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Physicochemical, thermodynamic and thermal properties of linalyl acetate-ethanol-water system

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Abstract: Some physicochemical, thermodynamic and thermal properties of linalyl acetate – ethanol - water solutions with different ethanol concentrations (70%, 75%, 80%, 85%, 90%, and 95%) in three ratios (1:5, 1:6, and 1:7) were determined. The properties were calculated to describe the stability of the system. Multiply linear regression model was obtained for surface tension prediction. Good correlation was observed between calculated and experimental surface tension values.

1 Introduction

Linalyl acetate ($C_{12}H_{20}O_2$, M_t 196,29, $bp_{101,3\ kPa}$ 220°C, n_D^{20}25 1.4480) occurs as its (-)-isomer as the main component of many essential oil, for example lavender, lavandin, bergamot, clary sage, *etc*. (±)-Linalyl acetate is synthesized by two methods: esterification of linalool and convertion of dehydrolinalool. It is a colorless liquid with a distinct bergamot lavender odor. Linalyl acetate is an excellent fragrance material for perfumery products, soaps and detergents [1]. Linalyl acetate has antimicrobial action [2-6] and anti-inflammatory activity [7].

In the European Cosmetic Directive is in the list of allergens as natural constituent of plant essential oil or other natural flavoring. These allergens must not exceed the permissible concentration of 0.01% in shower gels and rinse-off products and must not be higher than 0.001% in body oils, massage oils and creams. Sarkic and Stappen [8] reported for dermatitis of the linalool and linalool derivates.

Some physicochemical and thermodynamic properties were studied from different authors. Density, viscosity, refractive index and surface tension in different system and at different temperatures were determined [9-12]. A mathematical model was using to investigate physicochemical properties as surface tensions. The model was based on the multiple linear regressions fits [13, 14]. The thermal properties were investigated and presented by [15-17].

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The aim of this research is an experimental and theoretical study on the some properties for oil dissolve in solutions with different ethanol concentrations and application in different areas.

2 Material and methods

2.1 Materials

All solutions are prepared with distilled water. (±)-Linalyl acetate was provided by F. Hoffmann la Roche (n_D^{20} 1.4630) and 95% ethanol by FILLAB, Bulgaria.

2.1.1 Experiments and procedures

It is determined the surface tension of 18 samples of linalyl acetate:ethanol mixture. Six series of experiments are prepared. The prime composition of all samples is presented in Table 1. From the 95% starting ethanol, 70%, 75%, 80%, 85%, 90% ethanol are diluted with distilled water. The preparation of solutions and the experimental procedure are described [18].

Table 1. Prime composition of three components for of linalyl acetate - ethanol - water system.

Sample	ratio: linalyl acetate - ethanol	Linalyl acetate, %	Ethanol, %	Water, %
1	1:5	30	44	26
2	1:6	25	47	28
3	1:7	20	50	30
4	1:5	30	50	20
5	1:6	25	54	21
6	1:7	20	57	23
7	1:5	30	56	14
8	1:6	25	59	16
9	1:7	20	64	16
10	1:5	30	60	10
11	1:6	25	65	10
12	1:7	20	69	11
13	1:5	30	64	6
14	1:6	25	69	6
15	1:7	20	73	7
16	1:5	30	70	0
17	1:6	25	75	0
18	1:7	20	80	0

2.1.2 Infrared spectroscopy of linalyl acetate

The infrared spectrum was recorded using a Nicolet iS 50 Thermo Scientific FT-IR spectrometer in the frequency region of 4000–400 cm^{-1}, with the samples presented in KBr matrixes.

To obtain model for surface tension prediction the multiple linear regression method was applied. Some thermodynamic and thermal properties were calculated to determine the stability of the system. The obtained surface tension model and thermodynamic and thermal properties were described from authors [14]. The studied physicochemical properties of the solutions (density, refraction and surface tension) are performed at the temperature of 25 ^{0}C and the pressure of 1.10^5 Pa (atmosphere pressure).

The thermodynamic parameters (free energy of Gibb's, entropy, enthalpy, and activation energy) are criterion for thermodynamic stability of system. The calculations for thermodynamic parameters were given for 1 mol according [16, 19].

2.2 Calculation

Specific heat capacity, thermal conductivity and diffusivity were determined according [20].

The reaction rate theory for the dynamic viscosity [21-23] according Eyring was determined by free energy of Gibb's with following equation:

$$\mu = \frac{N.h}{V} e^{\frac{\Delta G}{R.T}} \tag{1}$$

Where: μ is dynamic viscosity, Pa.s; V is molar volume, m^3.mol^{-1}; N is Avagadro's number, mol^{-1}; h is Planck's constant, m^2.kg.s^{-1}; ΔG is free energy of Gibb's, J.kg^{-1}; R is universal gas constant, J.kg^{-1}.K^{-1} and T is temperature, K.

