

Investigation of the thermodynamic and physicochemical properties of lavender oil (*Lavandula angustifolia* Mill.)-ethanol-water system

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Abstract: The thermodynamic and physicochemical properties of lavender oil (*Lavandula angustifolia* Mill.)-ethanol-water system were measured. The chemical composition of solutions of the lavender oil in 70%, 75%, 80%, 85%, 90%, and 95% ethanol was determined using GC/MS analysis. The main compounds in the solutions are oxygenated monoterpenes (β -linalool, terpinen-4-ol, α -terpineol, and linalyl acetate), followed by monoterpene hydrocarbons ((*Z*)- β -ocimene and (*E*)- β -ocimene), and sesquiterpene hydrocarbons (β -caryophyllene and (*E*)- β -farnesene). The ternary phase diagrams were constructed. By multiply linear regression model for surface tension prediction was applied. The thermodynamic and kinetic parameters of lavender oil – ethanol - water system were calculated (energy of Gibb's, enthalpy, entropy, energy of activation, and coefficient of diffusion).

1.Introduction

Lavender essential oil is obtained by steam distillation of freshly cut, flowering tops of (*Lavandula angustifolia* Mill. (kind Lamiaceae). The solutions of the lavender essential oil in ethanol with concentration from 70% to 95% are used in different perfumery and pharmaceutical products. The major constituents of the oil are the oxygenated monoterpenes linalyl acetate, β -linalool, terpinen-4-ol, α -terpineol, and lavandulol acetate [1-3]. Influence of the temperature and the pressure on the thermodynamic and thermal properties of solution of different terpenic compounds, for example α - and β -pinene, linalool, borneol, etc., were investigated from different authors [4-11].

The essential oil content in the inflorescence of lavender cultivated in the mid hills of Uttarakhand was investigated. The quality of lavender oil produced in India was found to be comparable to that produced in Hungary, France, China, Bulgaria, Russia, and the USA [12].

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Different studies were provided for described the antibacterial properties of lavender essential oil. Besides, no data exist on its ability to activate human macrophages during the innate response against *Staphylococcus aureus* [13].

Lavender essential oil was used since antiquity as natural active constituents in products designed for dealing with a broad range of issues including those related to human hygiene, health and personal care, and those concerned with organic agriculture and pest management.

Lane and Mahmoud [14] report on the composition and insect repellent properties of the essential oils obtained from 12 varieties of the two most commonly cultivated lavender species (*L. angustifolia* and *L. intermedia*), grown in an experimental plot in the Okanagan Valley of British Columbia, Canada. The oil composition for three lavender oil samples was also analyzed. The results shown that the locally grown plants produce essential oils that are similar to those found in other parts of the world in terms of the overall olfactory properties, and in that they contain the same constituents found in comparable lavender oils.

The extracts obtained from lavender, which were grown in Burdur Örtülü locality, was determined using HPLC and GC-MS analysis. The anti-microbial effect of the essential oil was also investigated. The dried flowers were extracted and the essential oil was distilled from the remaining part. 31 different compounds were determined by GC-MS analysis: Linalool and linalyl acetate have the highest concentration. It was observed that the lavender essential oil could completely remove the contamination caused by the microorganisms as of the 14th day. The essential oil, can be used either directly or incorporated into the cosmetics without the necessity for any other extra preservative [15].

Lavender essential oil was approved by the European Medicines Agency as herbal medicine to relieve anxiety and stress. The capability of the oil to relieve other nervous system disorders such as neuropathic pain has never been established. Oral administration of lavender oil could represent a therapeutic approach in the management of neuropathic pain states [16].

The aim of this study is to be investigating some thermodynamic and thermal properties in the ternary lavender essential oil–ethanol–water system.

2. Material and methods

2.1. Material. For preparation of solutions was used distilled water, lavender essential oil was provided by Kateko Ltd, Bulgaria and 95% ethanol was provided by FILLAB, Bulgaria.

The lavender essential oil was exhibited light yellow color. The main oil has the following properties: density which is determined to 0.8623 ± 0.0 and a refractive index (n_D^{20}) which is determined to 1.4635 ± 0.0 .

2.1.1. Solutions preparation.

To investigate the system 18 solutions between ethanol and lavender essential oil with different quantity of water were prepared. The solutions were divided in six series according the ethanol percent. First series were started with 70% and proceed with step of 5%. Last series solutions were prepared only with 95% pure ethanol.

The prepared solutions were investigated with the ratios between lavender oil and ethanol equals to: 1:5, 1:6 and 1:7. The primary composition of the samples is presented in Table 1.

