

Thermodynamic investigation of methyl salicylate/1-pentanol binary system in the temperature range from 278.15 K to 303.15 K

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Abstract

Densities (ρ), speeds of sound (u), isentropic compressibilities (k_s), refractive indices (n_D), and surface tensions (σ) of binary mixtures of methyl salicylate (MSL) with 1-pentanol (PEN) have been measured over the entire composition range at the temperatures of 278.15 K, 288.15 K, and 303.15 K. The excess molar volumes (V^E), excess surface tensions (σ^E), deviations in speed of sound (Δu), deviations in isentropic compressibility (Δk_s), and deviations in molar refraction (ΔR) have been calculated. The excess thermodynamic properties V^E , σ^E , Δu , Δk_s , and ΔR were fitted to the Redlich–Kister polynomial equation and the A_k coefficients as well as the standard deviations (d) between the calculated and experimental values have been derived. The surface tension (σ) values have been further used for the calculation of the surface entropy (S^S) and the surface enthalpy (H^S) per unit surface area. The lyophobicity (β) and the surface mole fraction (x_2^S) of the surfactant component PEN have been also derived using the extended Langmuir model. The results provide information on the molecular interactions between the unlike molecules that take place at the surface and the bulk.

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1. Introduction

The knowledge of the fundamental thermodynamic properties of binary liquid mixtures is essential in many industrial applications. Solvent properties, such as the density, the speed of sound, the isentropic compressibility, the refractive index, and the surface tension, are often used for the determination of the excess thermodynamic properties of binary liquid mixtures. Considering that the calculated excess thermodynamic quantities (excess molar volume, excess surface tension, deviations in speed of sound, deviations in isentropic compressibility, and deviations in molar refraction) provide information on the extent of the specific intermolecular interactions between the components in bin-

ary systems, it is easy to understand the importance of the availability of these solvent properties.

The research activities of our laboratory comprise among others the systematic measurements of the excess thermodynamic properties of different groups of organic compounds [1–3]. In our previous papers, we have reported the excess thermodynamic properties of a wide number of binary mixtures containing 1-pentanol [4,5]. In continuation of our previous work, we report experimental values of density (ρ), speed of sound (u), isentropic compressibility (k_s), refractive index (n_D), and surface tension (σ) of binary mixtures of methyl salicylate (MSL) with 1-pentanol (PEN) over the entire composition range at 278.15 K, 288.15 K, and 303.15 K. From the experimental data, the excess molar volumes (V^E) and surface tensions (σ^E) and the deviations in speed of sound (Δu), isentropic compressibility (Δk_s), and molar refraction (ΔR) have been calculated and fitted by the Redlich–Kister polynomial relation. The surface entropies (S^S) and the surface

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enthalpies (H^S) per unit surface area have been obtained as well. The surface mole fractions (x_2^S) and the lyophobicity (β) of the surfactant PEN have been also derived using the extended Langmuir model.

A survey in the literature showed that binary mixtures of PEN with tetraethylene glycol dimethyl ether [6], ethyl acetate [7], *tert*-butyl methyl ether and *tert*-amyl methyl ether [8], 2-propoxyethanol and 2-isopropoxyethanol [9], heptane [10], *p*-chlorotoluene [11], and anisole [12] have been already studied. To the best of our knowledge, extensive data of excess thermodynamic properties of binary mixtures of PEN with MSL at the experimental conditions of this study are not available in the literature.

2. Experimental

2.1. Materials

The reagents methyl salicylate, MSL (Merck, *p.a.*, mass fraction >99.5%) and 1-pentanol, PEN (Fluka, *p.a.*, mass fraction >99.5%) were used without further purification. The solvents were stored over 0.4 nm molecular sieves. The purity of the liquids was assessed by comparing the experimental values of density (ρ), refractive index (n_D), and speed of sound (u) at 278.15 K, 288.15 K, and 303.15 K with those reported in the literature. The experimental and literature ρ , n_D , and u values are tabulated in table 1. The agreement was satisfactory. The binary mixtures of MSL with PEN were prepared by mass on an analytical balance (Mettler A210P) with a precision of ± 0.0001 g. The possible error in the mole fraction was estimated to be ± 0.0001 in all cases.

2.2. Apparatus and procedures

Densities (ρ) were measured with an Anton Paar (Model DMA 58, Austria) microcomputer-controlled precision densimeter with a built-in solid-state thermostat controlled to ± 0.01 K and a capacity of *ca.* 1.0 cm³. The densimeter was calibrated with dry air and distilled water at the exper-

imental temperatures. The densities of water and air at different temperatures were selected from the literature [13]. The estimated uncertainty of the measured densities was ± 0.00005 g · cm⁻³.

The surface tensions (σ) were measured using the ring method by a Du Nouy Tensiometer (A. Krüss, model K8600, Germany) equipped with a platinum–iridium ring having a diameter of 0.37 mm. The platinum–iridium ring was cleaned with chromosulfuric acid and boiling distilled water. The samples were 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 was found to be less than ± 0.1 mN · m⁻¹.

