U.P.B. Sci. Bull., Series B, Vol. 82, Iss. 1, 2020 ISSN 1454-2331

VAPOR PRESSURE OF TWO FATTY ACIDS ALKYL ESTERS: EXPERIMENTAL VS. PREDICTED DATA

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This paper contributes to enrichment databases with vapor pressure for two pure methyl linoleate and ethyl oleate, measured with a vapor-liquid equilibrium apparatus Fischer® Labodest® VLE 50 bar, for vacuum conditions, pressures between 1-30 mbar. Predicted data are calculated using three methods: correlation models based on experimental data, group contribution methods and corresponding states principle based on compound properties. Experimental vs. predicted vapor pressure data, for both fatty alkyl esters are compared in terms of RMSD (0.256 vs. 0.708 for correlation method, 5.7935 vs. 2.7649 for contribution methods and 1.3066 vs. 1.1860 for corresponding states principle methods).

Keywords: methyl linoleate, ethyl oleate, vapor pressure experimental data, correlation models, group contribution method, corresponding states principle

1. Introduction

Fatty acids methyl esters (FAME) and fatty acid ethyl esters (FAEE) are being used quite extensively as biodiesel, but different studies shown that some esters can be separated as valuable compounds to be used in food, pharmaceuticals (as omega polyunsaturated fatty acids) [1] and cosmetics fields (as fragrance and emollient esters) [2]. Accurate boiling temperatures and properties as vapor pressure, density, heat of vaporization, viscosity of pure fatty acids esters are required for separation engineering of these kind of mixtures [3]. Traditional distillation methods cannot be applied to separate FAME or FAEE compounds in normal conditions, due to their high boiling temperatures which exceed their decomposition temperatures. Most experimental measurements of the properties were performed especially for short-chain fatty acids esters, while for heavy ones, their properties were calculated based on the concept of group contributions. The first measurements for these compounds were performed by

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Althouse and Triebold [4] who determined vapor pressure for saturated FAME (C6:0, C8:0, C10:0, C12:0, C14:0, C16:0) and for two heavier unsaturated and polyunsaturated FAME (C18:1, C18:2) at pressures from 2.7 to 54.4 mbar. Other authors present measurements of vapor pressure and other properties as density for saturated fatty acids alkyl esters at different pressure ranges as: between 2.7-136 mbar [5], 0.13-13.60 mbar [6], 13.60-326.50 mbar [7], for C16:0 methyl esters in the range 20-65.70 mbar and C18:2 methyl esters in the range 19.72-40.40 mbar [8], 13.60-95.23 mbar [9], using different methods as differential scanning calorimetry [9] or thermogravimetric methods [10]. For compounds with higher number of carbon atoms, the measurements were performed at lower pressure due to their decomposition. For other pressure ranges, vapor pressure data for FAME both light and heavy esters are predicted by many authors using group contribution methods. Ceriani and Meireilles [11,13] proposed a group contribution model to estimate vapor pressure for fatty acids alkyl esters of major compounds found in the edible oil industry (1220 fatty compounds consisting in saturated and unsaturated fatty acids, fatty esters, fatty alcohols and glycerides), reporting an absolute average deviation as 5.04% for FAME and 8.60% for FAEE. Yuan [12] modelled the vapor pressure and normal boiling temperature of fourteen pure FAME (saturated C8:0-C18:0, unsaturated C18:1, C18:2, C18:3, saturated and unsaturated C20-C22) and nineteen biodiesel fuels using Ceriani and Meireilles group contribution model and Wang et al. [14] predicted vapor pressure of methyl, ethyl, propyl and butyl esters. Other models are based on prediction using compounds properties as normal boiling temperature, critical temperature and critical pressure: an analytical correlation based on the three parameter correspondent states principle (reduced temperature and pressure, acentric factor) which can be applied to a large group of compounds (nonpolar, or slightly polar and their mixtures) [15], or a model based on Clapeyron equation of state [16] to establish the equation coefficients A, B, C, D from four vapor pressure points of normal paraffins. Saxena et al. [17] evaluated different predictive models for vapor pressure estimation (Yuan [12], Peng Robinson equation of state at zero pressure fugacity, Othmer and Yu [18], Lee-Kesler [15], Pitzer [19] and Ceriani-Meireilles [11]), using experimental data reported by [5-7] and compared the models depending on their strengths, weakness and applicability. Castellanos [20] modelled the vapor pressure for FAME using Cox equation and constrained the equation parameters to match the heat capacity and an advance equation of state model was developed (APR EOS) for the representation of vapor pressure and heat capacity of FAME and biodiesel fuels [21]. The other author presented experimental data for different pure esters (ethyl myristate [22]), or mixture of FAME (methyl palmitate and methyl stearate at lower pressure as 1 mbar, 10.20 mbar, 51 mbar and 102 mbar [23]).

In this paper, experimental measurements of vapor pressure for two pure unsaturated fatty acids esters as methyl linoleate and ethyl oleate, using a Fisher vapor-liquid equilibrium equipment are performed to complete existing data, in the range of pressure between 0.1-30 mbar. Vapor pressure is also calculated using three methods (four correlation equations based on experimental data, one group contribution method considering the chemical structure, and one corresponding states principle method using predicted critical properties and normal boiling temperature). Experimental and predicted vapor pressure data for both unsaturated fatty acids alkyl esters are compared based on Root mean square deviation (RMSD) to assess data accuracy.

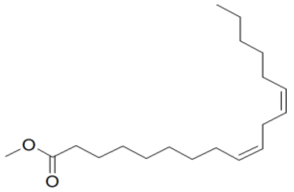
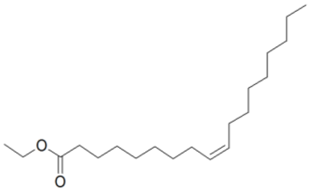
2. Experimental determination of vapor pressure

2.1 Materials

Methyl linoleate (≥99% purity) and ethyl oleate (≥95% purity) from Sigma Aldrich (Germany) are used for the vapor pressure measurements. Their structure, CAS number, and molecular weight are presented in Table 1.