Table 1. Molar ratio lavender oil: ethanol and prime composition in percent's of 18 solutions

N ^o	Lavender oil: ethanol	ethanol, %	Lavender oil, %	Water, %
1	1:5	70.0	3.3	26.7
2	1:6	70.0	2.5	27.5
3	1:7	70.0	2.5	27.5
4	1:5	75.0	2.5	22.5
5	1:6	75.0	1.7	23.3
6	1:7	75.0	1.7	23.3
7	1:5	80.0	3.3	16.7
8	1:6	80.0	3.4	16.6
9	1:7	80.0	3.4	16.6
10	1:5	85.0	4.2	10.8
11	1:6	85.0	3.4	11.6
12	1:7	85.0	3.4	11.6
13	1:5	90.0	4.2	5.8
14	1:6	90.0	3.4	6.6
15	1:7	90.0	3.4	6.6
16	1:5	95.0	5.0	0.0
17	1:6	95.0	5.0	0.0
18	1:7	95.0	5.0	0.0

2.1.2.Determination of surface tension.

The surface tension of prepared solutions was determined using maximum bubble pressure method. This method is connected with pressure P_{max} indicated as maximum pressure. In following to blow appeared a small bubble in solutions from the end of the capillary. The air bubble was flushed at a constant velocity through the capillary. Pressure was created by means of an aqueous pressure gauge. Surface tension is determined by equation (1)

$$\gamma = \frac{rg}{2}(\Delta H\rho_0 - r\rho) \tag{1}$$

where: *r* – capillary radius in (m), *g* – gravity in (m.s⁻²), *ΔH* – maximum difference in the two gauges of the gauge, *ρ₀*, *ρ*– density of the manometric (water) and test liquid in (kg.m⁻³).

2.1.3.Determination of density in solutions.

The density of liquids was determined by a pycnometer. A well-dried pycnometer was weighed. It is filled with the test liquid of which the density will be determined. After drying, the pycnometer is weighed with the test liquid. It is then emptied, rinsed with ethanol and filled with ethanol. Then, it is weighed again. The density is determined by the equation (2).

The density of the liquids was determined by a pycnometer according to the equation (2).

$$\rho = \frac{m_1 - m}{V} = \frac{m_1 - m}{\frac{m_1 - m}{\rho_1}} = \frac{m_1 - m}{m_2 - m} \rho_1 \quad (2)$$

where: ρ – the density of the test liquid in ($\text{kg}\cdot\text{m}^{-3}$), ρ_1 – the density of ethanol in ($\text{kg}\cdot\text{m}^{-3}$), m – mass of the pycnometer in (g), m_1 – mass of the pycnometer with the test liquid in (g), m_2 – mass of the pycnometer with ethanol in (g).

2.1.4. Determination of refractive index and molar refraction.

Measurements of the refractive index (n_D) were performed at a wavelength equal to 589.3 nm using an Abbe type refractometer. The measurements were used to calculate molar refraction by equation (3).

$$R_m = \frac{(n_D^2 - 1)(x_1 M_1 + x_2 M_2 + x_3 M_3)}{(n_D^2 + 2)\rho} \quad (3)$$

where: R_m – molar refraction in ($\text{m}^3\cdot\text{mol}^{-1}$), ρ – density of the test liquid in ($\text{kg}\cdot\text{m}^{-3}$), n_D – refractive index, x – mole fraction of components, M – molar mass of the component in (kg).

2.1.5. Gas Chromatograph (GC) analysis.

The GC analysis was provided for six samples at all ethanol concentrations in ratio 1:5, which is the highest content of essential oil. This series were contained the following ratio of lavender oil: ethanol = 1:5. The samples contained the largest amount of lavender oil and for this reason they were preferred as quantity of essential oil has an influence in the perfumery.

The GC analysis was performed using a GC Agilent 7890A, an HP-5 ms column (30 m x 250 μm x 0.25 μm), temperature: 35 °C/3 min, 5 °C/min to 250 °C for 3 min, total: 49 min; helium as a carrier gas at 1mL/min constant speed, and 30:1 split ratio.

The GC/MS analysis was carried out on an Agilent 5975C mass spectrometer, using helium as a carrier gas, and the same column and temperature as in the GC analysis.

The identification of chemical compounds was done by comparison to their relative retention indexes and library data. The identified constituents were arranged in order of retention time and quantity in percentage.

2.1.6. Linear regression model.

The surface tension prediction was provided by using of two pressures obtained after providing experiment. Maximum bubble pressure (ΔP) and Laplace pressure were included in the regression model. Their determinations were calculated by the equations (4-5):

$$P_{\max} = \rho g \Delta H \quad (4)$$

$$\Delta P = P_{\max} - P_L \quad (5)$$

where: P_{\max} – maximum bubble pressure in (MPa), P_L – Laplace pressure in (MPa), g – gravity in ($\text{m}\cdot\text{s}^{-2}$), ρ – density in ($\text{kg}\cdot\text{m}^{-3}$).