The speeds of sound (u) were measured with an Anton Paar (Model DSA 48, Austria) sound analyzer with a built-in solid-state thermostat controlled to ± 0.01 K. The sound analyzer was calibrated with dry air and distilled water at the experimental temperatures. The estimated uncertainty of the measured speeds of sound was ± 1 m · s⁻¹. The isentropic compressibility (k_s) was calculated from density (ρ) and speed of sound (u) data using the Laplace equation [14], $k_s = 1/(u^2 \cdot \rho)$. The isentropic compressibility determined was accurate to within ± 1 TPa⁻¹.

The refractive indices (n_D) at the sodium *D*-line were measured with a thermostatted Abbe refractometer (Model A. Krüss, Germany) with a built-in light source for the prism with an accuracy of ± 0.0001 . The thermostat temperature was constant to ± 0.01 K.

3. Results and discussion

The experimental values of density (ρ), speed of sound (u), isentropic compressibility (k_s), refractive index (n_D), and surface tension for MSL and PEN binary mixtures at 278.15 K, 288.15 K, and 303.15 K are given in table 2.

TABLE 1

Comparison of the experimental values of density (ρ), refractive index (n_D), and speed of sound (u) of MSL and PEN with the literature values at the temperatures (278.15, 288.15, and 303.15) K

Liquid	T (K)	ρ (g · cm ⁻³) (exp)	ρ (g · cm ⁻³) (ref)	n_D (exp)	n_D (ref)	u (m · s ⁻¹) (exp)	u (m · s ⁻¹) (ref)
PEN	278.15	0.82572	0.8259 ^a 0.8261 ^c	1.4160	1.4159 ^a	1348.6	1342 ^d
PEN	288.15	0.81890	0.8189 ^a	1.4118		1312.5	
PEN	303.15	0.80739	0.8073 ^a 0.8072 ^b	1.4070	1.40573 ^a	1258.2	1258 ^d
MSL	278.15	1.19892	1.1984 ^c	1.5420	1.5438 ^c	1483.9	1488 ^c
MSL	288.15	1.18890		1.5379		1446.9	
MSL	303.15	1.17380	1.1729 ^c	1.5324	1.5329 ^c	1391.2	1393 ^c

^a Reference [23].

^b Reference [24].

^c Reference [25].

^d Reference [26].

^e Reference [6].

TABLE 2

Densities (ρ), speeds of sound (u), isentropic compressibilities (k_s), refractive indices (n_D), and surface tensions (σ) of MSL (1)/PEN (2) binary mixtures at the temperatures (278.15, 288.15, and 303.15) K

x_1	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$u/(\text{m} \cdot \text{s}^{-1})$	$k_s/(\text{TPa}^{-1})$	n_D	$\sigma/(\text{mN} \cdot \text{m}^{-1})$
$T = 278.15 \text{ K}$					
0.0000	0.82572	1348.6	666	1.4160	27.5
0.0478	0.84690	1350.4	647	1.4230	27.8
0.1061	0.87220	1358.4	621	1.4311	28.0
0.1532	0.89220	1364.1	602	1.4378	28.2
0.2173	0.91887	1371.8	578	1.4471	28.4
0.2654	0.93848	1377.3	562	1.4538	28.6
0.3428	0.96934	1387.8	536	1.4643	28.8
0.4205	0.99945	1398.1	512	1.4743	29.5
0.5156	1.03520	1408.5	487	1.4863	30.7
0.5870	1.06120	1418.8	468	1.4949	31.6
0.6977	1.10012	1434.8	442	1.5085	33.7
0.8110	1.13835	1452.2	417	1.5215	36.1
0.8824	1.16160	1464.2	402	1.5290	37.8
1.0000	1.19892	1483.9	379	1.5420	41.0
$T = 288.15 \text{ K}$					
0.0000	0.81890	1312.5	709	1.4118	26.7
0.0478	0.83988	1316.4	687	1.4188	26.9
0.1061	0.86494	1323.7	660	1.4269	27.1
0.1532	0.88477	1329.2	640	1.4336	27.3
0.2173	0.91120	1336.7	614	1.4429	27.6
0.2654	0.93063	1342.3	596	1.4497	27.9
0.3428	0.96119	1352.3	569	1.4602	28.2
0.4205	0.99103	1362.2	544	1.4701	29.0
0.5156	1.02639	1373.3	517	1.4821	30.2
0.5870	1.05213	1383.5	497	1.4907	31.2
0.6977	1.09073	1399.0	468	1.5043	33.2
0.8110	1.12867	1416.4	442	1.5175	35.6
0.8824	1.15180	1427.9	426	1.5248	37.2
1.0000	1.18890	1446.9	402	1.5379	40.3
$T = 303.15 \text{ K}$					
0.0000	0.80739	1258.2	782	1.4070	25.5
0.0478	0.82804	1265.2	754	1.4140	25.6
0.1061	0.85278	1271.4	725	1.4222	25.8
0.1532	0.87242	1276.8	703	1.4290	26.0
0.2173	0.89861	1284.0	675	1.4381	26.4
0.2654	0.91785	1289.8	655	1.4445	26.8
0.3428	0.94810	1298.9	625	1.4550	27.4
0.4205	0.97763	1308.3	598	1.4652	28.3
0.5156	1.01261	1320.5	566	1.4772	29.5
0.5870	1.03809	1330.6	544	1.4860	30.6
0.6977	1.07630	1345.3	513	1.4995	32.5
0.8110	1.11395	1362.6	484	1.5117	34.8
0.8824	1.13699	1373.4	466	1.5198	36.3
1.0000	1.17380	1391.2	440	1.5324	39.2

