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## Studies Of Physicochemical And Thermal Properties Of Linalool-Ethanol-Water System

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### ABSTRACT

Some physicochemical and thermal properties of ( $\pm$ ) linalool - ethanol - water solutions with different ethanol concentrations were determined. The molar refraction was calculated and determined that decrease with increase of ethanol solvent in each series of solutions. Thermodynamic and thermal properties were calculated to describe the stability of the system. Multiply linear regression model was obtain for surface tension prediction. Good correlation was observed between calculated and experimental surface tension values.

**Keywords:** ( $\pm$ ) Linalool, Surface tension, Heat capacity, Thermal conductivity, Thermal diffusivity

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## INTRODUCTION

Linalool ( $C_{10}H_{18}O$ , 3,7-dimethyl-1,6-octenedien-3-ol, CAS № 78-70-6, Mw154.25), is terpene alcohol. It is colorless liquid with a flowery-fresh odor, reminiscent of lily of the valley [1, 2]. It occurs naturally in many essential oils from different plants [3-7]. Also it can be obtained by isolation from essential oils [4, 8] or synthesis from pinene or methyl heptenone [1, 6]. The essential oils which contained (+) or (-) linalool are with established antimicrobial effect [2, 4, 9-14]. At that reason they find broad application in perfumery, cosmetic and medicine.

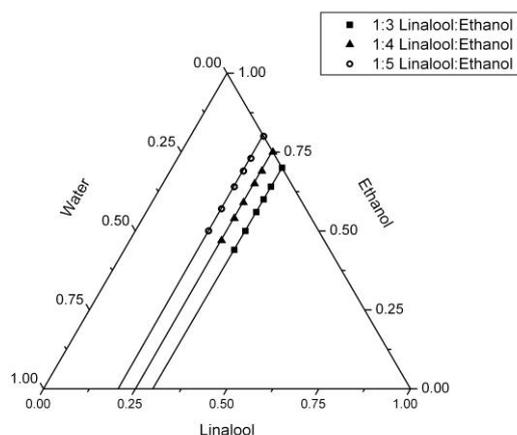
In the perfumery and cosmetic as well the aromatic products so separate aromatic compounds were used in ethanol-water solutions. Concentration of ethanol perfumery may vary from country to country and to brand. Influences of some factors – temperature, pressure, concentration of solvent into solutions of different terpenic compounds were investigated from different authors [15-22]. Density, viscosity, refractive index and surface tension were measured in water-alcohol system. Viscosities and densities at  $T = 298.15$  K, of the phases formed after deterpenation of bergamot, lemon and mint essential oils were determined [23]. Density and viscosity at temperature range between 293.15–373.15 K of pure 1-pentanol, R-(+)-limonene were described by [16] and in binary mixture of {(±)-linalool (1) + propan-1-ol (2)} by [17]. A mathematical model was prepared to investigate physical properties applying the surface tensions of different vegetable oils according the authors [24]. The model was based in the multiple linear regressions fits, based on the experimental data. According Bozikova and Hlavac [25] the thermophysical properties such as temperature, thermal conductivity and thermal diffusivity are very important properties, and there are properties that characterize the heat transfer behavior. The average heat convection coefficients were determined by methodology based on criteria equations for heat transfer processes between air flow in a steel pipe [26].

The aim of this study is to be investigating in deals the thermodynamic and thermal properties in the ternary linalool–ethanol–water system, because the linalool is terrene alcohol, sensitive to light and thermal degradation.

## MATERIALS AND METHODS

Water was distilled, (±) linalool was provided by F. Hoffmann la Roche and 95% ethanol by FILLAB, Bulgaria.

Linalool-ethanol-water solutions: Six series of experiments are being prepared. From the 95% starting ethanol, 70%, 75%, 80%, 85%, 90% ethanol are diluted with distilled water. The last samples were prepared with 95% pure ethanol. Alcoholic solutions were separated in three series of experiments the following ratio of coriander oil:ethanol 1:5, 1:6 and 1:7. In each series we have six samples with the same quantity of coriander oil and different quantities of ethanol+water. The primary composition of the samples is presented in Figure 1.



**Figure 1: Initial composition of six series solutions of linalool-ethanol-water system**

Surface tension, density and refractive index were determined experimentally in previous research. The methods are presented in [27].