2.1.6. Thermodynamic and thermal parameters calculations.

Some thermodynamic and thermal properties (Gibbs energy, entropy, enthalpy, thermal conductivity, thermal diffusivity and specific heat capacity) were calculated to determine the stability of the system of lavender oil-ethanol-water [17].

According to the transition state theory are determined activation thermodynamic parameters (equilibrium constant, activation free energy of Gibb's, activation enthalpy and entropy) by known equations [18-22].

Specific heat capacity, thermal conductivity and diffusivity were determined according [22-23].

The molecular diffusion coefficient was calculated according to the Wilke - Chang equation given in [20, 24].

2.1.7. Statistical analysis.

It should be noted that the experiments performed were repeated three times. The results were presented by OriginPro 7.0 software.

3. Results and discussion

Physicochemical properties of lavender oil (*L. angustifolia*)-ethanol-water system as density, surface tension and refractive index were determined experimentally. The obtained results are presented in Table 2. Density and refractive index were used to calculate molar refraction in the system.

Table 2. Density, surface tension, refractive index and molar refraction of 18 experimental solutions

N ^o	Density, ρ , 10^{-3} kg.m ⁻³	Surface tension, γ , mN.m ⁻¹	Refractive index, n_D^{20}	Molar refraction, R_m , 10^{-6} m ³ .mol ⁻¹
1	0.853±0.02	18.555±0.17	1.3827±0.01	10.726±0.11
2	0.849±0.02	14.885±0.13	1.3800±0.01	10.282±0.11
3	0.845±0.02	13.665±0.12	1.3766±0.01	9.983±0.12
4	0.853±0.02	19.780±0.18	1.3820±0.01	11.243±0.12
5	0.852±0.02	14.881±0.13	1.3798±0.01	10.844±0.12
6	0.851±0.02	13.658±0.12	1.3760±0.01	10.565±0.10
7	0.834±0.02	18.578±0.17	1.3827±0.01	11.733±0.12
8	0.833±0.02	16.130±0.15	1.3810±0.01	11.463±0.12
9	0.831±0.02	14.907±0.12	1.3780±0.01	11.188±0.13
10	0.825±0.02	16.139±0.15	1.3820±0.01	12.313±0.12
11	0.822±0.02	14.918±0.13	1.3790±0.01	11.867±0.11
12	0.819±0.02	13.697±0.12	1.3771±0.01	11.607±0.11
13	0.816±0.02	19.825±0.18	1.3801±0.01	12.731±0.13
14	0.812±0.02	18.605±0.17	1.3791±0.01	12.327±0.12
15	0.808±0.02	16.160±0.15	1.3769±0.01	12.041±0.13
16	0.801±0.02	17.884±0.16	1.3808±0.01	13.208±0.13
17	0.799±0.02	16.171±0.15	1.3786±0.01	12.896±0.11
18	0.798±0.02	14.947±0.13	1.3772±0.01	12.677±0.12

The presented results in Table 2 have shown that all physicochemical dimensions decreased their values when ethanol in solutions increased as quantity. Surface tension and

refractive index for pure ethanol are: $\gamma = 22.80 \text{ mN.m}^{-1}$ and $\rho = 0.789 \text{ kg.m}^{-3}$ [17]. The values of refractive index presented some small variations in the last solutions prepared with 90% and 95% ethanol. The refractive index in pure ethanol is 1.3617. In this reason probably decreasing of values of refractive index of solutions with increasing quantity of ethanol led to values closed of pure ethanol.

The surface tension of eighteen experimental solutions was measured. The obtained results are presented in Table 2. It was seen that with increased of quantity of ethanol in solutions, the surface tension decreases. Some of the highest surface tension values is approximately 19.825 mN.m^{-1} . Some low value is approximately 13.697 mN.m^{-1} . The obtained experimental values is in agree with surface tension in pure ethanol equal to 22.80 mN.m^{-1} and water equal to 72.75 mN.m^{-1} [25]. It's known that in perfumery and cosmetics are preferred solutions with high ethanol percent. These results presented ethanol and lavender essential oil as components as stabilized system.

The molar refraction R_m was calculated, too. The molar mass of lavender essential oil was determined experimentally by GC analysis. By application of equation 3, the mole fractions of three main components were calculated and used, too. The results which are shown in Table 2 for molar refraction it's obvious that all values increased with increasing of ethanol percent in solutions. In solutions with 70% ethanol the values is $9.983.10^6 \text{ m}^3.\text{mol}^{-1}$ but in solutions with 95% pure ethanol is $13.208.10^6 \text{ m}^3.\text{mol}^{-1}$. According [6] the molar refraction of mixtures exhibited values between $17\text{-}20.10^6 \text{ m}^3.\text{mol}^{-1}$. The determination of molar refraction of pure water ($3.88.10^6 \text{ m}^3.\text{mol}^{-1}$) and ethanol ($12.54.10^6 \text{ m}^3.\text{mol}^{-1}$) and a mixture of ethanol-water solutions with different concentrations [26] compared with results obtained in this work ($13.208.10^6 \text{ m}^3.\text{mol}^{-1}$) and good agreement was observed.