refer to the mixture property and to the respective property of the i th pure component, and the term c_i is the mixture composition expressed in mole fraction (x_i) for the calculation of V^E , Δu , and σ^E and in volume fraction (φ_i) for the calculation of ΔR and Δk_s . The calculated values of V^E , σ^E , Δu , Δk_s and ΔR are presented in table 3. The derived values of V^E , σ^E , Δu , Δk_s and ΔR were accurate to $\pm 0.006 \text{ cm}^3 \cdot \text{mol}^{-1}$, $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$, $\pm 0.1 \text{ m} \cdot \text{s}^{-1}$, $\pm 4 \text{ TPa}^{-1}$, and $\pm 0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively.

TABLE 3

Excess molar volumes (V^E), excess surface tensions (σ^E), deviations in speed of sound (Δu), deviations in isentropic compressibility (Δk_s), and deviations in molar refraction (ΔR) of MSL (1)/PEN (2) binary mixtures at the temperatures (278.15, 288.15, and 303.15) K

x_1	$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\Delta u/(\text{m} \cdot \text{s}^{-1})$	$\Delta k_s/(\text{TPa}^{-1})$	$\Delta R/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\sigma^E/(\text{mN} \cdot \text{m}^{-1})$
$T = 278.15 \text{ K}$					
0.0000	0.000	0.0	0	0.000	0.0
0.0478	-0.023	-4.7	-2	-0.105	-0.4
0.1061	-0.046	-4.5	-9	-0.233	-1.0
0.1532	-0.058	-5.2	-13	-0.306	-1.4
0.2173	-0.073	-6.2	-16	-0.369	-2.1
0.2654	-0.084	-7.2	-18	-0.412	-2.5
0.3428	-0.101	-7.2	-20	-0.464	-3.3
0.4205	-0.113	-7.4	-21	-0.505	-3.7
0.5156	-0.125	-9.9	-19	-0.514	-3.8
0.5870	-0.125	-9.3	-17	-0.506	-3.8
0.6977	-0.105	-8.2	-14	-0.410	-3.3
0.8110	-0.070	-6.1	-9	-0.289	-2.4
0.8824	-0.036	-3.8	-6	-0.214	-1.6
1.0000	0.000	0.0	0	0.000	0.0
$T = 288.15 \text{ K}$					
0.0000	0.000	0.0	0	0.00	0.0
0.0478	-0.021	-2.5	-5	-0.106	-0.5
0.1061	-0.041	-3.1	-11	-0.234	-1.0
0.1532	-0.053	-3.8	-15	-0.308	-1.5
0.2173	-0.067	-5.0	-19	-0.371	-2.1
0.2654	-0.076	-5.8	-20	-0.409	-2.4
0.3428	-0.089	-6.3	-22	-0.460	-3.2
0.4205	-0.100	-6.8	-23	-0.507	-3.4
0.5156	-0.103	-8.4	-21	-0.515	-3.5
0.5870	-0.098	-7.9	-19	-0.505	-3.5
0.6977	-0.081	-7.2	-15	-0.410	-3.0
0.8110	-0.050	-5.1	-11	-0.278	-2.1
0.8824	-0.025	-3.1	-7	-0.218	-1.5
1.0000	0.000	0.0	0	0.000	0.0
$T = 303.15 \text{ K}$					
0.0000	0.000	0.0	0	0.000	0.0
0.0478	-0.007	0.6	-9	-0.099	-0.6
0.1061	-0.020	-0.9	-15	-0.217	-1.1
0.1532	-0.035	-1.8	-19	-0.284	-1.6
0.2173	-0.054	-3.1	-23	-0.356	-2.1
0.2654	-0.064	-3.7	-25	-0.415	-2.3
0.3428	-0.077	-5.0	-26	-0.462	-2.8
0.4205	-0.087	-5.9	-26	-0.488	-3.0
0.5156	-0.086	-6.3	-25	-0.490	-3.1
0.5870	-0.079	-5.7	-24	-0.465	-3.0
0.6977	-0.058	-5.7	-18	-0.370	-2.6
0.8110	-0.034	-3.5	-13	-0.297	-1.8
0.8824	-0.021	-2.2	-8	-0.190	-1.3
1.0000	0.000	0.0	0	0.000	0.0

The calculations of the excess molar volume (V^E), excess surface tension (σ^E), deviation in speed of sound (Δu), deviation in isentropic compressibility (Δk_s), and deviation in molar refraction (ΔR) were carried out from the general equation:

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

where ΔY refers to $V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$, $\sigma^E/(\text{mN} \cdot \text{m}^{-1})$, $\Delta u/(\text{m} \cdot \text{s}^{-1})$, $\Delta k_s/(\text{TPa}^{-1})$, and $\Delta R/(\text{cm}^3 \cdot \text{mol}^{-1})$, Y_m and Y_i

Each set of the calculated values ΔY (V^E , σ^E , Δu , Δk_s , and ΔR) was fitted by the Redlich–Kister [15] polynomial equation to derive the binary coefficients A_k :

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

A nonlinear least-squares method was used to estimate the parameters A_k . In each case, the optimum number m of the A_k coefficients ($m = n + 1$) was determined through an examination of the variation of standard deviation (d) according to the equation:

$$d = \left[\sum (\Delta Y_{\text{Calc}} - \Delta Y_{\text{Exp}})^2 / (p - m) \right]^{1/2}, \quad (3)$$

where p represents the number of measurements and m the number of coefficients used for fitting the experimental data in equation (2). The estimated values of A_k and d for V^E , σ^E , Δu , Δk_s , and ΔR are presented in table 4. In all the cases, the best fit in equation (2) was found by using three adjustable fitting coefficients ($m = 3$, $n = 2$). The agreement between the measured excess quantities and those calculated from the Redlich–Kister relation was found to be satisfactory.