Table 1

Compounds characteristics

Compound	Structure	CAS No.	Molecular weight (kg/kmole)
Methyl linoleate		112-63-0	294.5
Ethyl oleate		111-62-6	310.5

2.2 Equipment

Vapor pressure measurements are performed using a vapor-liquid-equilibrium apparatus *Fischer*$^{®}$ *Labodest*$^{®}$ *VLE 50 bar* produced by i-Fischer Engineering GmbH, Waldbuettelbrunn (Germany). The measurement method is based on the "*Circulation*" principle. The area of measurement ranges from 1 mbar to 50 bars. A part of the liquid mixture is evaporated by means of an immersed electric heater and the ascending vapors also carry part of the boiling liquid in a tubular contact zone called Cottrell pump. The liquid-vapor mixture is separated into two component phases in the separation chamber. The constant recirculation of the liquid phase and the condensed vapor and the simultaneous mixing of the recirculated phases in the mixing chamber ensure the achievement of the equilibrium state. After some hours, the status of equilibrium is reached by constant recycling of liquid phase and condensed vapor phase. The principle is based on measuring boiling temperature (with a precision of ±0.01 K) of pure component at a setting up pressure (with a precision of ±0.1 mbar). The vapor pressure measurement range depends on maximum temperature recommended by the manufacturers for device operation (500ºC) and on compounds thermal decomposition. Samples of 200 mL pure fatty acid alkyl ester are used for each experiment. All data are measured three times in order to control errors.

3 Vapor pressures prediction

For vapor pressure of unsaturated fatty acids alkyl esters prediction, the following methods are proposed: correlations based on experimental data, group contribution methods which consider the contribution of each functional group and corresponding states principle approach that use as input parameters the properties of compounds as critical properties and boiling temperatures. Year by year, these methods became more accurate, many authors contributing in this field to calculate properties for systems that cannot be easily measured.

Correlation methods (CM). Based on experimental data, the parameters of vapor pressure-temperature dependence are determined using four regression empirical models: Clapeyron (*eq. 1*), Antoine (*eq. 2*), Riedel (*eq. 3*) and extended Antoine (*eq. 4*). A four steps algorithm for vapor pressure prediction is proposed (Fig. 1) using:

Clapeyron model:

$$\log P_{vj} = A_j + \frac{B_j}{T} \tag{1}$$

Antoine model:

$$\log P_{vj} = A_j - \frac{B_j}{T + C_j} \tag{2}$$

Riedel model:

$$\log P_{vj} = A_j + \frac{B_j}{T} + C_j \cdot \log(T) + D_j \cdot T^2 \tag{3}$$

Extended Antoine model:

$$\ln P_{vj} = A_j + \frac{B_j}{T + C_j} + D_j \cdot T^{F_j} + E_j \cdot \ln T \qquad (4)$$

where: $P_{v,j}$ is the vapor pressure of ester j (mbar), T is temperature (K), A_j, B_j, C_j, D_j, E_j, F_j are component specific constants, j (1, 2) index of ester. For each model, the vapor pressure are predicted following next steps (Fig.1). The constants are calculated using mean square method which estimates the minimum errors sum between experimental and calculated values.

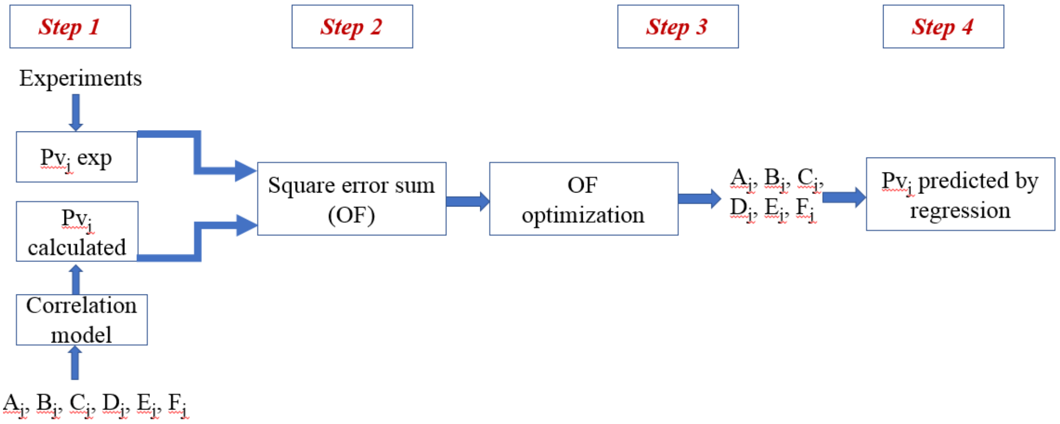


Fig. 1 CM algorithm for vapor pressure prediction for ester j

Group contribution method (GCM). Vapor pressure of methyl linoleate and ethyl oleate are predicted using *Ceriani-Gani-Lu* group contribution method [13], with equations *5-8*. Functional groups, based on chemical structure of each ester, which contribute to the vapor pressure calculation are chosen.

$$\ln(P_{vj}) = A_j + \frac{B_j}{T} + C_j \cdot \ln(T) \qquad (5)$$

$$A_j = \sum_i N_{ij} \cdot (A_{1i} + M_j \cdot A_{2i}) + (s_0 + N_{CSj} \cdot s_1) + \alpha \cdot (f_0 + N_{CSj} \cdot f_1) \qquad (6)$$

$$B_j = \sum_i N_{ij} \cdot (B_{1i} + M_j \cdot B_{2i}) + \beta \cdot (f_0 + N_{Cj} \cdot f_1) \qquad (7)$$

$$C_j = \sum_i N_{ij} \cdot (C_{1i} + M_j \cdot C_{2i}) \qquad (8)$$

where P_{vj} is the vapor pressure (Pa), T is the temperature (K), N_{ij} is the number of groups i in the j ester molecule, M_j is ester j molecular weight, N_{CSj} is the number of carbons of the alcoholic part of ester j, N_{Cj} is the total number of carbons atoms in the molecule of ester j, A_{1i}, A_{2i}, B_{1i}, B_{2i}, C_{1i}, C_{2i}, α, β, s_0, s_1 are the parameters obtained by regression, j is the ester index. The calculation algorithm for this method is presented din Fig. 2.