Six from all solutions were investigated with GC analysis. The experimental results for chemical compositions of lavender essential oil: ethanol = 1:5 are presented in Table 3. The solutions contained the largest amount of lavender essential oil were preferred because the investigation is connected with the perfumery.

- In the solution prepared with lavender essential oil with 70% ethanol was identified 42 components representing 99.43% of the total content. Six of them were in concentrations above 1% and the rest 36 constituents were in concentrations under 1%. The main components in the solution (above 2%) were: β -linalool (48.30%), linalyl acetate (26.14%), terpinen-4-ol (5.40%), and α -terpineol (5.05%).

- In the solution prepared with lavender essential oil with 75% ethanol was identified 42 components representing 98.98% of the total content. Eight of them were in concentrations above 1% and the rest 34 constituents were in concentrations under 1%. The main components in the solution (above 2%) were: β -linalool (54.13%), linalyl acetate (20.81%), terpinen-4-ol (6.24%), and α -terpineol (3.82%).

- In the solution prepared with lavender essential oil with 80% ethanol was identified 42 components representing 98.39% of the total content. Six of them were in concentrations above 1% and the rest 34 constituents were in concentrations under 1%. The main components in the solution (above 2%) were: β -linalool (51.14%), linalyl acetate (23.80%), terpinen-4-ol (6.04%), and α -terpineol (3.52%).

- In the solution prepared with lavender essential oil with 85% ethanol was identified 42 components representing 98.67% of the total content. Seven of them were in concentrations above 1% and the rest 35 constituents were in concentrations under 1%. The main components in the solution (above 2%) were: β -linalool (49.07%), linalyl acetate (25.00%), terpinen-4-ol (5.89%), and α -terpineol (3.25%).

- In the solution prepared with lavender essential oil with 90% ethanol was identified 42 components representing 97.95% of the total content. Six of them were in concentrations above 1% and the rest 36 constituents were in concentrations under 1%. The main

components in the solution (above 2%) were: β -linalool (46.20%), linalyl acetate (28.30%), terpinen-4-ol (5.73%), and α -terpineol (2.96%).

- In the solution prepared with lavender essential oil with 95% ethanol was identified 42 components representing 97.37% of the total content. Seven of them were in concentrations above 1% and the rest 35 constituents were in concentrations under 1%. The main components in the solution (above 2%) were: β -linalool (38.75%), linalyl acetate (33.10%), terpinen-4-ol (4.92%), lavandulol acetate (2.40%), and α -terpineol (2.38%).

Table 3. Chemical composition of the six investigated samples between lavender essential oil and ethanol after GC analysis

Name	70% ethanol	75% ethanol	80% ethanol	85% ethanol	90% ethanol	95% ethanol
n-Hexanol	0.08±0.0	0.09±0.0	0.08±0.0	0.07±0.0	0.06±0.0	0.04±0.0
α -Pinene	0.08±0.0	0.17±0.01	0.14±0.01	0.12±0.01	0.18±0.01	0.13±0.01
Camphene	0.07±0.0	0.11±0.01	0.09±0.0	0.07±0.0	0.12±0.01	0.11±0.01
Sabinene	0.08±0.0	0.04±0.0	0.05±0.0	0.03±0.0	0.04±0.0	0.07±0.0
β -Pinene	0.06±0.0	0.06±0.0	0.05±0.0	0.04±0.0	0.07±0.0	0.13±0.01
n-Octan-1-en-3-ol	0.73±0.06	0.86±0.07	0.82±0.07	0.76±0.06	0.72±0.06	0.55±0.05
n-Octanone-3	0.54±0.04	0.59±0.05	0.57±0.05	0.60±0.05	0.56±0.04	0.60±0.05
Myrcene	0.18±0.01	0.16±0.01	0.19±0.01	0.22±0.01	0.28±0.02	0.35±0.03
n-Butyl butyrate	0.05±0.0	0.04±0.0	0.07±0.0	0.05±0.0	0.06±0.0	0.08±0.0
n-Octan-2-ol	0.12±0.01	0.13±0.01	0.15±0.01	0.11±0.01	0.12±0.01	0.14±0.01
n-Hexyl acetate	0.32±0.02	0.30±0.02	0.35±0.03	0.38±0.03	0.40±0.03	0.43±0.03
<i>p</i> -Cymene	0.05±0.0	0.07±0.0	0.04±0.0	0.06±0.0	0.07±0.0	0.16±0.01
Limonene	0.07±0.0	0.07±0.0	0.05±0.0	0.07±0.0	0.08±0.0	0.17±0.01
Eucalyptol	0.55±0.04	0.58±0.05	0.51±0.04	0.57±0.05	0.59±0.05	0.73±0.07
β -(Z)-Ocimene	0.80±0.07	0.52±0.04	0.69±0.05	0.86±0.07	0.94±0.08	1.81±0.17
β -(E)-Ocimene	0.27±0.02	0.18±0.01	0.24±0.02	0.30±0.02	0.33±0.02	0.57±0.04
<i>cis</i> -Linalyl oxide	0.38±0.03	0.52±0.04	0.41±0.03	0.39±0.03	0.34±0.03	0.28±0.02
<i>trans</i> -Linalyl oxide	0.24±0.02	0.32±0.02	0.26±0.01	0.23±0.01	0.20±0.01	0.17±0.01
β -Linalool	48.30±4.50	54.13±5.50	51.14±5.00	49.07±4.80	46.20±4.50	38.75±3.50
Ethyl heptanoate	0.94±0.08	0.85±0.07	0.97±0.08	1.08±0.09	1.24±0.10	1.42±0.12
Heptyl acetate	0.04±0.0	0.06±0.0	0.08±0.0	0.06±0.0	0.04±0.0	0.09±0.0
Camphor	0.35±0.03	0.38±0.03	0.37±0.03	0.35±0.03	0.34±0.03	0.30±0.02
Lavandulol	0.86±0.07	1.05±0.09	0.98±0.08	0.91±0.08	0.85±0.07	0.66±0.05
Borneol	1.51±0.13	1.83±0.17	1.68±0.15	1.61±0.15	1.48±0.13	1.17±0.10
Terpinen-4-ol	5.40±0.50	6.24±0.60	6.04±0.58	5.89±0.55	5.73±0.53	4.92±0.45
Cryptone	0.68±0.05	1.02±0.09	0.77±0.06	0.68±0.05	0.59±0.04	0.49±0.03
n-Butyl hexanoate	0.08±0.0	0.10±0.0	0.10±0.0	0.21±0.02	0.17±0.01	0.28±0.02

