibrium, the relation between the surface volume fraction (ϕ_1^S) and the bulk volume fraction (ϕ_1) of the surfactant component (in the present work 4-methyl-2-pentanone) is given by the following equation:

$$\phi_1^S = \frac{\beta \phi_1}{1 + (\beta - 1) \phi_1} \quad (8)$$

where β is a measure of the lyophobicity of the surfactant component (4-methyl-2-pentanone), which represents its tendency to be adsorbed at the surface. A value

of β close to unity shows the same affinity of the surfactant component for both the bulk region and the surface, whereas $\beta > 1$ or $\beta < 1$ demonstrates the greater affinity of the surfactant component for the surface or the bulk region, respectively. This model has been successfully applied by Azizian and Bashvard^(36–38) for the analysis of the surface tension data of binary mixtures containing ethylene glycol. The bulk volume fraction of 4-methyl-2-pentanone (ϕ_1) is obtained from the following equation:

$$\phi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2} \quad (9)$$

where x_1 and V_1 are the mole fraction and molar volume of 4-methyl-2-pentanone, and x_2 and V_2 are the mole fraction and molar volume of ethyl benzoate, respectively.

According to this model, the surface tension of the mixture is related to the surface volume fractions of 4-methyl-2-pentanone and ethyl benzoate by means of the following equation:

$$\sigma = \phi_1^S \sigma_1 + \phi_2^S \sigma_2 - \lambda \phi_1^S \phi_2^S (\sigma_1 - \sigma_2) \quad (10)$$

where σ_1 and σ_2 are the surface tensions of 4-methyl-2-pentanone and ethyl benzoate, respectively, and ϕ_1^S and ϕ_2^S are the surface volume fractions of 4-methyl-2-pentanone and ethyl benzoate, respectively. The factor λ represents the effect of unlike-pair interactions on the surface tension of the mixture that are related to structural changes. If we assume that the structural changes occurring during mixing are insignificant (λ becomes 0), then Eq. (10) simplifies to:

$$\sigma = \phi_1^S \sigma_1 + \phi_2^S \sigma_2 \quad (11)$$

Equation (11) allows us to calculate the surface volume fractions of the two components. Combining Eqs. (8) and (11) leads to the following relation:

$$\frac{(\sigma - \sigma_2)}{(\sigma_1 - \sigma)} = \beta \left(\frac{\phi_1}{\phi_2} \right) \quad (12)$$

For the 4-methyl-2-pentanone + ethyl benzoate binary mixtures, the plot of $(\sigma - \sigma_2)/(\sigma_1 - \sigma)$ versus ϕ_1/ϕ_2 is linear in the concentration range of $0.9520 \geq x_1 \geq 0.1121$, suggesting that the effect of unlike-pair interactions on the surface tension of the mixture is negligible ($\lambda = 0$) in this concentration range (see Fig. 1). The slope of $(\sigma - \sigma_2)/(\sigma_1 - \sigma)$ versus ϕ_1/ϕ_2 is equal to the value of lyophobicity (β) of 4-methyl-2-pentanone. The obtained β values at 278.15, 288.15, 298.15 and 308.15 K are listed in Table VI.

The surface volume fractions of 4-methyl-2-pentanone (ϕ_1^S) in the composition range of $0.9520 \geq x_1 \geq 0.1121$ were calculated from the following equation:

$$\phi_1^S = \frac{(\sigma - \sigma_2)}{(\sigma_1 - \sigma_2)} \quad (13)$$

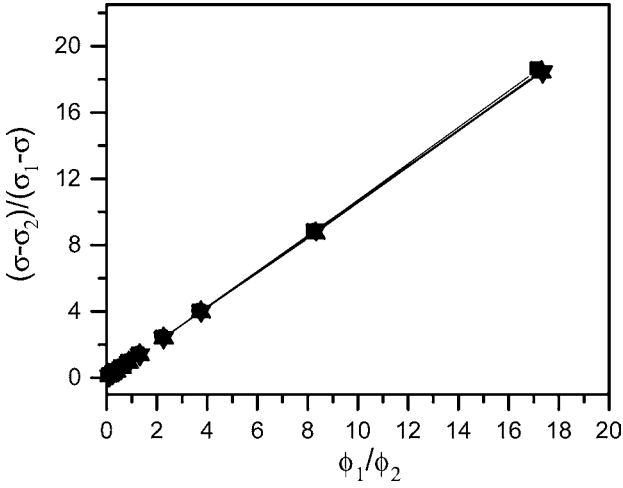


Fig. 1. Plot of the surface enthalpy per unit area (H^S) versus the mole fraction of 4-methyl-2-pentanone (x_1) for binary mixtures of 4-methyl-2-pentanone + ethyl benzoate in the temperature range from 278.15 to 308.15 K.

which results from Eq. (11) after rearrangement and considering that $\phi_1^S + \phi_2^S = 1$. The surface volume fractions (ϕ_1^S) of 4-methyl-2-pentanone have been converted to the surface mole fractions (x_1^S) using the following equation:

$$\phi_1^S = \frac{x_1^S V_1}{x_1^S V_1 + x_2^S V_2} \tag{14}$$

where x_1^S and x_2^S are the surface mole fractions of 4-methyl-2-pentanone and ethyl benzoate, respectively. The obtained x_1^S values at 278.15, 288.15, 298.15 and 308.15 K are listed in Table VII.

Table VI. Values of Lyophobicity (β) of 4-Methyl-2-Pentanone in Ethyl Benzoate in the Temperature Range 278.15–308.15 K

T (K)	β
278.15	1.08
288.15	1.07
298.15	1.06
308.15	1.06

Table VII. Bulk Mole Fractions (x_1) and Surface Mole Fractions (x_1^S) of 4-Methyl-2-Pentanone in the Temperature Range 278.15–308.15 K

x_1	x_1^S			
	$T = 278.15 \text{ K}$	$T = 288.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 308.15 \text{ K}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.1121	0.1170	0.1166	0.1162	0.1176
0.2100	0.2184	0.2177	0.2163	0.2182
0.3010	0.3113	0.3099	0.3092	0.3102
0.4050	0.4169	0.4158	0.4149	0.4151
0.5020	0.5147	0.5136	0.5127	0.5120
0.6020	0.6155	0.6144	0.6136	0.6130
0.7220	0.7348	0.7340	0.7333	0.7335
0.8110	0.8207	0.8201	0.8195	0.8212
0.9050	0.9103	0.9099	0.9090	0.9107
0.9520	0.9554	0.9549	0.9548	0.9547
1.0000	1.0000	1.0000	1.0000	1.0000

4. DISCUSSION

The curves of the excess molar volume (V^E) versus the composition of the 4-methyl-2-pentanone + ethyl benzoate mixtures are illustrated in Fig. 2. The V^E values are negative over the entire range of composition, display a minimum at

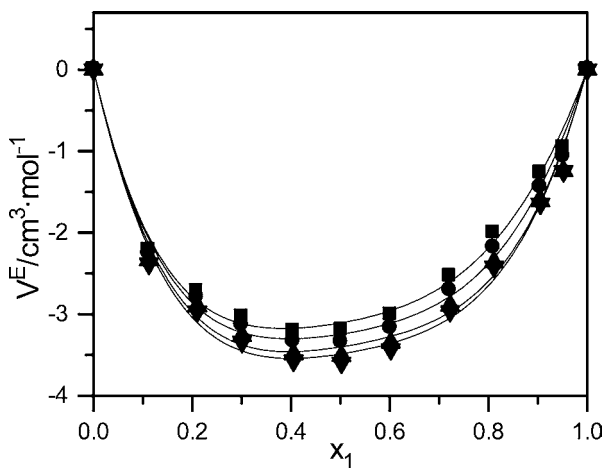


Fig. 2. Plot of $(\sigma - \sigma_2)/(\sigma_1 - \sigma)$ versus the ratio of the bulk volume fractions (ϕ_1/ϕ_2), Eq. (12), for binary mixtures of 4-methyl-2-pentanone (1) + ethyl benzoate (2) at 278.15 (■), 288.15 (●), 298.15 (▲), and 308.15 K (▼).