Between dynamic and kinematic viscosity appeared connection which presented for equation:

$$\nu = \frac{\mu}{\rho} \tag{2}$$

Where: ν is kinematic viscosity, m^2.s^{-1}; μ is dynamic viscosity, Pa.s; ρ is density at the corresponding temperature, kg.m^{-3}.

3 Results and discussions

The experimental FT-IR spectrum of linalyl acetate is presents in Fig. 1. From the oil spectrum (Fig. 1) there is a clear line at 2972 cm^{-1} and 2930 cm^{-1}, which is proof of linear γ_{as} CH_3 и γ_{as} $–CH_2–$ bonds. The bands at 3090 cm^{-1} and 1644 cm^{-1} responsible for the presence of $\gamma_{C–H}$ average absorption band, characteristic of R'RC=CH$_2$. There are also characteristic stripes 1739 cm^{-1}, corresponding to oscillation of γC=O conjugated aliphatic esters. A distinctive characteristic strip is outlined 1249 cm^{-1}, characteristic of an ester, which is further confirmed by the strip 1110 cm^{-1}, 1044 cm^{-1} and 1092 cm^{-1}, typical of vinyl =C–O–C, γ^s C–O–C. The IR spectrum of linalyl acetate is presents in Table 2.

The experimental data for properties of solutions of (±)-linalyl acetate and ethanol are presented in Table 2. According the experimental results was obtained that with increasing of dilution, independent on concentration of ethanol, the values of density and surface tension decreasing but the values of refractive index increase. In solutions prepared with ethanol 95%, observed some low values close to density and surface tension of pure ethanol at temperature 20 ^{0}C (ρ_1 = 0,789 kg.m^{-3} and γ = 22,80 mN.m^{-1}) [19].

Table 2. The IR spectrum of linalyl acetate.

Characteristic bands, cm^{-1}		Group type
Linalyl acetate	Reference data	
3455	550 – 3400 3590 – 3420	γOH intramolecular H – bond

3090	3095 – 3075	$\gamma_{C–H}$ average absorption band characteristic of R'RC=CH_2
2972	2970 – 2950	linear γ_{as} CH_3
2930	2940 – 2915	γ_{as} –CH_2–
1739	1740 – 1720	γC=O conjugated aliphatic esters
1644	1648 – 1640	non-conjugated C=C, low intensity. HRC=CH_2 and vinyl
1450	1450 – 1250	some informative stripes δ (OH) for R–O–H
1413	1435 – 1405	- CH_2–CO– vibrations of ketones, δ CH_2
1368	1385 – 1370	a structural fragment of the type $C(CH_3)_2$
1249	1260 – 1240	γ^{as} C–O–C, ether bond
1173	1175 – 1165	absorption band characteristic of a group of type CH_3–CH–CH_3
1110	1150 – 1050	strip characteristic of the γ^{as} C–O–C bond
1092	1150 – 1050	strip characteristic of the γ^{as} C–O–C bond
1044	1070 – 1020	=C–O–C, γ^{s} C–O–C, aromatic and vinyl
923	925 – 905	C–H bond in alkenes of the type HRC=CH_2

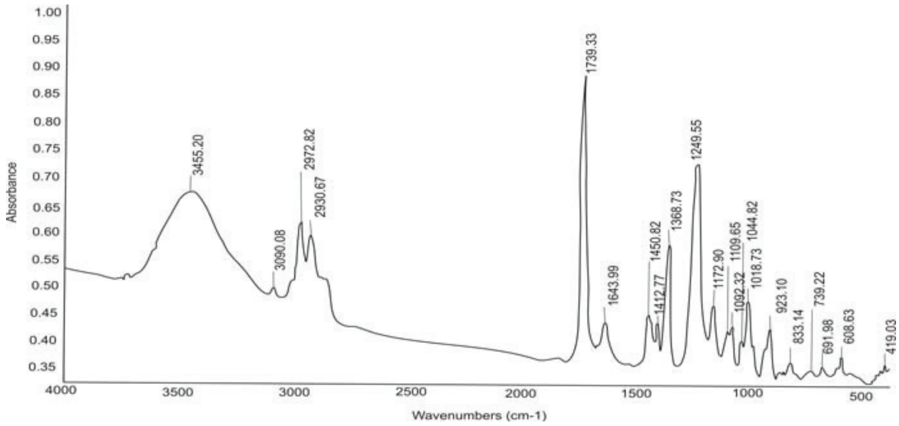

Fig. 1. IR spectrum of linalyl acetate essential oil.