α -Terpineol	5.05±0.49	3.82±0.37	3.52±0.42	3.25±0.30	2.96±0.25	2.38±0.25
Ethyl octanoate	0.18±0.01	0.20±0.01	0.20±0.01	0.20±0.01	0.10±0.0	0.10±0.0
Nerol	0.53±0.04	0.56±0.04	0.60±0.05	0.50±0.04	0.50±0.04	0.30±0.02
Geraniol	0.29±0.01	0.31±0.02	0.30±0.02	0.20±0.01	0.20±0.01	0.20±0.01
Linalyl acetate	26.14±0.2 5	20.81±0.1 9	23.80±0.2 2	25.00±0.2 4	28.30±0.2 7	33.10±0.3 1
Name	70% ethanol	75% ethanol	80% ethanol	85% ethanol	90% ethanol	95% ethanol
<i>p</i> -Menth-1-en-7-al	0.16±0.01	0.12±0.01	0.0	0.10±0.0	0.0	0.10±0.0
Lavandulol acetate	1.52±0.14	1.33±0.12	1.60±0.15	1.80±0.17	2.00±0.19	2.40±0.23
Linalool propanoate	0.26±0.02	0.39±0.03	0.20±0.01	0.20±0.01	0.10±0.0	0.24±0.02
Neryl acetate	0.23±0.02	0.20±0.01	0.20±0.01	0.30±0.02	0.40±0.03	0.41±0.03
Geranyl acetate	0.52±0.04	0.46±0.03	0.56±0.04	0.60±0.05	0.68±0.06	0.96±0.08
β -Caryophyllene	0.43±0.03	0.25±0.02	0.33±0.03	0.40±0.03	0.58±0.05	1.52±0.14
β -(Z)-Farnesene	0.11±0.01	0.14±0.01	0.08±0.0	0.10±0.0	0.16±0.01	0.51±0.04
β -(E)-Farnesene	0.14±0.01	0.10±0.0	0.06±0.0	0.08±0.0	0.09±0.0	0.12±0.01
Caryophyllene oxide	0.23±0.02	0.11±0.01	0.25±0.02	0.30±0.02	0.33±0.03	0.58±0.05
α -Cadinol	0.07±0.0	0.16±0.01	0.10±0.0	0.13±0.01	0.10±0.01	0.14±0.01
oxygenated hydrocarbons, %	3.81	4.26	4.21	4.35	4.21	4.40
monoterpene hydrocarbons, %	1.63	1.33	1.52	1.74	2.06	3.41
oxygenated monoterpenes, %	93.52	93.58	93.41	92.82	92.38	89.10
phenyl propanoids%	0.05	0.07	0.04	0.06	0.07	0.16
sesquiterpene hydrocarbons, %	0.69	0.49	0.47	0.59	0.84	2.19
oxygenated sesquiterpene, %	0.30	0.27	0.36	0.44	0.44	0.74

In this study, the oxygenated monoterpenes and oxygenated hydrocarbons were the dominant groups of chemical components in the solutions according to Table 3. From obtained experimental data it can be seen that low composition of hydrocarbons at small ethanol concentrations is connected with their difficult solubility. With increase of ethanol concentration, the oxygen monoterpenes content decreased but hydrocarbons increased.