The curves of the excess molar volume (V^E) versus the composition of the binary mixtures of MSL with PEN are illustrated in figure 1. The V^E values are negative over the entire range of composition, display a minimum at the composition of $x_1 \approx 0.5$ – 0.6 and become slightly less negative as the temperature increases. The negative V^E values indicate that there is a volume contraction upon mixing which can result from the specific interactions between MSL and PEN molecules in the bulk. The specific interactions amplified at the composition of $x_1 \approx 0.5$ – 0.6 and weakened with the rise of the temperature.

The deviations in isentropic compressibility (Δk_s) are plotted versus the volume fraction of MSL (ϕ_1) in figure 2.

TABLE 4

Parameters of the Redlich–Kister equation (A_k), equation (2), and standard deviations (d), equation (3), of excess functions of MSL/PEN binary mixtures at the temperatures (278.15, 288.15, and 303.15) K

Function	T/(K)	A_0	A_1	A_2	d
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	278.15	-0.488	-0.016	0.110	0.006
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	288.15	-0.408	0.056	0.116	0.003
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	-0.347	0.056	0.232	0.002
$\Delta u/(\text{m} \cdot \text{s}^{-1})$	278.15	-34.62	-1.281	-16.42	1.132
$\Delta u/(\text{m} \cdot \text{s}^{-1})$	288.15	-30.86	-3.397	-3.247	0.576
$\Delta u/(\text{m} \cdot \text{s}^{-1})$	303.15	-25.22	-6.409	15.97	0.393
$\Delta k_s/(\text{TPa}^{-1})$	278.15	-81.69	14.46	13.53	0.899
$\Delta k_s/(\text{TPa}^{-1})$	288.15	-89.30	19.48	2.237	0.481
$\Delta k_s/(\text{TPa}^{-1})$	303.15	-104.4	28.07	-18.64	0.430
$\Delta R/(\text{cm}^3 \cdot \text{mol}^{-1})$	278.15	-2.037	-0.140	-0.185	0.012
$\Delta R/(\text{cm}^3 \cdot \text{mol}^{-1})$	288.15	-2.036	-0.125	-0.170	0.015
$\Delta R/(\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	-1.959	-0.064	-0.092	0.010
$\sigma^E/(\text{mN} \cdot \text{m}^{-1})$	278.15	-15.50	-2.882	4.495	0.082
$\sigma^E/(\text{mN} \cdot \text{m}^{-1})$	288.15	-14.23	-1.655	3.186	0.068
$\sigma^E/(\text{mN} \cdot \text{m}^{-1})$	303.15	-12.23	-0.014	0.194	0.029

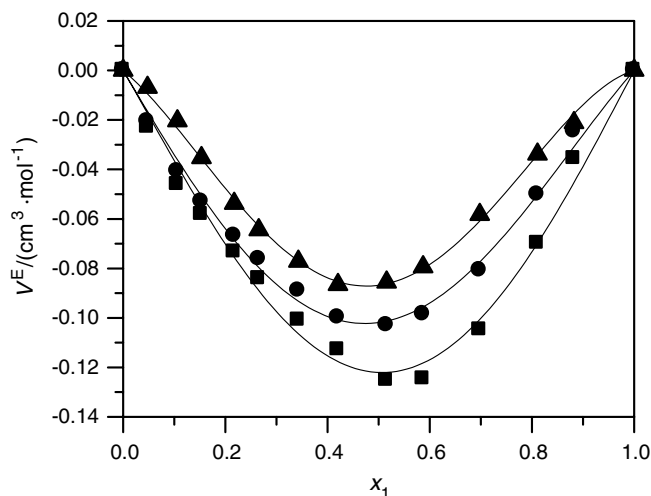


FIGURE 1. Plot of the excess molar volume (V^E) versus the mole fraction of MSL (x_1) for binary mixtures of MSL/PEN at 278.15 K (■), 288.15 K (●) and 303.15 K (▲). The lines correspond to the calculated V^E values according to equation (2).

The observed Δk_s values are negative over the entire concentration range and display a minimum at the composition of $x_1 \approx 0.5$ – 0.6 . The results reveal that the compressibility of the solution diminishes upon mixing which suggests the existence of specific interactions between unlike molecules in the bulk as was indicated by the V^E results. The results for the deviations in molar refraction (ΔR) versus the volume fraction of MSL (ϕ_1) which are displayed in figure 3 exhibit almost the same dependence as the V^E and Δk_s values supporting once more the explanation given above. The ΔR values are independent of the temperature as predicted by the theory, according of which, ΔR depends only on the wavelength of the light used for the measurement [16].