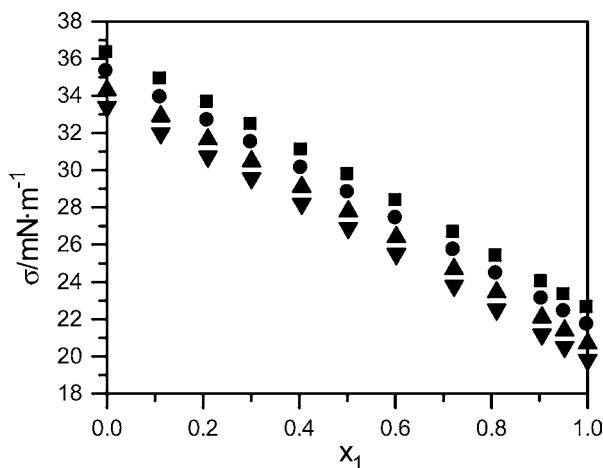


Fig. 3. Plot of the excess molar volume (V^E) versus the mole fraction of 4-methyl-2-pentanone (x_1) for binary mixtures of 4-methyl-2-pentanone + ethyl benzoate at 278.15 (■), 288.15 (●), 298.15 (▲), and 308.15 K (▼).

$x_1 \approx 0.5$ and become slightly more negative as the temperature increases. The negative V^E values indicate that there is a volume contraction upon mixing, which can result from specific interactions between unlike molecules.⁽³⁹⁾ The interactions between the molecules appear to predominate at the equimolar composition, suggesting the formation of 1:1 type molecular complexes. As was already observed, binary mixtures containing 4-methyl-2-pentanone or ethyl benzoate show negative deviations of V^E from ideality and this has been explained by the presence of interactions involving the polar carbonyl group.^(12,40–42)

The experimental values of the surface tension (σ) of binary 4-methyl-2-pentanone + ethyl benzoate mixtures are graphically shown in Fig. 3. The surface tension increases nonlinearly with an increase in the ethyl benzoate concentration at constant temperature. Furthermore, the surface tension decreases linearly with increasing temperature. Application of the principle of least squares to the surface tension–temperature data leads to linear equations of the form $\sigma = a - bT$, in agreement with the reports by Jasper and others.^(43–45) The slope b is temperature-independent and is the surface entropy per unit surface area according to Eq. (6). A comparison of the values of the surface tension of the pure components shows that the σ value of ethyl benzoate is about $\sim 38\%$ larger than that of 4-methyl-2-pentanone. Because the surface tension is the energy per unit area required to bring the molecules from the bulk region to the surface, the values of this difference demonstrate that the interactions between the ester molecules in the bulk region are stronger than the interactions between the ketone molecules. Figure 4 shows the

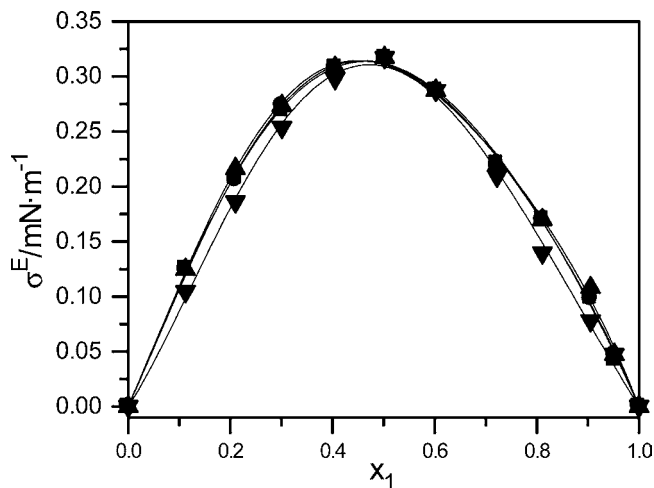


Fig. 4. Plot of the surface tension (σ) versus the mole fraction of 4-methyl-2-pentanone (x_1) for binary mixtures of 4-methyl-2-pentanone + ethyl benzoate at 278.15 (■), 288.15 (●), 298.15 (▲), and 308.15 K (▼).