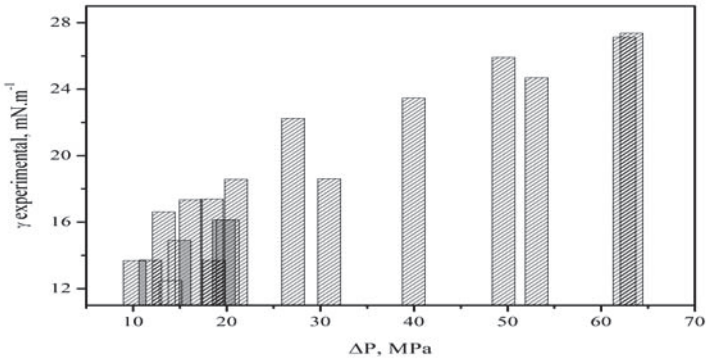

Fig. 2. Dependence of surface tension from Laplace pressure ΔP.

In Fig. 2 the dependences between experimental surface tension and Laplace pressure [14] are presented. It is observed good correlation between them. Small Laplace pressure was observed at small pressure in solutions with high percent ethanol. The studied physicochemical properties of the solutions (density, surface tension, and refraction) are presented in Table 3. The studies were performed at the temperature of 25 ^{0}C and the pressure of 1.10^{5} Pa (atmosphere pressure).

Table 3. Thermodynamic properties of linalyl acetate - ethanol - water solutions.

Ethanol, %	ratio of (±)-linalyl acetate - ethanol	Density, ρ, 10^{-3} kg.m^{-3}	Surface tension, γ, mN.m^{-1}	Refractive index, n_D^{20}
70	1:5	0.854	25.904	1.3788
70	1:6	0.849	17.335	1.3783
70	1:7	0.847	16.112	1.3768
75	1:5	0.848	25.911	1.3803
75	1:6	0.846	23.464	1.3792
75	1:7	0.842	22.244	1.3717
80	1:5	0.837	18.575	1.3807
80	1:6	0.836	17.351	1.3789
80	1:7	0.835	16.617	1.3771
85	1:5	0.835	16.127	1.3820
85	1:6	0.829	14.909	1.3794
85	1:7	0.827	13.687	1.3772
90	1:5	0.825	16.139	1.3815
90	1:6	0.820	13.696	1.3808
90	1:7	0.814	11.253	1.3782
95	1:5	0.807	18.611	1.3818
95	1:6	0.803	17.391	1.3859
95	1:7	0.799	13.721	1.3789

To estimate the surface tension from different pressures a multiple linear regression model was developed. The obtained linear regression based on the equations of authors [13, 14] for the Laplace pressure ΔP and maximum bubble pressure.

It is determined the linear regression equations y = a + b.x, where *a* and *b* are constant, but *x* is Laplace pressure ΔP.

$$y = 11.49 + 0.26.x \qquad (3)$$

For eq. (3) the standard error was calculated for two constant - a = ± 0.76 and b = ± 0.02. The correlation coefficient (R^2 = 0.891) and average value of the correlation coefficient (Adj. R^2 = 0.885) was determined.

Eq. (4) gives possibilities to determine the maximum bubble pressure values P_{max}.

$$y = -0.95 + 0.25.x \qquad (4)$$

The same calculations were prepared as eq. in (4). The standard error for two constant are:a = ± 0.01and b = ± 2.10^{-4}). The correlation coefficient (R^2 = 0.999) and average value of the correlation coefficient (Adj. R^2 = 0.999) was present.

A high coefficient of correlation for eqs. 3 and 4 indicates the excellent correlation between experimental and calculated values. The standard error for each constants show a low error for the results.

The thermodynamic parameters Gibbs free energy, enthalpy and entropy were calculated for the obtained solutions. According different ethanol percent in solutions data are presented in Fig. 3.

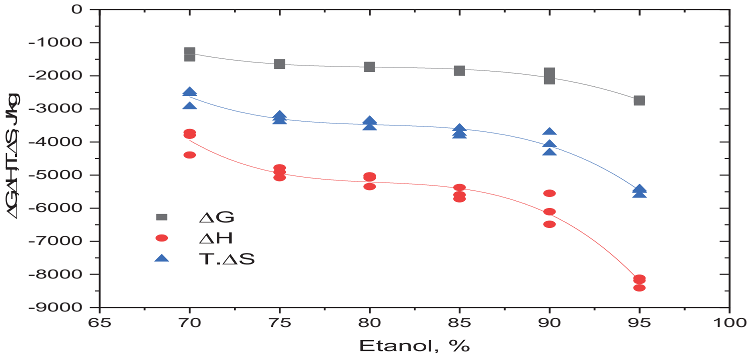

Fig. 3. Thermodynamic parameters of solutions linalyl acetate - ethanol - water system at different ethanol percent.