GC analysis of six solutions the main components were determined. In the solutions they are oxygenated monoterpenes: β -linalool, terpinen-4-ol, α -terpineol, linalyl acetate with up to 5%. The results are used to construct experimental phase diagrams. Two phase diagrams for solutions prepared with 75% and 80% ethanol are presented in Figs. 1-2. These two solutions were preferred because the main components β -linalool and linalyl acetate exhibited highest values in these solutions. Fig. 1 presented results for the solution with 75% ethanol. The symbols denoted the point of equilibrium between each tree component (oil-ethanol-water) total compositions of each sample. In the phase diagram four primary compounds were observed: β -linalool, terpinen-4-ol, α -terpineol, linalyl acetate and the equilibrium points they form with ethanol and water. The lines shown the tie-lines for the components connected with the equilibrium state in the system. Fig. 2 presented the same phase diagram at 80% ethanol and the components: β -linalool, terpinen-4-ol, α -terpineol, linalyl acetate and equilibrium points between these and ethanol. The lines presented again the tie-lines connected with the equilibrium state in the system.

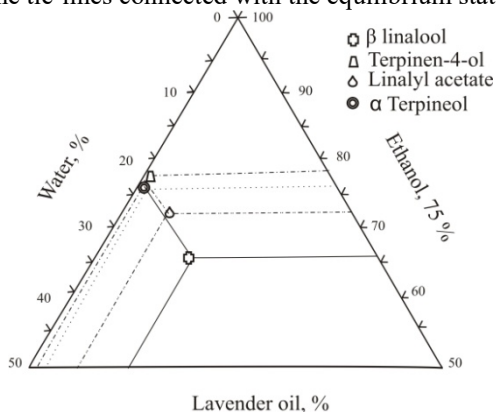


Fig. 1 Partial phase diagram for solution prepared with 75% ethanol in lavender essential oil-ethanol-water system

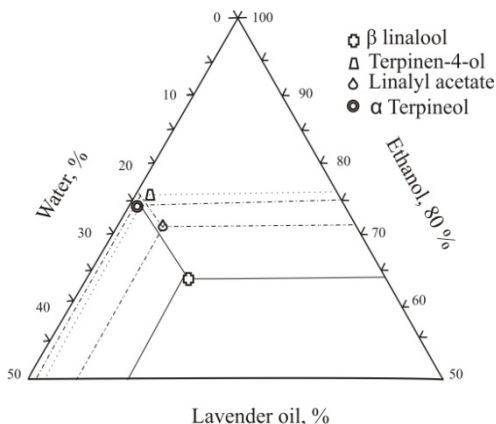


Fig. 2 Partial phase diagram for solution prepared with 80% ethanol in lavender essential oil-ethanol-water system

Between figures 1 and 2 appeared small differences in component β -linalool. At solution prepared with 75% the component is equal to 54.13% but at solution with 80% ethanol is 51.14%. With increasing of ethanol percent the β -linalool percent decreased. Opposite values for linalyl acetate increased with increasing of ethanol percent. At solution prepared with 75% is 20.81% but at solution with 80% ethanol is 23.80%. These differences in chemical compositions are connected with different properties and stability of the systems, probably.

Multiple linear regression. To estimate the surface tension from two pressures, a multiple linear regression model was developed [14] using the values shown in Figs. 3 and 4. Fig. 3 presented values of surface tension with dependence of density and Laplace pressure. Fig. 4 presented values of surface tension with dependence of density and maximum bubble pressure. Almost linear dependence and preferable correlation has been observed. As can be seen from the figure, there is a preferable correlation between the two tensions. According to these results two equations were obtained. In the equations “x” interacts in equation (6) with a maximum bubble pressure and in equation (7) with Laplace pressure. A high coefficient of correlation ($R^2 = 0.999$ and $R^2 = 0.905$) indicates the excellent correlations between experimental and calculation values of surface tension.

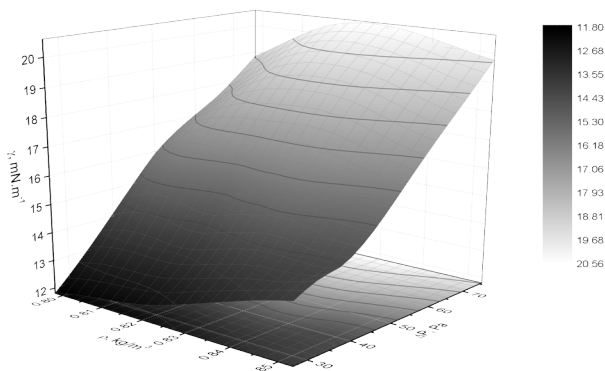


Fig. 3 Presents values of surface tension with dependence of density and Laplace pressure.