dependence of the excess surface tension (σ^E) on the mole fraction of 4-methyl-2-pentanone (x_1) at 278.15, 288.15, 298.15 and 308.15 K. The σ^E values are positive at all temperatures and compositions, pass through a maximum at $x_1 \approx 0.5$, and tend to be less positive as the temperature increases. In other words, the energy required to increase the surface area of the liquid is higher in binary mixtures compared with those of the pure components. These results reveal the formation of hetero-aggregated adducts in the bulk region, which become significant at the equimolar composition. This conclusion is supported by the report of other researchers^(46,47) that the σ^E values tend to be positive for binary mixtures in which the molecular interactions in the bulk region are significant. The σ^E results confirm the explanation given for the V^E .

The values of the surface entropy per unit surface area, S^S , are plotted versus the mole fraction of 4-methyl-2-pentanone (x_1) in Fig. 5. The S^S values demonstrate that the surface becomes more disordered with an increase of the ethyl benzoate concentration. As reported by Gliński *et al.*,⁽⁴⁸⁾ a minimum value of S^S originates from the formation of molecular complexes at the surface. The absence of a minimum value of S^S in the present binary system indicates that the interactions between unlike molecules that take place in the bulk region and predominate at the equimolar composition, do not occur at the surface. The last conclusion is in complete agreement with the positive values found for the excess surface tension.

The values of the surface enthalpy per unit surface area, H^S , increase with increasing ethyl benzoate concentration (Fig. 6). A comparison of the H^S values of the pure components shows that H^S of ethyl benzoate is about $\sim 23\%$ larger

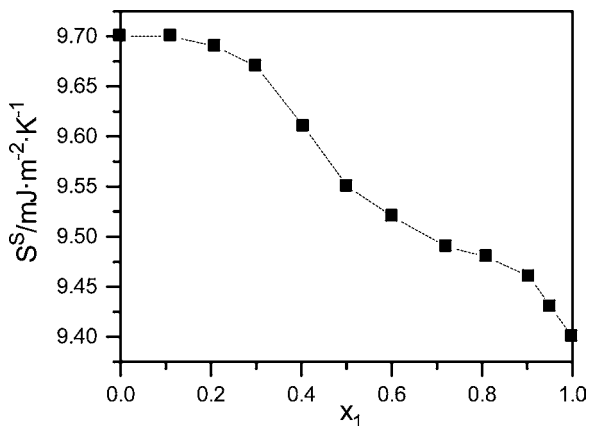


Fig. 5. Plot of the excess surface tension (σ^E) versus the mole fraction of 4-methyl-2-pentanone (x_1) for binary mixtures of 4-methyl-2-pentanone + ethyl benzoate at 278.15 (■), 288.15 (●), 298.15 (▲), and 308.15 (▼).

than that of 4-methyl-2-pentanone, which is a further indication of stronger intermolecular interactions occurring between ester molecules in the bulk region than those occurring between the ketone molecules.

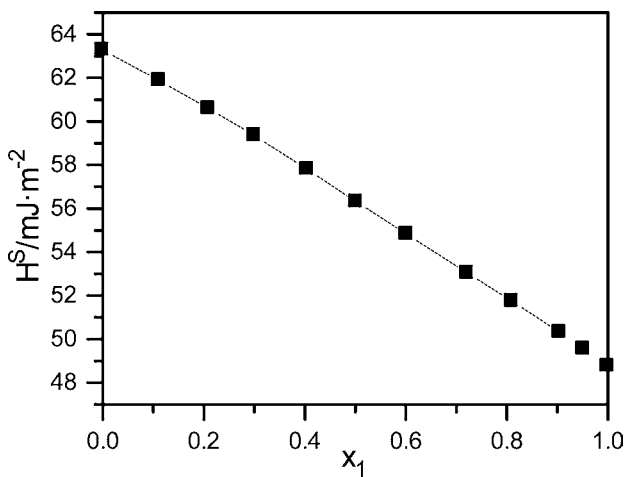


Fig. 6. Plot of the surface entropy per unit area (S^S) versus the mole fraction of 4-methyl-2-pentanone (x_1) for binary mixtures of 4-methyl-2-pentanone + ethyl benzoate in the temperature range from 278.15 to 308.15 K.