According graphical dependence from Fig. 3 all thermodynamic parameters are negative and process of dissolution is determined as a spontaneously and irreversible.

Based on the presented graphical dependence, third degree polynomial equations with the average correlation coefficients and the correlation coefficient of each equation are derived to determine the thermodynamic parameters depending on the ethanol concentration in the solution presented in Table 4. The activation energy is calculated too. The determined value is $E_a = -11.42$ kJ.mol^{-1}.

Table 4. Polynomial equations of solutions linalyl acetate - ethanol - water system.

Equations	R^2	Stand. error
$\Delta G = 151268 - 568357.x + 704685.x^2 - 291633.x^3$	0.837	± 0.02
$\Delta H = 454050 - 2.10^6.x + 2.10^6.x^2 - 875374.x^3$	0.837	± 0.06
$T\Delta S = 302782 - 1.10^6.x + 1.10^6.x^2 - 0.58.x^3$	0.837	± 0.09

For the linalyl acetate - ethanol -water system thermal parameters (specific heat capacity, thermal conductivity coefficient, thermal diffusivity coefficient, dynamic, and kinematic viscosity) are calculated and presented in Table 5.

Table 5. Thermal parameters of solutions linalyl acetate - ethanol - water system.

Ethanol, %	Heat capacity, c, kJ.mol^{-1}.K^{-1}	Coefficient of conductivity, $\lambda.10^3$, W.m^{-1}.K^{-1}	Coefficient of thermal diffusivity, $a,10^6$, m^2.s^{-1}	Dynamic viscosity, $\mu.10^{12}$, Pa.s	Kinematic viscosity, $\nu.10^{15}$, m^2.s^{-1}
70	35.90	330.36	10.78	22.51	26.36
70	33.89	330.37	11.48	26.84	31.61
70	32.10	330.37	12.15	30.32	35.78
75	39.00	330.37	9.99	19.99	23.57
75	37.15	330.37	10.51	22.44	26.52
75	35.01	330.37	11.21	25.36	30.12
80	42.69	330.37	9.25	18.65	22.29
80	39.89	330.37	9.91	21.45	25.66
80	38.50	330.37	10.38	23.48	28.12
85	45.56	330.37	8.68	17.48	20.93
85	43.76	330.38	9.11	19.28	23.26

85	41.44	330.38	9.64	21.93	26.52
90	48.85	330.38	8.20	15.38	18.64
90	46.78	330.38	8.61	17.57	21.42
90	44.15	330.38	9.19	20.76	25.50
95	54.79	330.39	7.47	11.40	14.13
95	52.20	330.39	7. 88	12.86	16.02
95	52.26	330.39	7.91	13.92	17.43

From the data of Table 5 can be seen that with increasing of ratio linalyl acetate:ethanol in the solutions with the same percentage concentration of ethanol there is a decreasing in the specific heat capacity, and an increasing in the coefficient of thermal conductivity, as well as the dynamic and kinematic viscosity. This was explained by the fact that these coefficients are additive values and the chemical composition of the substance affects their values. Only the coefficient of thermal conductivity remains the same when the ratio of linalyl acetate: ethanol changes, which means that this coefficient is independent of the nature of the chemical composition of the substances.

In reference [14] are investigated physicochemical and thermal properties of the linalool. The three thermal parameters according calculations obtained in [14] work are: λ = 0.33 W.m-1 K^{-1}, Cp = 2.7 - 3.8 кJ.mol^{-1}K^{-1}and a = 7.94.10^{-6} - 12.41.10^{-6} m^{2}.s^{-1}. The results can't compare with the data for the same parameters in this paper because linalool and linalyl acetate are two compounds with different functional groups: linalool is alcohol and linalyl acetate is ester. In this case it is normal to obtained different values for heat capacities.

4 Conclusion

Different properties of linalyl acetate-ethanol-water system with different ethanol concentrations (70%, 75%, 80%, 85%, 90%, and 95%) were determined. Infrared spectrum analysis was performed and surface tension for all solutions was measured. Multiply linear regression model was obtained for surface tension prediction. Good correlation was observed between calculated and experimental surface tension values. The thermodynamic parameters (Gibbs free energy, enthalpy and entropy) and thermal parameters (specific heat capacity, thermal conductivity coefficient, thermal diffusivity coefficient, dynamic and kinematic viscosity) were determined.

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