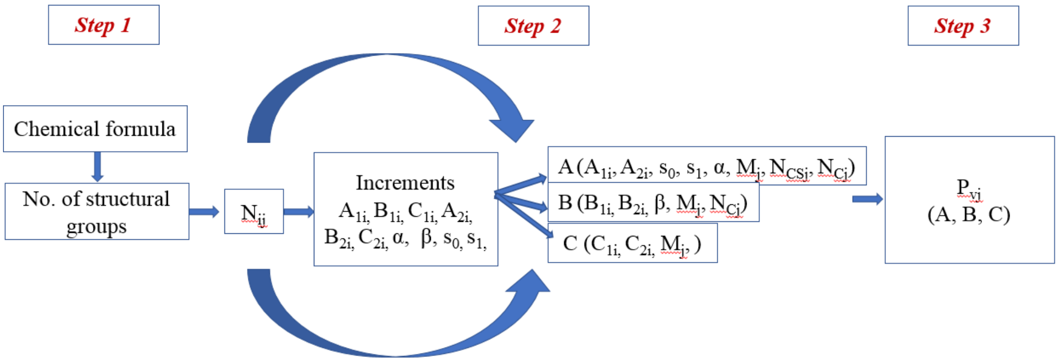


Fig. 2 GCM algorithm for vapor pressure prediction

Step 1 Evaluation of structural groups of each ester. Unsaturated fatty acid alkyl esters have a long chain of 18 carbon atoms, with one or two double bonds. Methyl linoleate and ethyl oleate have the same structural groups but different number of -CH2- and =CH- groups, as presented in Table 2.

Table 2

Fatty acids alkyl esters structural groups

Structural group	**Ethyl oleate** ($C_{20}H_{38}O_2$)	**Methyl linoleate** ($C_{19}H_{34}O_2$)
-COO-	1	1
-CH2-	15	12
=CH-	2	4
-CH3	2	2

Step 2 Constants equation calculation. A_j, B_j, C_j constants are calculated according to equations 6-8 using the *Ceriani-Gani-Lu* adjusted parameters from Table 3.

Table 3

Adjusted parameters

Structural group	**-COO-**	**-CH2-**	**=CH-**	**-CH3**
A_{1i}	3.6559	-3.1789	-2.6923	1.0583
A_{2i}	-0.012577	0.0000082404	0.00000824	0.2891
B_{1i}	4880.9	1756.7	1664.6	1780.8
B_{2i}	-1.2848	-0.11714	-0.11857	-87.312
C_{1i}	-3.896	-0.64358	-0.64371	0.011484
C_{2i}	0.0024548	0.0000474	0.000048389	-0.000038837
Class of compound		s_0		s_1
Fatty esters		-0.658		0.12

Step 3 Vapor pressure calculation. Knowing A_j, B_j, C_j constants equation, vapor pressure of pure unsaturated fatty acid alkyl esters can be calculated, using eq. 5.

Corresponding states principle method (CSPM). For vapor pressure prediction of pure unsaturated fatty acid alkyl ester, the method proposed by *Reynes and Thodos* [16] is chosen. Reduced vapor pressure is calculated using (*eq. 9*):

$$\log(P_{vr\,j}) = \left(\frac{B_j}{T_{c\,j}}\right)\cdot\left(\frac{1}{T_{r\,j}}-1\right)+\left(\frac{1{,}80\cdot B_j}{T_{c\,j}}+2{,}67\right)\cdot\log T_{r\,j}+0{,}1832\cdot\left(\frac{P_{vr\,j}}{T_{r\,j}^{\,2}}-1\right) \qquad (9)$$

where P_{vrj} is the reduced vapor pressure, T_{cj} is the critical temperature (K), T_{rj} is the reduced temperature and B_j is an adjustment parameter calculated from a known vapor pressure at a known T_{bj}, j is the ester index. Vapor pressure can be determined with (*eq. 10):*

$$P_{v\,j} = P_{vr\,j}\cdot P_{c\,j} \qquad (10)$$

where P_{cj} is the critical pressure of ester j (bar).

For *Reynes and Thodos* model, a four steps algorithm for vapor pressure prediction is proposed (Fig. 3).

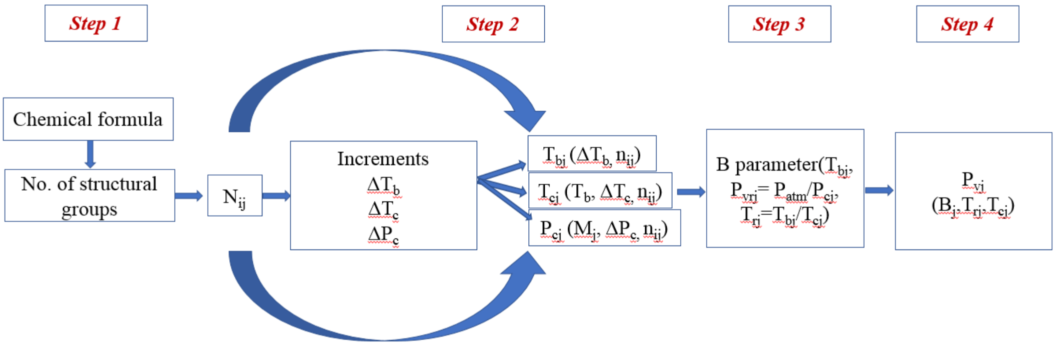


Fig. 3 *CSPM* algorithm for vapor pressure prediction

Step 1. Evaluation of structural groups of each ester. Structural groups are presented in Table 2.

Step 2. Prediction of boiling temperature and critical properties. These properties can be calculated using different models, based on the value of each structural groups [24-26]. Normal boiling temperature of unsaturated fatty acid alkyl esters is predicted using *Joback and Reid* equation with group increments of Stein and Brown [24]:

$$T_{bj} = 198.2 + \sum_i n_{ij}\cdot\Delta T_{bi} \qquad (11)$$

with a correction added by Stein and Brown [24] (*eq.12*):

$$T_{bj}(corr) = T_{bj} + 282.7 - 0.5209 \cdot T_{bj} \tag{12}$$

where n_{ij} is number of structural groups and ΔT_{bi} is a group increment value for normal boiling temperature, *j* is ester index and *i* is a structural group type.