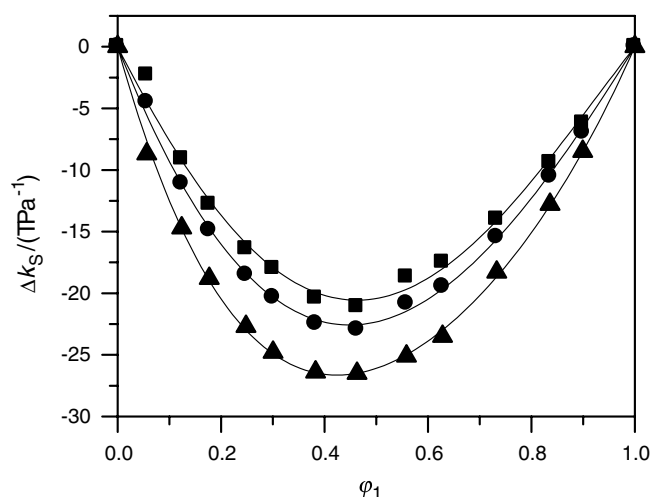


FIGURE 2. Plot of the deviation in isentropic compressibility (Δk_s) versus the volume fraction of MSL (ϕ_1) for binary mixtures of MSL/PEN at 278.15 K (■), 288.15 K (●) and 303.15 K (▲). The lines correspond to the calculated Δk_s values according to equation (2).

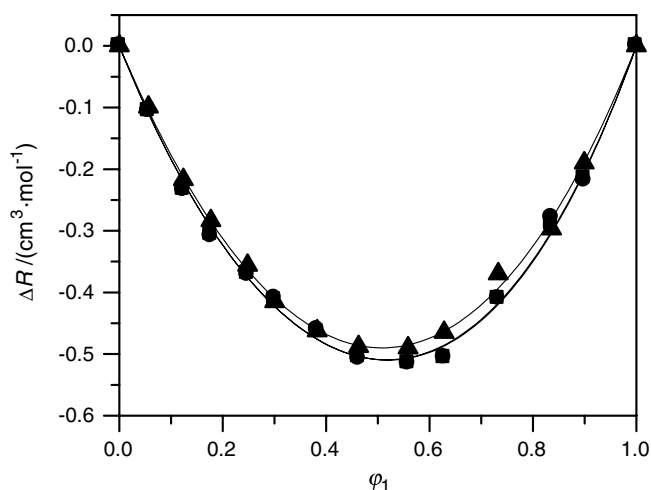


FIGURE 3. Plot of the deviation in molar refraction (ΔR) versus the volume fraction of MSL (ϕ_1) for binary mixtures of MSL/PEN at 278.15 K (■), 288.15 K (●) and 303.15 K (▲). The lines correspond to the calculated ΔR values according to equation (2).

The excess surface tensions (σ^E) are plotted as a function of the composition of the binary mixtures in figure 4. The σ^E values are negative at the whole composition range, pass through a minimum at $x_1 \approx 0.5$ –0.6 and tend to become less negative as the temperature increases. This behaviour is explained by the difference in the distribution of the molecules between the surface and the bulk region of the liquid [17]. It is obvious that the surface concentration of PEN, which is the surfactant component, is higher than its bulk concentration. The attraction of the PEN by the surface can be explained by means of the existence of specific interactions at the surface leading probably to PEN-rich adducts. The specific interactions at the surface appear to be amplified at the composition of $x_1 \approx 0.5$ –0.6 and weakened with the rise of the temperature. This conclusion

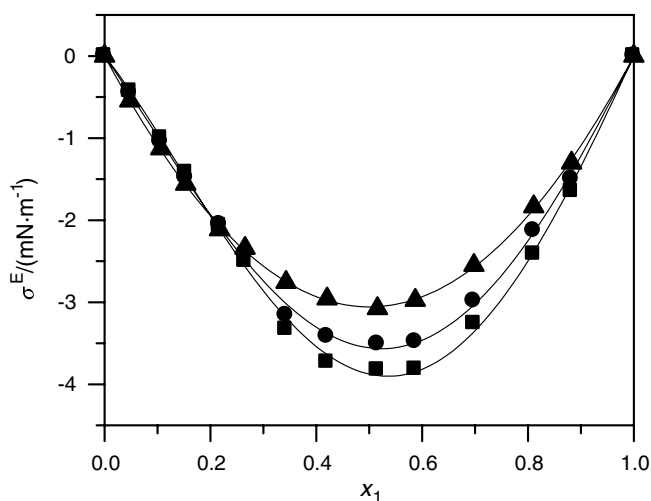


FIGURE 4. Plot of the excess surface tension (σ^E) versus the mole fraction of MSL (x_1) for binary mixtures of MSL/PEN at 278.15 K (■), 288.15 K (●) and 303.15 K (▲). The lines correspond to the calculated σ^E values according to equation (2).

is supported from the values of the surface entropy per unit surface area (S^S) as well as the values of the lyophobicity (β) of PEN, which are given below.