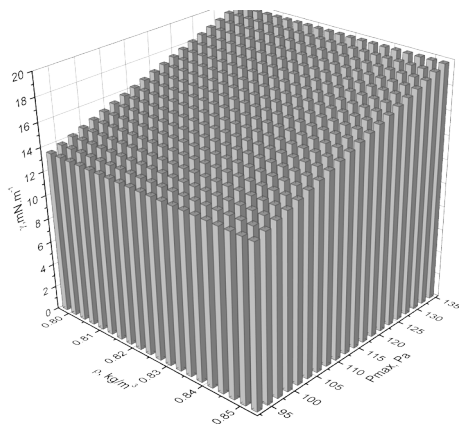


Fig. 4 Presents values of surface tension with dependence of density and maximum bubble pressure.

$$P_{\max} = -0.371 + 0.150.x, R^2 = 0.999 \tag{6}$$

$$\Delta P = 9.00 + 0.433.x, R^2 = 0.905 \tag{7}$$

To estimate the surface tension from composition of oxygenated monoterpenes, a multiple linear regression model was developed using the values showed in Table 2 and Table 3. The model is shown in equation 8. Coefficient of correlation is $R^2 = 0.832$.

$$\gamma = -211.878 + 5.284.L - 19.393.T-4-ol - 5.284.T + 3.970.La. \tag{8}$$

where: γ – surface tension; L – β -linalool; T-4-ol – terpinen-4-ol; T - α -terpineol; La - linalyl acetate.

According to the transport theory, the values of the activating enthalpy, entropy and Gibbs energy for the transition state and for the final state of the investigated solutions of lavender oil-ethanol-water are calculated and are presented in Table 4. The value of the activating energy was calculated according to [19], which is 5726.07 kJ.mol⁻¹. As can be seen from the presented results in the transient state, the values of the activating thermodynamic parameters are negative and decrease with increasing lavender oil: ethanol ratio of the tested solutions.

Table 4. Thermodynamic parameters of experimental lavender solutions

№	K [#]	$\Delta G^\#$	$\Delta S^\#$	$\Delta H^\#$	ΔG	ΔS	ΔH
		kJ.mol ⁻¹	kJ.mol ⁻¹ K ⁻¹	kJ.mol ⁻¹	kJ.mol ⁻¹	kJ.mol ⁻¹ K ⁻¹	kJ.mol ⁻¹
1	3.052	-2705.956	-9.076	-2715.032	-2765.837	9.929	194.398
2	2.447	-2169.726	-7.277	-2177.003	-2217.740	11.767	1290.592
3	2.273	-1991.770	-6.680	-1998.450	-2035.847	12.377	1654.379
4	3.580	-3093.215	-10.375	-3103.590	-3161.666	8.601	-597.259
5	2.609	-2326.068	-7.802	-2333.870	-2377.542	11.231	970.987
6	2.412	-2134.816	-7.160	-2141.976	-2182.058	11.887	1361.956
7	3.588	-3098.340	-10.392	-3108.732	-3166.904	8.583	-607.737
8	3.032	-2689.772	-9.022	-2698.794	-2749.295	9.984	227.482
9	2.787	-2485.651	-8.337	-2493.988	-2540.657	10.684	644.758
10	3.255	-2862.425	-9.601	-2872.026	-2925.768	9.392	-125.465
11	2.976	-2645.158	-8.872	-2654.030	-2703.694	10.137	318.685
12	2.722	-2428.495	-8.145	-2436.640	-2482.236	10.880	761.601
13	4.637	-3720.434	-12.478	-3732.912	-3802.765	6.451	-1879.457
14	4.218	-3490.448	-11.707	-3502.155	-3567.690	7.239	-1409.307
15	3.490	-3031.359	-10.167	-3041.527	-3098.441	8.813	-470.811
16	4.326	-3551.819	-11.913	-3563.731	-3630.418	7.029	-1534.764
17	3.759	-3211.219	-10.770	-3221.989	-3282.281	8.197	-838.490
18	3.400	-2967.899	-9.954	-2977.853	-3033.577	9.031	-341.081

K[#] - equilibrium constant of the transition state; $\Delta G^\#$ - is the activation free energy or Gibb's energy, kJ.mol⁻¹; $\Delta S^\#$ - is the activation entropy, kJ.mol⁻¹K⁻¹; $\Delta H^\#$ - is the activation enthalpy, kJ.mol⁻¹; ΔG - the free energy or Gibb's energy, kJ.mol⁻¹; ΔS - is the entropy, kJ.mol⁻¹K⁻¹; ΔH - is the enthalpy, kJ.mol⁻¹.