Critical properties are predicted using *Lydersen* method [25], a correlation between number of structural groups n_{ij}, group increments ΔT_{ci} and normal boiling temperature T_{bj} is proposed to evaluate critical temperature (*eq. 13*):

$$T_{cj} = \frac{T_{bj}}{0.567 + \sum_i n_{ij} \cdot \Delta T_{ci} - (\sum_i n_{ij} \cdot \Delta T_{ci})} \tag{13}$$

On the other hand, critical pressure (bar) depends on the same parameters, number of structural groups and the increments groups values ΔP_{ci}, but also by molecular weight M_j (*eq. 14*) with an average absolute percent error of 6.9%:

$$P_{cj} = \frac{M_j}{(0.34 + \sum_i n_{ij} \cdot \Delta P_{ci})^2} \cdot 1.0133 \tag{14}$$

Group increments values are obtained from experimental value by Ghasemitabar [26]. The generated group increments values are obtained through optimization of experimental data for 2036 organic compounds having a structure with 1-36 carbon atoms and molecular weight between 26-555 kg/kmol. In Table 4 group increments values for each structural group specific to ethyl oleate and methyl linoleate for three sources [24-26] are presented. For normal boiling temperature, two group increments values, for critical temperature and critical pressure only one value is used.

Step 3 Evaluation of B parameter. Considering the vapor pressure at atmospheric pressure as a known value, parameter B_j can be found by solving (*eq.9*).

Table 4

Group increments values

Structural group	-COO-	-CH2-	=CH-	-CH3
ΔT_b [26]	97.4615	22.9831	23.7995	13.0945
ΔT_b [24]	78.85	24.22	27.95	21.98
ΔT_c [25]	0.047	0.020	0.018	0.020
ΔP_c [25]	0.47	0.227	0.198	0.227

Step 4 Vapor pressures calculation. Knowing B_j parameter and critical/reduced temperatures, vapor pressures of pure unsaturated fatty acid esters can be calculated, using eq. 9 and 10.

4 Results and discussion

Vapor pressure measurements. Measurement results for the two unsaturated fatty acids alkyl esters are presented in Fig. 4. All data are measured three times and the uncertainty of the experimental measurements is between ± 0.26% and ± 0.45%. In case of methyl linoleate, for pressure between 1 and 30 mbar, boiling temperature are measured in the range 435-493.3 K. The vapor pressure data are consistent with experimental data reported in literature, as presented in Fig. 4. Althouse [4] performed the measurements in the pressure range 2.67-13.33 mbar using a hand-made apparatus, Scott [6] covered the smaller pressures range 0.15-6.47 mbar, using a Hickman tensimeter and Goodwin [8] determined the vapor pressure at higher pressure between 19.33-39.60 mbar, using a vapour-liquid equilibria equipment.

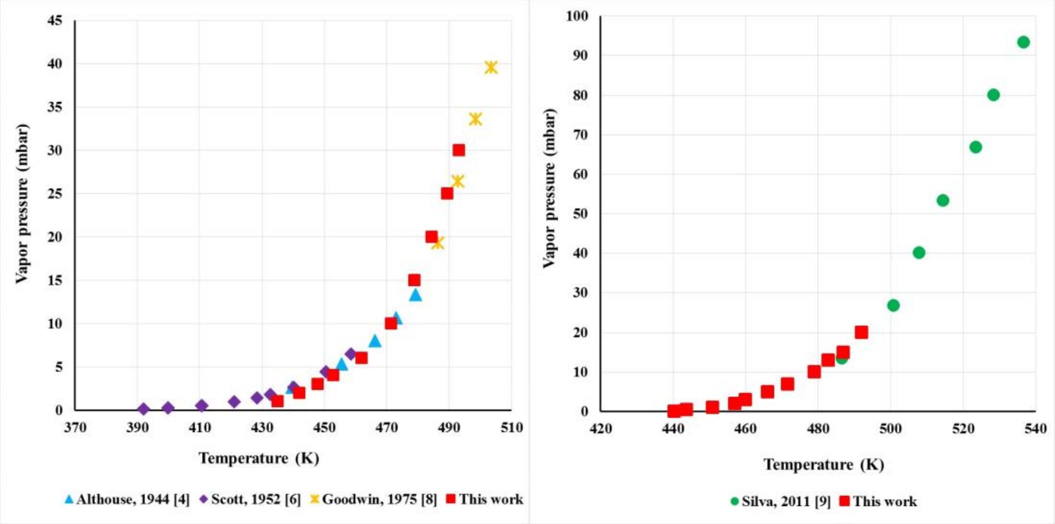


Fig. 4 Experimental vapor pressures a) methyl linoleate; b) ethyl oleate

The data measured in this work (ten points in the range 1-30 mbar) are fitted the same shape of vapor pressure variation with temperature, with small errors. Concerning ethyl oleate, experimental data obtained by Silva [10] using differential scanning calorimetry technique complete the experimental data series obtained in this work (Fig. 4.b). The measured eleven points, in a range 1-20 mbar are placed on a same curve as for other esters.

Vapor pressure estimation by correlation methods (CM). The estimated coefficients for both pure fatty acid alkyl esters are presented in Table 5. Dependence calculated/experimental vapor pressure values vs. temperature, for methyl linoleate are presented in Fig. 5a-d for *Clapeyron*, *Antoine*, *Riedel* and *extended Antoine* models. RMSD is calculated to indicate which model can predict with higher reliability the vapor pressure of methyl linoleate (Table 5). An accepted correlation between experimental and calculated data are obtained for *extended Antoine* equation, with RMSD=0.256.

