Available online at www.sciencedirect.com

ScienceDirect

J. Chem. Thermodynamics 39 (2007) 1110–1117

JCT

www.elsevier.com/locate/jct

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

Nikos G. Tsierkezos [a,*], Ioanna E. Molinou [b,*]

[a] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, D-12489 Berlin, Germany

[b] Physical Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis, Athens 15771, Greece

Received 20 October 2006; received in revised form 10 January 2007; accepted 11 January 2007
Available online 23 January 2007

## Abstract

Densities ($\rho$), speeds of sound ($u$), isentropic compressibilities ($k_s$), refractive indices ($n_D$), and surface tensions ($\sigma$) 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 ($\sigma^E$), deviations in speed of sound ($\Delta u$), deviations in isentropic compressibility ($\Delta k_s$), and deviations in molar refraction ($\Delta R$) have been calculated. The excess thermodynamic properties $V^E$, $\sigma^E$, $\Delta u$, $\Delta k_s$, and $\Delta R$ 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 ($\sigma$) 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 ($\beta$) 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.


*Keywords:* Excess thermodynamic properties; Extended Langmuir model; Lyophobicity; Methyl salicylate; 1-Pentanol

## 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 binary 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 ($\rho$), speed of sound ($u$), isentropic compressibility ($k_s$), refractive index ($n_D$), and surface tension ($\sigma$) 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 ($\sigma^E$) and the deviations in speed of sound ($\Delta u$), isentropic compressibility ($\Delta k_s$), and molar refraction ($\Delta R$) have been calculated and fitted by the Redlich–Kister polynomial relation. The surface entropies ($S^S$) and the surface

* Corresponding authors. Tel.: +49 30 20937440; fax: +49 30 20937468 (N.G. Tsierkezos).
*E-mail addresses:* tsierkezos@chemie.hu-berlin.de (N.G. Tsierkezos), imolinou@chem.uoa.gr (I.E. Molinou).

0021-9614/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2007.01.008

enthalpies ($H^S$) per unit surface area have been obtained as well. The surface mole fractions ($x_2^S$) and the lyophobicity ($\beta$) 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 ($\rho$), 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 $\rho$, $n_D$, 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 $\pm 0.0001$ g. The possible error in the mole fraction was estimated to be $\pm 0.0001$ in all cases.

### 2.2. Apparatus and procedures

Densities ($\rho$) were measured with an Anton Paar (Model DMA 58, Austria) microcomputer-controlled precision densimeter with a built-in solid-state thermostat controlled to $\pm 0.01$ K and a capacity of *ca.* 1.0 cm$^3$. 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 [13]. The estimated uncertainty of the measured densities was $\pm 0.00005\ \mathrm{g \cdot cm^{-3}}$.

The surface tensions ($\sigma$) 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 $\pm 0.01$ 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 $\pm 0.1\ \mathrm{mN \cdot m^{-1}}$.

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 $\pm 0.01$ 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 $\pm 1\ \mathrm{m \cdot s^{-1}}$. The isentropic compressibility ($k_s$) was calculated from density ($\rho$) 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 $\pm 1\ \mathrm{TPa^{-1}}$.

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 $\pm 0.0001$. The thermostat temperature was constant to $\pm 0.01$ K.

## 3. Results and discussion

The experimental values of density ($\rho$), 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 ($\rho$), 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) | $\rho/(\mathrm{g \cdot cm^{-3}})$ (exp) | $\rho/(\mathrm{g \cdot cm^{-3}})$ (ref) | $n_D$ (exp) | $n_D$ (ref) | $u/(\mathrm{m \cdot s^{-1}})$ (exp) | $u/(\mathrm{m \cdot s^{-1}})$ (ref) |
|---|---|---|---|---|---|---|---|
| PEN | 278.15 | 0.82572 | 0.8259[a] <br> 0.8261[e] | 1.4160 | 1.4159[a] | 1348.6 | 1342[d] |
| PEN | 288.15 | 0.81890 | 0.8189[e] | 1.4118 | | 1312.5 | |
| PEN | 303.15 | 0.80739 | 0.8073[a] <br> 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].