The entropies of the surface formation per unit surface area ($S^S/\text{J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$) have been calculated from the thermodynamic equation of Clapeyron [18,19] modified for liquid surfaces:

$$S^S = -(\partial\sigma/\partial T)_p, \quad (4)$$

where S^S represents the variation of the entropy per unit surface area due to interface formation, which according to equation (4) is equal to the negative temperature coefficient of the surface tension. Considering that the surface enthalpy ($H^S/\text{J} \cdot \text{m}^{-2}$) is the sum of the surface free 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 MSL and PEN binary mixtures have been calculated according to the following equation:

$$H^S = \sigma - T(\partial\sigma/\partial T)_p = \sigma + TS^S. \quad (5)$$

The calculated surface entropies and enthalpies of the binary mixtures are listed in table 5. The values of S^S are plotted versus the mole fraction of MSL (x_1) in figure 5. The position of the minimum of the curve was found to be in the same composition range with that observed for σ^E ($x_1 \approx 0.5$ –0.6). The results demonstrate that the surface becomes less disordered at this composition region suggesting, therefore, the existence of specific interactions at the surface as was indicated by the σ^E results.

In order to study the influence of the bulk composition on the surface tension of the binary mixtures a new model reported by Piñeiro *et al.* [20] (the extended Langmuir model) was applied. This model has been successfully applied also by other researchers for the analysis of the surface tension data of binary mixtures [21,22]. According to this model, the surface of a liquid is considered to be a thin layer of finite depth. At equilibrium the relation between

TABLE 5
Surface entropies (S^S) and surface enthalpies (H^S) per unit surface area for MSL (1)/PEN (2) binary mixtures in the temperature range from 278.15 K to 303.15 K

x_1	$S^S/(\text{mJ} \cdot \text{m}^{-2} \cdot \text{K}^{-1})$	$H^S/(\text{mJ} \cdot \text{m}^{-2})$
0.0000	0.0820	50.38
0.0478	0.0864	51.79
0.1061	0.0864	52.00
0.1532	0.0863	52.22
0.2173	0.0822	51.24
0.2654	0.0735	49.04
0.3428	0.0558	44.47
0.4205	0.0475	42.70
0.5156	0.0463	43.94
0.5870	0.0431	43.66
0.6977	0.0474	46.91
0.8110	0.0521	50.48
0.8824	0.0605	54.63
1.0000	0.0734	61.46

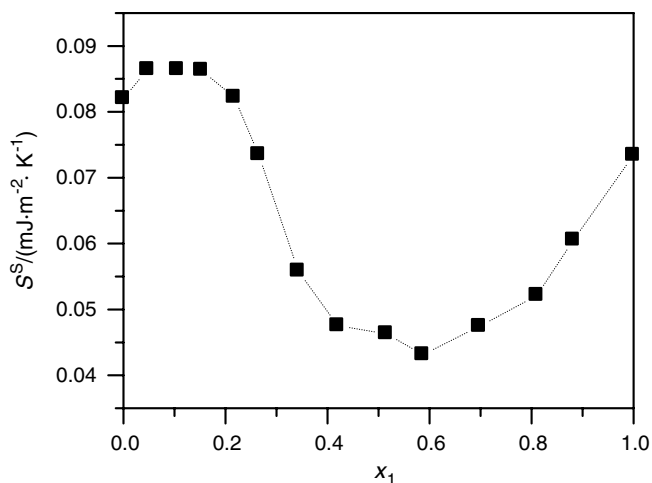


FIGURE 5. Plot of the surface entropy per unit area (S^S) versus the mole fraction of MSL (x_1) for binary mixtures of MSL/PEN in the temperature range from 278.15 K to 303.15 K.

the surface volume fraction (φ_2^S) and the bulk volume fraction (φ_2) of the surfactant component (in the present work PEN) is given by the following equation:

$$\varphi_2^S = \beta \varphi_2 / [1 + (\beta - 1)\varphi_2], \quad (6)$$

where β is a measure of the lyophobicity of the surfactant PEN, which represents its tendency to be adsorbed by 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 $\beta > 1$ demonstrates the greater affinity of the surfactant component for the surface.

According to this model, the surface tensions of the binary mixtures of MSL and PEN are related with the corresponding surface volume fractions by means of the following equation:

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2 - \lambda \varphi_1^S \varphi_2^S (\sigma_1 - \sigma_2), \quad (7)$$

where σ_1 , σ_2 and φ_1^S , φ_2^S are the surface tensions and the surface volume fractions of MSL and PEN, respectively. The factor λ represents the effect of the unlike-pair interactions on the surface tension of the mixture which are related to structural changes. If we assume that the structural changes upon mixing are insignificant (λ becomes 0), the equation (7) simplifies to:

$$\sigma = \varphi_1^S \sigma_1 + \varphi_2^S \sigma_2, \quad (8)$$

Equation (8) offers the opportunity to calculate the surface volume fractions of the two components of the binary mixtures. The combination of the equations (6) and (8) leads to the following relation:

$$(\sigma - \sigma_1)/(\sigma_2 - \sigma) = \beta(\varphi_2/\varphi_1). \quad (9)$$

For the MSL and PEN binary mixtures, the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus φ_2/φ_1 is linear in the concentration range of $0.7346 \geq x_2 \geq 0.1176$, suggesting that the effect of the unlike-pair interactions on the surface tension of the mixture is negligible ($\lambda = 0$) in this concentration range.