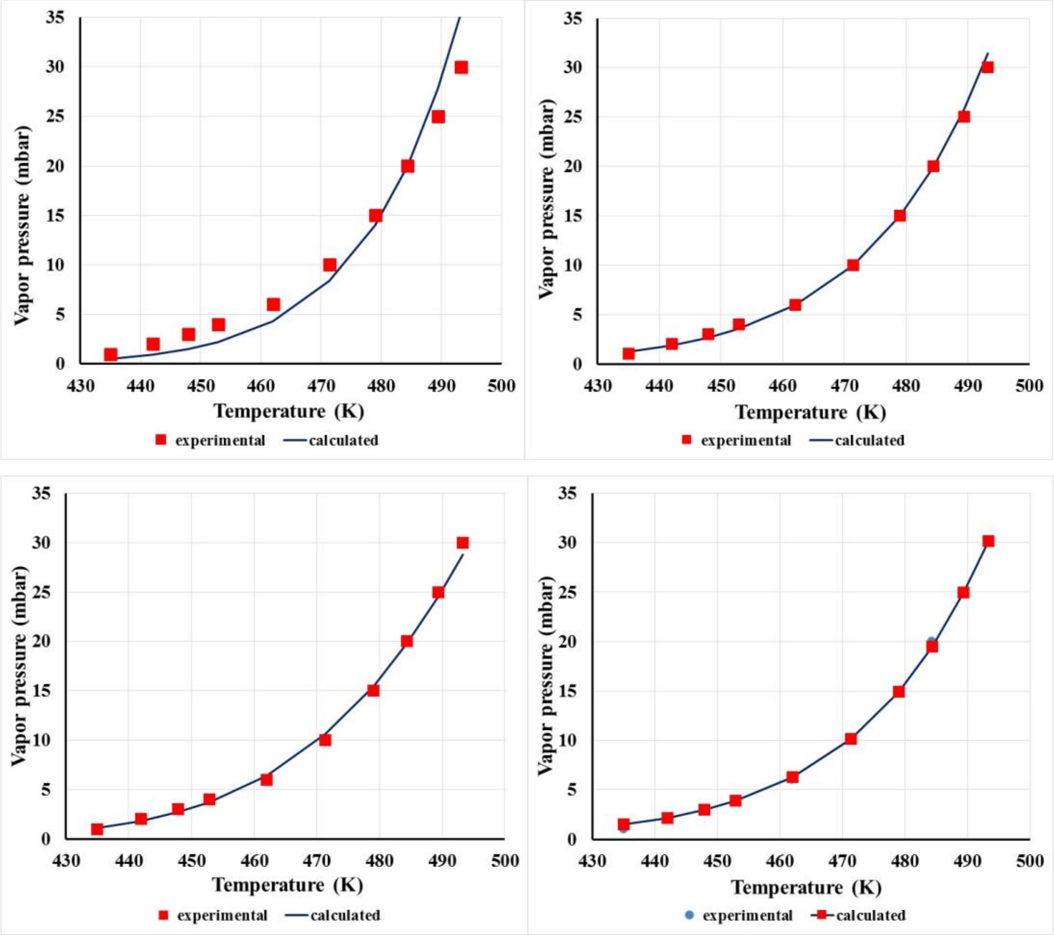


Fig. 5 Calculated vs experimental vapor pressures for pure methyl linoleate
a) *Clapeyron* model, b) *Antoine* model, c) *Riedel* model, d) *Extended Antoine* model

Table 5

Coefficients from different correlation methods of unsaturated fatty acids alkyl esters

Model	Methyl linoleate						Ethyl oleate					
	A	B	C	D	E	F	A	B	C	D	E	F
CM-C	15,1	-6673.0	-	-	-	-	15.9	-7138.8	-	-	-	-
CM-A	35.4	2289.3	141.1	-	-	-	5.5	204.1	-413.0	-	-	-
CM-R	-185.4	-18.9	77.8	-	-	-	-244.4	-18.4	96.8	0	-	-
CM-EA	-72.8	-2.0	5.0	72.4	23.9	-	-181.7	-9.8	5.0	0	28.9	0.7

CM-C is Clapeyron model, CM-A is Antoine model, CM-R is Riedel model and CM-EA is extended Antoine model