Molar refraction is calculated. Measurements of refractive index ( $n_D^{20}$ ) were performed at wavelength equal to 589.3 in nm using refractometer type Abbe. The measurements of refractive index ( $n_D^{20}$ ) and density [27] were used to calculate molar refraction on solutions eq. (1) [17].

$$R_m = \frac{(n_D^2 - 1)(x_1M_1 + x_2M_2 + x_3M_3)}{(n_D^2 + 2)\rho} \quad (1)$$

where:  $\rho$  is the density,  $n_D$  is the refractive index, both measured for the ternary mixture,  $x$  and  $M$  are the mole fraction and molar mass of the  $i$  component, respectively; index 1 – connected with linalool, 2 – with ethanol, 3 – with water.

To obtain model for surface tension prediction the multiple linear regression method was applied. For this purpose Microsoft Excel software was used. The two pressures maximum bubble pressure eq. (2) and Laplace pressure eq. (3) include in the regression model.

$$P_{\max} = \rho g H \quad (2)$$

$$\Delta P = P_{\max} - P_L \quad (3)$$

where:  $P_{\max}$  is maximum bubble pressure;  $P_L$  is Laplace pressure;  $g$  - acceleration of gravity;  $\rho$  is density of the test liquids.

Some thermodynamic and thermal properties were calculated to determine the stability of the system.

$$M = \sum_{i=1}^k m_i \quad (4)$$

The Gibbs energy determined by eq. (5)

$$G_{\text{mix}} = H - TS \quad (5)$$

The activation thermodynamic parameters were calculated in the following equations according to transition state theory [28-31].

The changes values of reaction rate constant can be described by the Arrhenius equation [28, 30]:

$$k = A e^{-E_a / R.T} \quad (6)$$

where:  $k$  is the reaction rate constant;  $E_a$  is the activation energy.

Specific heat capacity, thermal conductivity and diffusivity were determined according [32]. The dependence between them obtained by eq. (7).

$$a = \frac{\lambda}{\rho C_p} \quad (7)$$

where:  $a$  is thermal diffusivity;  $\lambda$  is thermal conductivity;  $C_p$  is specific heat capacity.

## RESULTS AND DISCUSSION

In Table 1 are presented calculated surface tension values using  $P_{\max}$  and  $\Delta P$  pressure according eqs. (2), (3). The calculations were obtained for all 18 samples – six series with different ratio linalool:ethanol.

Comparative analysis was done on Figure 2 and 3 between experimental determined surface tension [27] and calculations.

**Table 1: Eighteen samples with different linalool:ethanol ratio, surface tensions calculated by two types of pressure and calculated molar refraction**

Concentration of ethanol	Ratio linalool:ethanol	$\gamma_{P_{max}}$ mN.m <sup>-1</sup>	$\gamma_{\Delta P}$ mN.m <sup>-1</sup>	$R_m \cdot 10^6$ m <sup>3</sup> .mol <sup>-1</sup>
70	1:3	32.05±0.30	33.27±0.30	13.32±0.12
70	1:4	35.72±0.34	36.16±0.35	12.61±0.11
70	1:5	36.95±0.35	35.27±0.34	11.52±0.10
75	1:3	29.60±0.28	30.65±0.28	14.15±0.13
75	1:4	33.27±0.30	32.14±0.31	12.98±0.11
75	1:5	35.72±0.34	36.13±0.35	11.87±0.10
80	1:3	25.93±0.24	24.72±0.23	15.24±0.14
80	1:4	27.15±0.26	25.69±0.24	14.12±0.13
80	1:5	28.37±0.27	28.48±0.27	13.20±0.12
85	1:3	23.48±0.22	23.06±0.22	14.88±0.13
85	1:4	24.70±0.23	25.85±0.24	13.99±0.12
85	1:5	28.37±0.27	28.68±0.27	13.22±0.12
90	1:3	24.70±0.23	24.32±0.23	15.08±0.14
90	1:4	25.93±0.24	25.20±0.24	14.16±0.13
90	1:5	29.60±0.38	28.46±0.27	13.08±0.12
95	1:3	21.03±0.20	23.59±0.22	14.41±0.13
95	1:4	25.93±0.24	25.66±0.24	14.03±0.13
95	1:5	28.37±0.27	29.50±0.28	13.18±0.12