This means that in addition to the temperature as a factor influencing the thermodynamic parameters, the ratio of raw material: solvent in the studied solutions is also important. According to the obtained results, the negative values of activation entropy $\Delta S^\#$ indicated the process was less random and non-spontaneous. The formation of activated complex due to the association mechanism is responsible for negative values of entropy. The negative values for Gibbs free energy change of the solution for ternary system specific that process was spontaneous, as shown by the values for the transient and final

state. Which is probably due to better solubility of lavender oil in a solution with ethanol and water (better solubility of the main components of lavender oil in these solutions).

For the solutions of lavender oil-ethanol-water according to the Willie-Cheng equation, the internal molecular diffusion of the solutions at temperature ($T = 298.15 \text{ K}$) and solvent ethanol was calculated, the value of the diffusion coefficient is $D = 56.27 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

Based on the obtained values for the final state of enthalpy, the specific heat capacity of the lavender oil-ethanol-water solutions was calculated. The coefficient of thermal conductivity is calculated, which is a thermophysical characteristic of bodies and depends on many factors, but is usually determined by empirical dependencies. Using them [27], the thermal conductivity of a solution of lavender oil-ethanol-water was calculated.

The coefficient of thermal conductivity is also calculated, representing the ratio of the coefficient of thermal conductivity related to the specific heat capacity for the studied solutions.

The higher value of λ connected with the faster temperatures in the system equalize, or the faster given environment conducts heat. Thermal conductivity is a property of material [23]. According the experimental results the thermal properties of the system were calculated and presented in Table 5. The specific heat capacity increases with increasing ethanol concentration and with increasing lavender oil: ethanol ratio. The values for the specific heat capacity are similar to the values obtained with the linalyl acetate-ethanol-water solution presented in [22]. Due to the fact that linalyl acetate is one of the main components in lavender oil, probably. The difference between linalyl acetate and lavender solutions is based on lower values for specific heat capacity, which is probably due to the fact that lavender solutions involve the main components of lavender oil. The obtained results on the coefficient of thermal conductivity and thermal diffusivity for solutions of lavender oil-ethanol-water are close to the values for solutions of linalool-ethanol-water presented in [17, 22], which is explained by the fact that the components involved in the solutions are oxygen-containing monoterpenes.

Table 5. Thermal parameters of lavender oils solution

No	$c_p, \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\lambda \cdot 10^3, \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	$a \cdot 10^6, \text{ m}^2 \cdot \text{s}^{-1}$
1	35.073	330.364	9.419
2	33.279	330.366	9.927
3	31.661	330.368	10.435
4	37.985	330.364	8.697
5	36.379	330.364	9.081
6	34.459	330.365	9.587
7	41.494	330.374	7.962
8	39.012	330.374	8.468
9	37.840	330.375	8.731
10	44.157	330.379	7.482
11	42.669	330.38	7.743
12	40.658	330.382	8.126
13	47.294	330.384	6.986
14	45.582	330.386	7.248
15	43.287	330.388	7.632
16	52.635	330.392	6.277
17	50.554	330.393	6.535
18	48.632	330.393	6.794

c_p - specific heat capacity $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; λ - coefficient of thermal conductivity, $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$;
 a - coefficient of thermal diffusivity, $\text{m}^2 \cdot \text{s}^{-1}$.

Three thermal parameters according calculations obtained in this work: $\lambda = 0.33 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$; $C_p = 31.661 - 52.635 \text{ kJ} \cdot \text{mol}^{-1} \text{K}^{-1}$; $a = 6.277 - 10.435 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$. In literature are given results for same components of essential oil linalool and linalyl acetate, and the results compared with literature data for the same parameters, obtained experimentally [17, 22, 27].

4. Conclusions

Lavender oil-ethanol-water systems were investigated by different methods. Some physicochemical and thermal properties in the system were calculated. Density, surface tension and refractive index were determined experimentally. They are decreased when ethanol in solutions increased as quantity. These results presented lavender essential oil as component that stabilized system. Molar refraction of solutions was obtained with calculations. The values were between $9.98 \cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ in solutions with 70% ethanol and $13.21 \cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$ in solutions with 95% ethanol. Two phase diagrams are presence at 75% and 80% ethanol in solutions. In the two phase diagrams four main components β -linalool, terpinen-4-ol, α -terpineol, and linalyl acetate are presence. Three thermal parameters according calculations obtained in this work presented values: $\lambda = 0.33 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$; $C_p = 31.661 - 52.635 \text{ kJ} \cdot \text{mol}^{-1} \text{K}^{-1}$; $a = 6.277 - 10.435 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$. The multiple linear regressions, preferable correlation between experimental surface tension values was obtained. A high coefficient of correlations was observed in three dependent and independent variables; $R^2 = 0.999$ and $R^2 = 0.905$, for pressures and $R^2 = 0.832$ for chemical composition of monoterpenes.

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