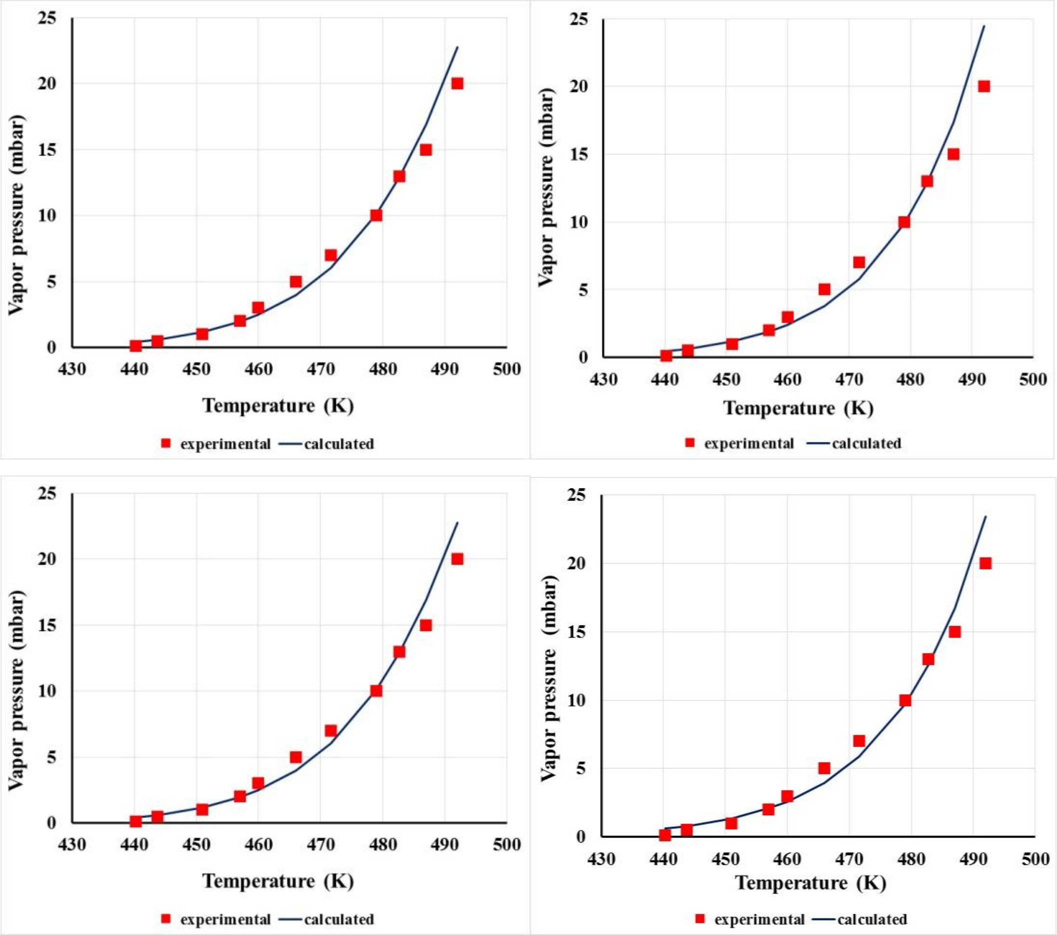


Fig. 6 Calculate vs experimental vapor pressures for pure ethyl oleate
a) *Clapeyron* model, b) *Antoine* model, c) *Riedel* model, d) *Extended Antoine* model

For ethyl oleate, a similar dependence of calculated and experimental vapor pressure values vs. temperature is presented in Fig. 6. An accepted correlation between experimental and calculated data is obtained for *Antoine* model, with RMSD=0.708. When the experimental points are plotted vs. calculated data with proposed models, as in Fig. 7a (for methyl linoleate) and in Fig. 7b (for ethyl oleate), the points are close to the diagonal for pressure less than 10 mbar (correlation coefficient - R^2 having a value closer to 1) for both esters (Table 6). Also *extended Antoine* and *Antoine* models show a good fitting for methyl linoleate and ethyl oleate, respectively.

Vapor pressure estimation by group contribution method (GCM).

Vapor pressure is calculated by *Ceriani-Gani-Lu* method using the algorithm presented in Fig. 2 and eq. 5-8. The results are compared with experimental data

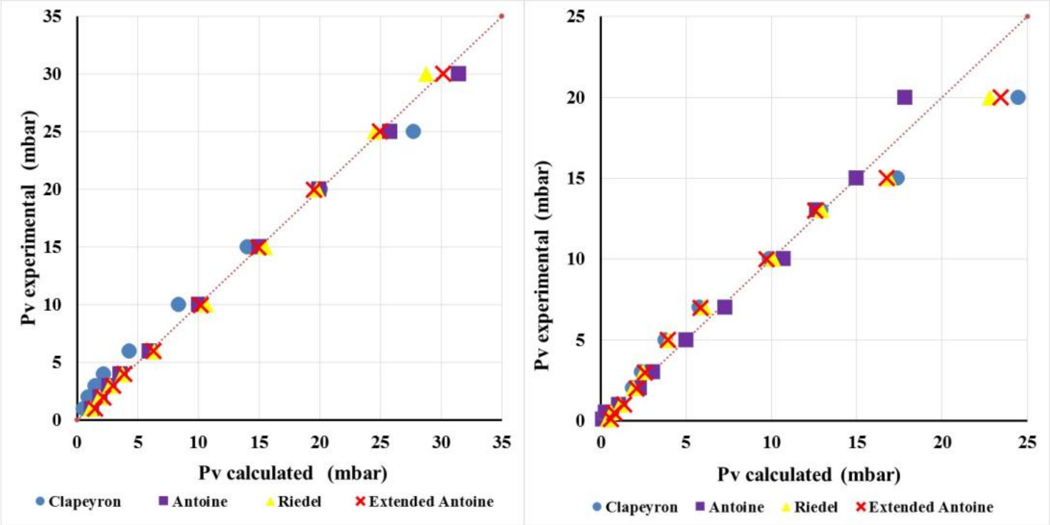


Fig. 7 Vapor pressure experimental vs. calculated data a) methyl linoleate; b) ethyl oleate

Table 6

Statistic parameters values for fitted data

Vapor pressure model	Methyl linoleate		Ethyl oleate			
	RMSD (p<35 mbar)	**R^2**	**RMSD** (p<35 mbar)	**R^2**	**RMSD** (p<10 mbar)	**R^2**
Clapeyron	2.2674	0.84	1.6289	0.83	0.6615	0.97
Antoine	0.5511	0.89	0.7083	0.94	0.3009	0.99
Riedel	0.5220	0.89	1.1160	0.85	0.5438	0.98
Extended Antoine	0.2560	0.92	1.2775	0.83	0.6230	0.98

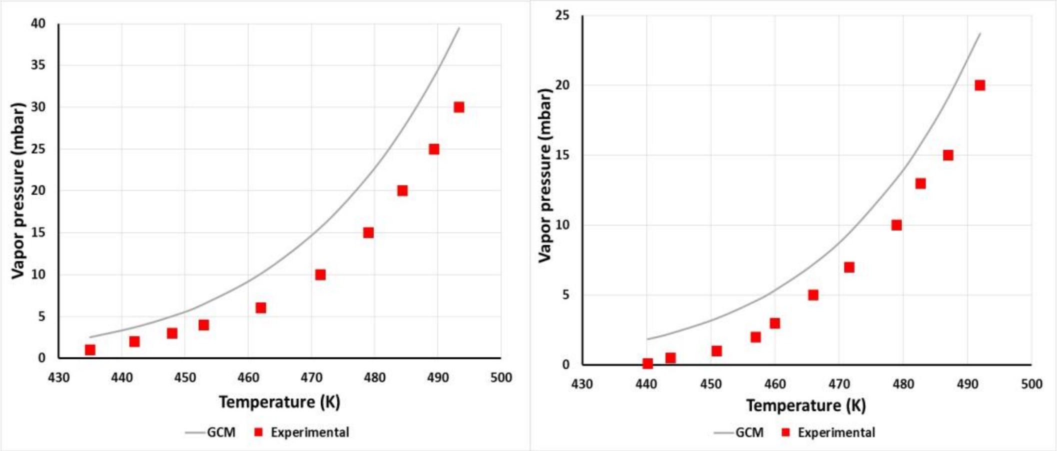


Fig. 8 Experimental vs calculated by GCM vapor pressure a) methyl linoleate; b) ethyl oleate

and are represented in Fig. 8. For methyl linoleate RMSD is 5.7935, while for ethyl oleate is lower (RMSD =2.7649).