To estimate the surface tension from different pressures a multiple linear regression model was developed. The obtained model is shown in the following equations [24]. A high coefficient of correlation ( $R^2 = 0.93$ ) indicates the excellent correlation between experimental and calculated values. The standard error (SE = 1.16) shows a low error for the results.

$$\gamma - \text{calculation: } \gamma = 15.64 + 0.23 \cdot x$$

$$\gamma - \text{experimental: } \gamma = 6.61 + 0.72 \cdot x - 0.01 \cdot x^2 + 4.55 \cdot 10^{-5} \cdot x^3$$

$$\text{Correlation coefficient is } R^2 = 0.94$$

Fig. 2 presented experimental and calculation values of surface tension with dependence of  $\Delta P$ . On the figure seen good correlation between two tensions.

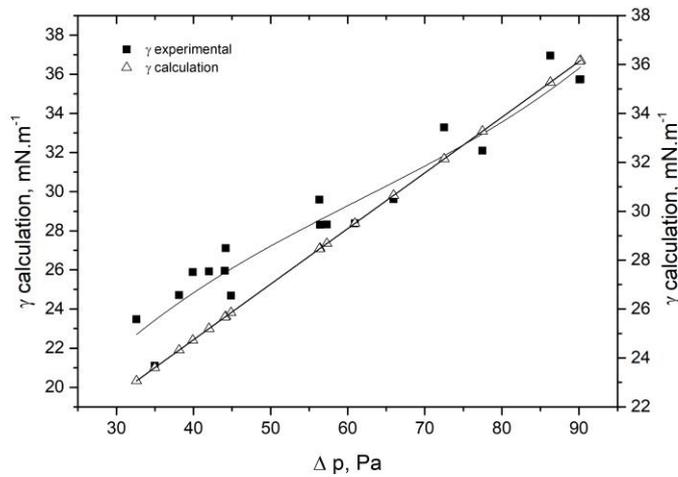


Figure 2: Comparison between experimental surface tension and with calculated values using  $\Delta p$

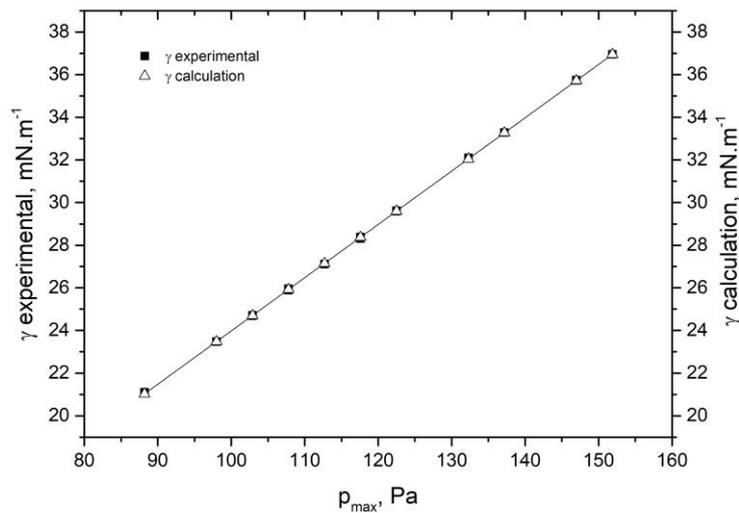


Figure 3: Comparison between experimental surface tension and with calculated values using  $P_{max}$

Fig. 3 presented experimental and calculation values of surface tension with dependence of maximum bubble pressure. It is observed linear dependence and good correlation. A high coefficients of correlation ( $R^2 = 0.99$ ) indicates the excellent correlations between experimental and calculation values of surface tension.

$$\gamma = -1.02 + 0.25.x$$

The molar refraction,  $R_m$ , for the ternary mixtures linalool-ethanol-water was obtained from the measured refractive indexes and density [27] eq. (1). The two parameters were measured for the ternary mixture. According the experimental results [27] the mole fraction ( $x$ ) was determined for each of third components.  $M$  is the molar mass of the components, respectively. The obtained values of molar refractions were between  $11.52 \cdot 10^6 - 15.24 \cdot 10^6$  in  $m^3 \cdot mol^{-1}$ . The results were in agreement with values of molar refraction according literature data. Authors [17] investigated binary mixture linalool-propanol and in a small mole fraction linalool in the system molar refraction exhibit values between  $17 \cdot 10^6 - 20 \cdot 10^6$  in  $m^3 \cdot mol^{-1}$ . According the literature data [33] determined molar refraction of pure water ( $3.88 \cdot 10^6$  in  $m^3 \cdot mol^{-1}$ ) and ethanol ( $12.54 \cdot 10^6$  in  $m^3 \cdot mol^{-1}$ ) and a mixtures ethanol-water with different concentrations. In solution with high % ethanol  $R_m = 13.21 \cdot 10^6$  in  $m^3 \cdot mol^{-1}$ .