The slope of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus φ_2/φ_1 is equal to the value of lyophobicity (β) of PEN. The obtained β values of PEN at 278.15 K, 288.15 K, and 303.15 K are listed in table 6 and plotted as a function of the temperature in figure 6. The obtained β values for PEN are greater than unity and decrease (almost linearly) with the temperature. The results show the greater affinity of PEN for the surface. Furthermore, the results confirm once more that the affinity of PEN for the surface weakens as the temperature increases, as was indicated by the σ^E results.

The surface volume fractions (φ_2^S) of PEN in the composition range $0.7346 \geq x_2 \geq 0.1176$ have been calculated from the following equation:

$$\varphi_2^S = (\sigma - \sigma_1)/(\sigma_2 - \sigma), \quad (10)$$

which results from equation (8) after rearrangement and considering that $\varphi_1^S + \varphi_2^S = 1$. The surface volume fractions (φ_2^S) of PEN have been converted to the surface mole fractions (x_2^S) using the following equation:

$$\varphi_2^S = x_2^S V_2 / (x_1^S V_1 + x_2^S V_2), \quad (11)$$

where x_1^S and x_2^S are the surface mole fraction of MSL and PEN, respectively. The results are tabulated in table 7. The values of the surface mole fraction (x_2^S) of PEN and plotted versus its bulk mole fractions (x_2) are shown in figure 7. The diagram shows that the surface concentration of

TABLE 6
Values of lyophobicity (β) of PEN at the temperatures (278.15, 288.15, and 303.15) K

$T/(K)$	β
278.15	5.45
288.15	4.80
303.15	4.19

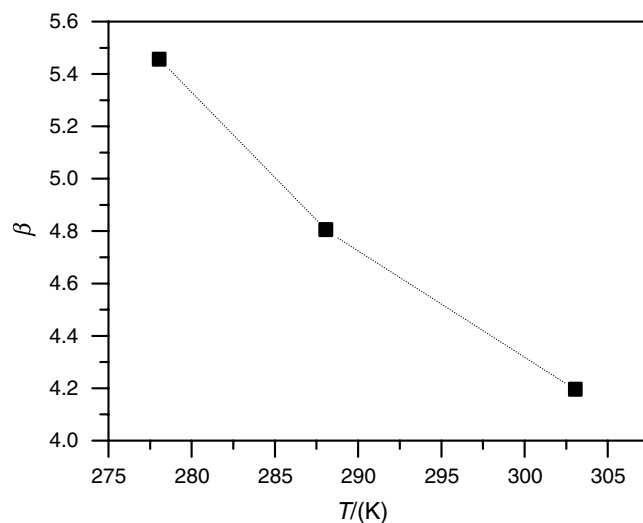


FIGURE 6. Plot of the lyophobicity (β) of PEN versus the temperature (T) in the temperature range from 278.15 K to 303.15 K.

TABLE 7

Bulk mole fractions (x_2) and surface mole fractions (x_2^S) of PEN at the temperatures (278.15, 288.15, and 303.15) K

x_2	x_2^S		
	$T = 278.15$ K	$T = 288.15$ K	$T = 303.15$ K
0.7346	0.9318	0.9247	0.9192
0.6572	0.9179	0.9055	0.8778
0.5795	0.8759	0.8537	0.8217
0.4844	0.7972	0.7741	0.7427
0.4130	0.7311	0.7061	0.6688
0.3023	0.5862	0.5647	0.5309
0.1890	0.4088	0.3855	0.3613
0.1176	0.2728	0.2596	0.2426

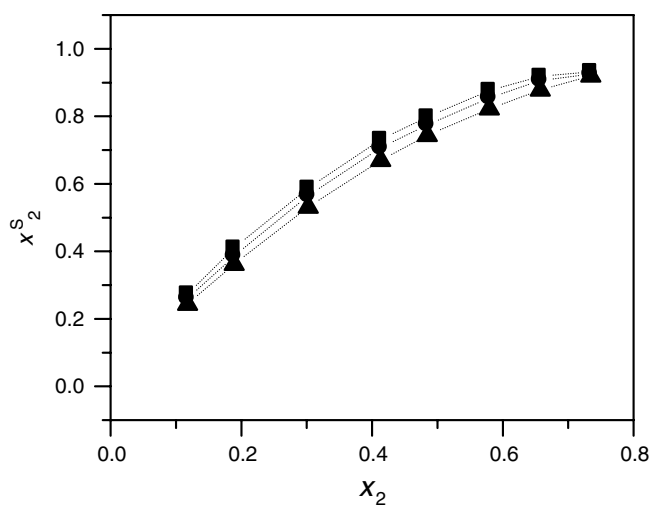


FIGURE 7. Plot of the surface mole fraction (x_2^S) versus the bulk mole fraction (x_2) of PEN in binary mixtures of MSL/PEN at 278.15 K (■), 288.15 K (●) and 303.15 K (▲).

PEN is higher than its bulk concentration indicating the greater affinity of PEN for the surface and confirming, once more, that the formed adducts at the surface are rich in PEN. Furthermore, the rise of the temperature leads to the decrease of x_2^S demonstrating that the attraction of PEN by the surface and thus the interactions at the surface, weaken as the temperature increases. This conclusion is in absolute agreement with the β values of PEN as well as with the σ^E results.