Vapor pressure estimation by corresponding states principle method (CSPM)

Vapor pressure is calculated according to the algorithm presented in Fig. 3 based on equations *9-10*, implemented in Mathcad. Considering the structure of both unsaturated fatty acid alkyl esters P_c, T_c and T_b are predicted. These values are compared with experimental data ([10], [27]) and estimated data with *Propred®* implemented models [28]: *Marrero&Gani (MG)*, *Constantinou & Gani (CG)*, *Joback &Reid (JR)*, *Wilson (W)* or *Lipids*. Results are presented in Tables 7-9.

Table 7

Normal boiling temperatures (K)

Method	**Calculated with increments from** *[24]*	**Calculated with increments from** *[26]*	**Experimental**	**ProPred (MG)**	**ProPred (CG)**	**ProPred (Lipids)**
Reference			*[10], [27]*	*[28a]*	*[28b]*	*[28c]*
Ethyl oleate	637.33	624.87	608.36	629.28	608.61	632.32
Methyl linoleate	629.30	614.64	639.00	615.06	595.67	623.06

Boiling temperatures are calculated with equations *11-12*, using the increments reported in references [24] and [26]. In normal conditions, ethyl oleate boil at 608.36K [10], the same value as predicted in *Propred®* with *CG method*. Values predicted in this work are with 29 K, respectively 19 K greater related to experimental data, but related to data estimated with *Lipids Propred®*, the errors are less than 5K. Also, for methyl linoleate, the predicted boiling temperature closer to *Lipids* values. Even if the structures of both esters are different, their normal boiling temperatures difference is almost 10K, that means these compounds are difficult to separate by distillation at atmospheric pressure.

Table 8

Critical temperatures (K)

Method	**Calculated with increments from** [25]*	**Calculated with increments from**[25]**	**ProPred (MG)**	**ProPred (CG)**
Reference			[28a]	[28b]
Ethyl oleate	785.79	770.42	777.65	748.64
Methyl linoleate	780	761.82	769.78	736.16

*[25]*Data calculated using T_b according [24]; [25]**Data calculated using T_b according [26];*

Critical temperature is determined with *eq.13* using the boiling temperature calculated with increments from [24] and [26]. Values predicted in this work are close to those estimated by *Propred®* with *MG method* for both unsaturated fatty acid alkyl esters. A difference of 50K is reported by *Propred® CG method*.

Table 9

Critical pressures (bar)

Method	**Calculated with increments from** [25]	**ProPred (MG)**	**ProPred (CG)**	**ProPred (JR)**	**ProPred (W)**
Reference		*[28a]*	*[28b]*	*[28d]*	*[28e]*
Ethyl oleate	12.26	11.13	10.30	10.53	11.39
Methyl linoleate	13.06	11.95	10.67	11.62	12.36

Critical pressure is calculated using *eq. 14*. Values predicted in this work are comparable with those estimated by *Propred®* with *Wilson method (W)*, for both unsaturated fatty acid alkyl esters.

Table 10

Properties prediction using combined methods

Prediction	**Ethyl oleate**			**Methyl linoleate**		
	T_b	**T_c**	**P_c**	**T_b**	**T_c**	**P_c**
Prediction 1	637.33[24]	785.79[25]*	10.30[28b]	629.3[24]	780[25]*	13.06[25]
Prediction 2	624.87[26]	770.42[25]**	12.26[25]	614.64[26]	761.82[25]**	13.06[25]
Prediction 3	608.36[10]	748.64[28b]	12.26[25]	639.00[27]	780[25]*	10.67[28b]
Prediction 4	629.28[28a]	785.79[25]*	10.30[28b]	639.00[27]	761.82[25]**	13.06[25
Prediction 5	629.28[28a]	777.65[28a]	11.13[28a]	615.06[28a]	769.78[28a]	11.95[28a]
Prediction 6	608.61[28b]	748.64[28b]	12.26[25]	615.06[28a	736.16[28b]	10.67[28b]
Prediction 7	632.32 [28c]	785.79[25]*	12.26 [25]	623.06[28c]	780[25]*	13.06[25]
Prediction 8	632.32 [28c]	770.42[25]**	10.30[28b]	623.06[28c]	761.82[25]**	13.06[25]

*[25]*Data calculated using T_b according[24]; [25]**Data calculated using T_b according[26]*

Normal boiling point and critical parameters have a significant influence on the predicted vapor pressure. Several predictions are made using different combination of T_b, T_c and P_c (Table 10) which are further used in equation *9*. Experimental measurements result for ethyl oleate and for methyl linoleate are compared with predicted vapor pressure data obtained with the eight predictions (Fig. 9). Also, another dataset is added with predicted data with *Multiflash®* software [29]. Vapor pressure is calculated with extended Antoine equation and the coefficients are estimated with *Predictive Soave-Redlich-Kwong* (PSRK) group contribution equation of state in *Multiflash*®, using DIPPR database.