The thermodynamic parameters, obtained for ternary mixture linalool-ethanol-water system are presented in Table 2. When investigated mix systems  $G_{\text{mix}}$  exhibit positive values, connected with endothermic process. The activation energy was calculated [29] and exhibit values about 2450 in  $\text{kJ}\cdot\text{mol}^{-1}$ . The activation thermodynamic parameters were calculated according the transition state theory [28-31]. The activation enthalpy  $\Delta H^\ddagger$  and the activation entropy  $\Delta S^\ddagger$  are the reaction enthalpy and reaction entropy of a hypothetical chemical reaction reactants  $\leftrightarrow$  activated complex [34]. According to the obtained results, the negative values of activation entropy  $\Delta S^\ddagger$  indicated that 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 positive values for Gibbs free energy change of the solution for ternary system specific that process was non-spontaneous. It was observed that with increasing the temperature,  $\Delta S$  and  $\Delta H$  values also increased. The above results are in consensus with study of authors [30, 31].

**Table 2: Thermodynamic parameters obtained for ternary mixture linalool-ethanol-water**

M	Ea $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta G^\ddagger$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\ddagger$ J.mol <sup>-1</sup> $^\circ\text{K}^{-1}$	$\Delta H^\ddagger$ $\text{kJ}\cdot\text{mol}^{-1}$	$G_{\text{mix}}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S$ kJ. $\text{mol}^{-1}\text{K}^{-1}$	$\Delta H$ $\text{kJ}\cdot\text{mol}^{-1}$
71.22	2462.31	-16.45	-55.18	-16.51	4265.12	63.41	35346.77
65.26	2460.82	-17.94	-60.16	-17.99	4907.81	68.38	38312.85
59.29	2460.34	-18.42	-61.77	-18.48	5303.34	69.98	39268.21
72.91	2461.33	-17.43	-58.48	-17.49	4165.77	66.69	37308.08
67.22	2459.34	-19.41	-65.10	-19.48	4851.17	73.31	41255.20
61.25	2458.32	-20.43	-68.53	-20.50	5400.60	76.74	43299.49
74.59	2460.99	-17.77	-59.59	-17.83	3884.62	67.81	37972.47
68.62	2460.97	-17.79	-59.67	-17.85	4145.36	67.89	38018.65
63.22	2459.86	-18.89	-63.37	-18.96	4546.22	71.58	40223.29
75.72	2460.74	-18.02	-60.44	-18.08	3696.32	68.66	38480.05
70.31	2459.80	-18.95	-63.57	-19.02	4031.89	71.78	40344.19
64.62	2457.38	-21.37	-71.68	-21.44	4781.19	79.88	45175.37
76.84	2457.34	-21.41	-71.80	-21.48	4101.09	79.99	45243.58
71.43	2456.42	-22.32	-74.86	-22.39	4445.86	83.05	47068.29
65.74	2453.89	-24.84	-83.32	-24.93	5221.44	91.50	52108.73
78.52	2456.40	-22.34	-74.94	-22.419	3827.21	83.14	47116.82
73.12	2451.69	-27.03	-90.67	-27.12	4835.84	98.833	56482.48
67.71	2449.38	-29.35	-98.43	-29.44	5472.91	106.58	61104.03