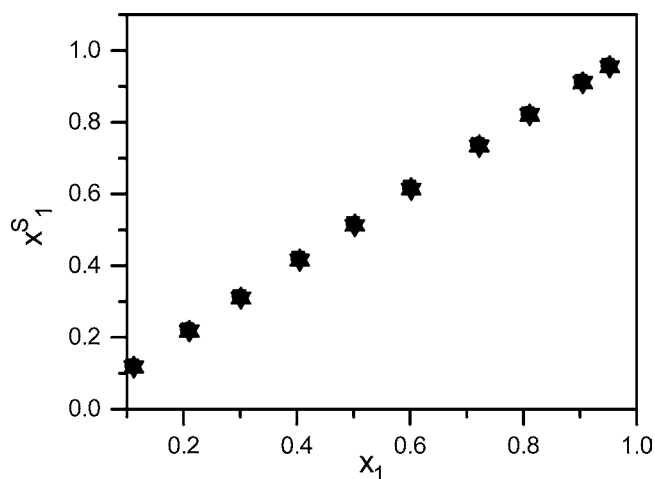


Fig. 7. Plot of the surface mole fraction (x_1^S) versus the bulk mole fraction (x_1) of 4-methyl-2-pentanone in binary mixtures of 4-methyl-2-pentanone + ethyl benzoate at 278.15 (■), 288.15 (●), 298.15 (▲), and 308.15 K (▼).

Figure 1 demonstrates the proportionality between $(\sigma - \sigma_2)/(\sigma_1 - \sigma)$ and ϕ_1/ϕ_2 , according to Eq. (12) for the 4-methyl-2-pentanone + ethyl benzoate binary mixtures. The obtained β values for 4-methyl-2-pentanone (Table V) are almost equal to unity and remain constant with increasing temperature. These results show that the affinity for 4-methyl-2-pentanone is the same for both the bulk region and surface.

The values of the surface mole fraction of 4-methyl-2-pentanone (x_1^S) are plotted against the bulk mole fractions (x_1) in Fig. 7 at the investigated temperatures. An increase of temperature has almost no effect on the surface composition. This diagram shows that the surface concentration of 4-methyl-2-pentanone does not differ much from its bulk concentration, indicating the same affinity of ketone for both the bulk region and the surface. This observation is in very good agreement with the β values ($\beta \approx 1$) of 4-methyl-2-pentanone (Table V). Because the affinity of the ketone for the liquid surface results from its lower surface Gibbs energy (the lower surface tension), the affinity for the bulk region can be explained only by the participation of the ketone molecules in the formation of the ketone–ester molecular complexes in the bulk region.

5. CONCLUSIONS

The present paper reports experimental densities (ρ) and surface tensions (σ) of binary mixtures of 4-methyl-2-pentanone + ethyl benzoate over the entire composition range at the temperatures 278.15, 288.15, 298.15 and 308.15 K. The

excess molar volumes (V^E) and excess surface tensions (σ^E) were calculated and correlated with the Redlich–Kister polynomial equation. The last equation reproduces the excess thermodynamic properties very satisfactorily. The V^E values are negative over the entire composition range and the deviation of V^E from ideality increase slightly with increasing temperature. Exactly the inverse trend is observed for the σ^E values. The negative V^E values demonstrate that volume contraction occurs upon mixing, which probably results from specific interactions between unlike molecules in the bulk region. The interactions in the bulk appear to be most important at the equimolar composition ($x_1 \approx 0.5$). The values of the surface entropy per unit surface area (S^S) reveal that interactions between unlike molecules do not extended to the surface. Calculation of the surface mole fraction of 4-methyl-2-pentanone (x_1^S) using the extended Langmuir model demonstrates that the ketone has the same affinity for both the bulk region and the surface, a conclusion that is in agreement with the positive deviation of σ^E from ideal behavior. The lyophobicity values of 4-methyl-2-pentanone ($\beta \approx 1$) reconfirm the last conclusion. According to these results, we conclude that hetero-association between ketone and ester molecules takes place in the bulk region and becomes most important at the equimolar composition. However, the hetero-association seems not to be extensive at the surface.

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