4. Conclusions

The present article reports experimental data of density (ρ), speed of sound (u), isentropic compressibility (k_s), refractive index (n_D), and surface tension (σ) of binary mixtures of methyl salicylate (MSL) with 1-pentanol (PEN) over the entire composition range at the temperatures of 278.15 K, 288.15 K, and 303.15 K. The excess molar volume (V^E), excess surface tension (σ^E), deviation in speed of sound (Δu), deviation in isentropic compressibility (Δk_s), and deviation in molar refraction (ΔR) have been calculated and correlated to the Redlich–Kister relation.

The V^E , Δk_s , and ΔR values are negative over the entire composition range demonstrating the existence of specific interactions between unlike molecules in the bulk. The specific interactions appear to be significant at the equimolar composition ($x_1 \approx 0.5$ – 0.6) and weaken with the rise of the temperature. The σ^E values are negative over the whole composition range indicating that the surface is enriched in the surfactant PEN. According to the σ^E results, specific interactions between unlike molecules extended also at the surface of the liquid, become more significant at the equimolar composition and weaken with the increase of the temperature. The surface entropy per unit surface area (S^S), the lyophobicity (β), and the surface mole fraction (x_2^S) of PEN support this conclusion. According to these results, we conclude that interactions between MSL and PEN leading to the formation of molecular adducts occur in both bulk and surface. The interactions become most significant at the equimolar composition and weaken with the rise of the temperature. The formed molecular adducts at the surface are rich in PEN.

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References

- [1] N.G. Tsierkezos, I.E. Molinou, J. Chem. Eng. Data 43 (1998) 989–993.
- [2] N.G. Tsierkezos, I.E. Molinou, J. Sol. Chem. 35 (2006) 279–296.
- [3] N.G. Tsierkezos, A.C. Filippou, J. Chem. Thermodyn. 38 (2006) 952–961.
- [4] N.G. Tsierkezos, I.E. Molinou, J. Chem. Eng. Data 44 (1999) 955–958.
- [5] N.G. Tsierkezos, M.M. Palaiologou, I.E. Molinou, J. Chem. Eng. Data 45 (2000) 272–275.
- [6] C.R. Schaefer, M.E. Ruiz Holgado, E.L. Arancibia, J. Chem. Eng. Data 47 (2002) 144–148.
- [7] J.M. Resa, C. Gonzalez, J.M. Goenaga, M. Iglesias, J. Chem. Eng. Data 49 (2004) 804–808.
- [8] A. Pal, G. Dass, J. Chem. Eng. Data 44 (1999) 1325–1329.
- [9] A. Pal, G. Dass, J. Chem. Eng. Data 45 (2000) 693–698.
- [10] L. Romani, J. Peleteiro, T.P. Iglesias, E. Carballo, R. Escudero, J.L. Lepido, J. Chem. Eng. Data 39 (1994) 19–22.
- [11] K.S. Kumar, P.R. Naidu, J. Chem. Eng. Data 38 (1993) 156–159.
- [12] W.L. Weng, J. Chem. Eng. Data 44 (1999) 63–66.
- [13] CRC Handbook of Chemistry and Physics, 74th ed., CRC Press, Boca Raton, FL, 1993–1994.
- [14] M.J.W. Povey, S.A. Hindle, J.D. Kennedy, Z. Stec, R.G. Taylor, Phys. Chem. Chem. Phys. 5 (2003) 73–78.
- [15] O. Redlich, A.T. Kister, J. Ind. Eng. Chem. 40 (1948) 341–345.
- [16] P.W. Atkins, Molecular Quantum Mechanics, Oxford University Press, Oxford, 1983.
- [17] C. Pan, C. Ouyang, J. Lin, Y. Rao, X. Zhen, G. Lu, Z. Huang, J. Chem. Eng. Data 49 (2004) 1744–1747.
- [18] R.S. Hansen, J. Phys. Chem. 66 (1962) 410–415.
- [19] M. Aratono, T. Toyomasu, M. Villeneuve, Y. Uchizono, T. Takiue, K. Motomura, N. Ikeda, J. Coll. Interface Sci. 191 (1997) 146–153.
- [20] A. Piñeiro, P. Brocos, A. Amigo, J. Gracia-Fadrique, M.G. Lemus, Langmuir 17 (2001) 4261–4266.

- [21] S. Azizian, N. Bashavard, *J. Chem. Eng. Data* 50 (2005) 1091–1094.
- [22] S. Azizian, N. Bashavard, *J. Coll. Interface Sci.* 286 (2005) 349–354.
- [23] R. Rigglo, H.E. Martlnez, H.N. Söllmo, *J. Chem. Eng. Data* 31 (1986) 235–238.
- [24] W.L. Weng, L.T. Chang, I.M. Shiah, *J. Chem. Eng. Data* 44 (1999) 994–997.
- [25] T.M. Aminabhavi, H.T.S. Phayde, R.S. Khinnavar, *Collect. Czech. Chem. Commun.* 59 (1994) 1511–1524.
- [26] A.F. Ribeiro, E. Langa, A.M. Mainar, J.I. Pardo, J.S. Urieta, *J. Chem. Eng. Data* 51 (2006) 1846–1851.

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