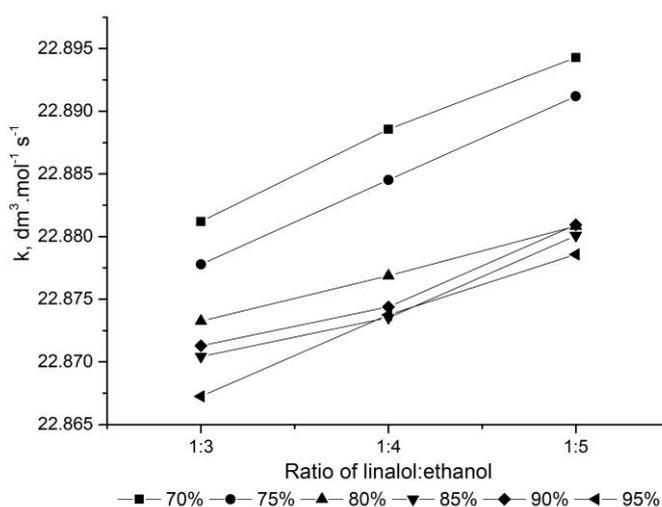
A general observation about liquid thermal conductivities was that they vary only slightly with temperature and are relatively independent of pressure [32]. The higher value of  $\lambda$  connected with the faster temperatures in the system equalize, or the faster given environment conducts heat. In heat transfer analysis, the ratio of the thermal conductivity to the heat capacity is an important property termed the thermal diffusivity ( $a$ ). According the experimental results [27] the thermal properties of the system were calculated and presented in Table 3. Heat capacity is no more change with change between ethanol-water, thermal conductivity had almost constant value, but thermal diffusivity decrease with increase of ethanol content.

**Table 3: Thermal parameters of ternary mixture linalool-ethanol-water**

$C_p$ $\text{kJ}\cdot\text{mol}^{-1}\text{K}^{-1}$	$\lambda$ $10^{-3}$ $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$	$a$ $10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$
3.07	330.39	11.71

3.52	330.38	11.92
3.79	330.37	12.41
2.99	330.38	10.46
3.46	330.38	10.93
3.86	330.37	11.49
2.78	330.36	9.11
2.97	330.35	9.62
3.25	330.34	9.73
2.65	330.37	8.87
2.88	330.37	9.07
3.39	330.35	9.18
2.91	330.38	8.37
3.14	330.37	8.57
3.67	330.37	8.98
2.71	330.41	7.97
3.39	330.38	7.94
3.82	330.38	8.15

Three thermal parameters according calculations obtained in this work are:  $\lambda = 0.33$  in  $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ ;  $C_p = 2.7\text{--}3.8$  in  $\text{kJ}\cdot\text{mol}^{-1}\text{K}^{-1}$ ;  $a = 7.94\cdot 10^{-6}\text{--}12.41\cdot 10^{-6}$  in  $\text{m}^2\cdot\text{s}^{-1}$ . The results compared with literature data for the same parameters, obtained experimentally [33], where  $\lambda = 0.11\text{--}0.28$  in  $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ ;  $C_p = 0.77\text{--}1.99$  in  $\text{kJ}\cdot\text{mol}^{-1}\text{K}^{-1}$ ;  $a = 2.32\cdot 10^{-7}\text{--}3.18\cdot 10^{-7}$  in  $\text{m}^2\cdot\text{s}^{-1}$ .



**Figure 4: Dependence between reaction rates constant, Arrhenius constant and quantity linalool in six series experiment**

The effect of temperature on the reaction rate constant was analysed using Arrhenius relation and presented in Figure 4. On the figure seen results for the rate constant. According the results the constant increase with increase linalool:ethanol ratio. The highest values of rate constant connected with low ethanol concentration, which described with good solubility of linalool in ternary linalool-ethanol-water system.

### CONCLUSIONS

The ternary linalool-ethanol-water system was investigated. Thermodynamic and thermal properties of system were obtained. Multiply linear regression model was developed for surface tension calculated with two pressures  $P_{\max}$  and  $\Delta P$ . High coefficients of correlations ( $R^2 = 0.99$  and  $R^2 = 0.94$ ) were observed. Molar refraction of solutions was calculated and obtained values were between  $13.18\text{--}15.24\cdot 10^6$  in  $\text{m}^3\cdot\text{mol}^{-1}$ . Thermal

conductivity  $\lambda$  and thermal diffusivity exhibit values  $330.38 \cdot 10^{-3}$ - $330.39 \cdot 10^{-3}$  in  $W \cdot m^{-1} \cdot K^{-1}$  and  $7.94 \cdot 10^{-6}$ - $12.41 \cdot 10^{-6}$  in  $m^2 \cdot s^{-1}$  respectively.

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