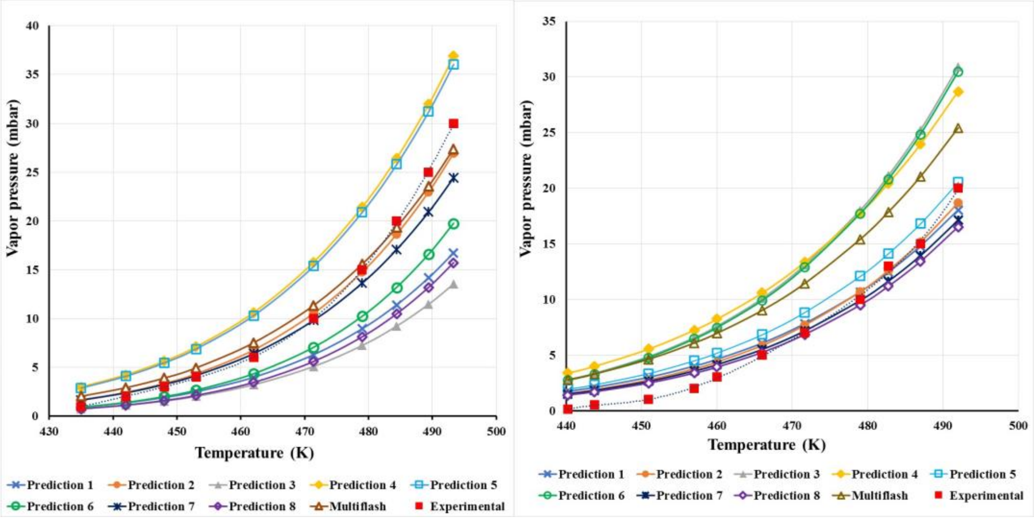


Fig. 9 Vapor pressure predictions a) methyl linoleate; b) ethyl oleate

In case of methyl linoleate, prediction 2 is in good agreement with the experimental data. Also, the data predicted with *Multiflash*® fit with the experimental measurements. Prediction 7 with the normal boiling temperature from *Lipids* database is also in good agreement with the experimental data, especially for pressures below 10 mbar. For the other predictions the errors are higher. It is to notice that at small pressure most predictions can accurately depict the vapor pressure, but the error increases in case of higher pressure.

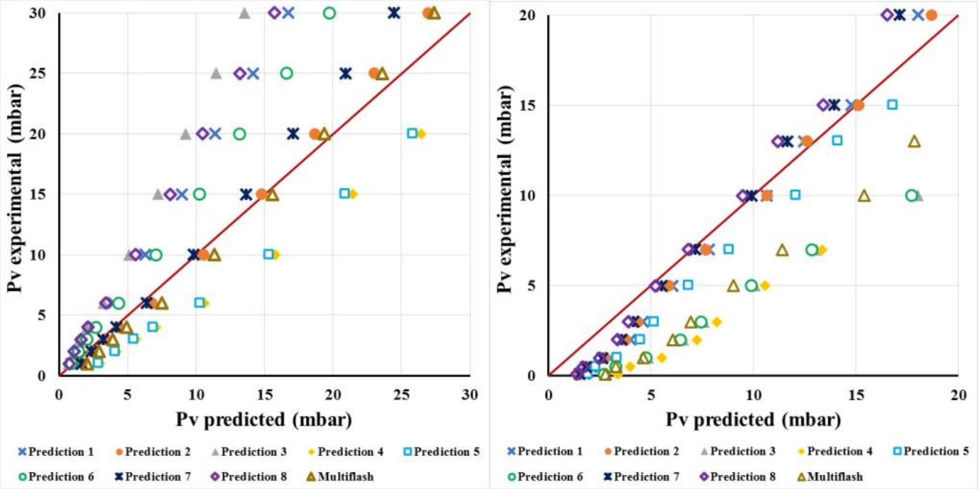


Fig. 10 Parity plot a) methyl linoleate; b) ethyl oleate

Concerning ethyl oleate, prediction 2 shows the best agreement with the experimental data. Predictions 7 and 8, using the normal boiling temperature from *Lipids*, also match the experimental data, but at pressure lower than 1 mbar the errors are higher, as the measuring device pressure control is difficult to handle.

The parity plots (Fig. 10) present a good correlation between the experimental and predicted vapor pressure values of methyl linoleate (prediction 2, 7 and *Multiflash*®). It is to notice that the errors increase at higher pressures. For ethyl oleate predictions 1, 2, 7 and 8 can be used to describe the vapor pressure.

RMSD is calculated to measure the differences between the values predicted by the model and by experiments (Table 11).

Table 11

RMSD values

	Methyl linoleate	Ethyl oleate
Prediction 1	6.5260	1.4184
Prediction 2	1.3066	1.1860
Prediction 3	8.1752	6.6659
Prediction 4	5.0848	6.3282
Prediction 5	4.6224	1.8807
Prediction 6	5.0906	6.4143
Prediction 7	2.4241	1.3987
Prediction 8	7.1695	1.5448
Multiflash	1.3188	4.4107

In Fig. 11 experimental and best predicted vapor pressure values using the three methods are presented.

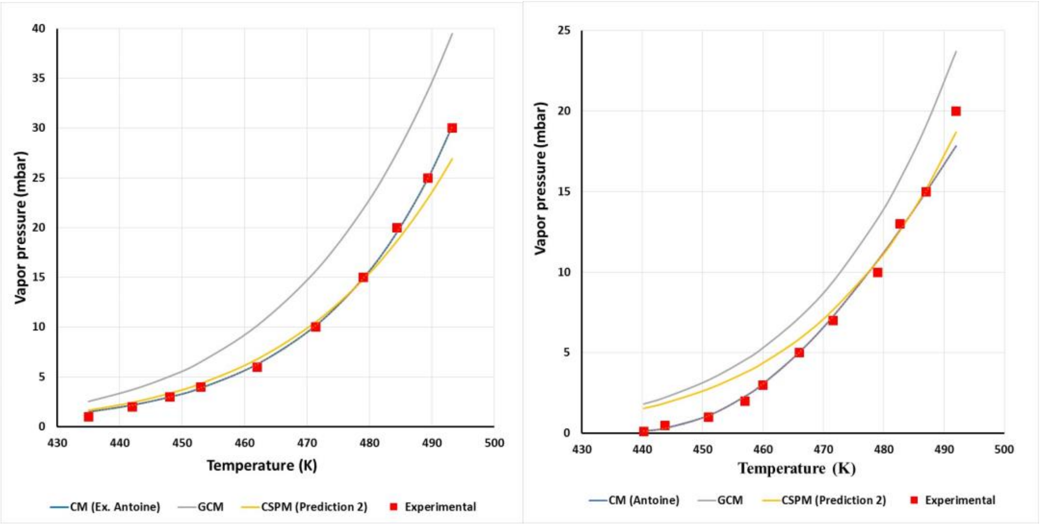


Fig 11. Experimental vs best predicted data by CM, GCM and CSPM
a) methyl linoleate; b) ethyl oleate

Prediction 2 gives good results for both methyl linoleate (RMSD=1.3066) and ethyl oleate (RMSD=1.1860).

5 Conclusions

Ethyl oleate and methyl linoleate vapor pressure is measured using a Vapour-Liquid-Equilibrium apparatus *Fischer® Labodest® VLE 50 bar*. Experimental data are compared with predicted data using three methods: four correlations based on experimental data (with Clapeyron, Riedel, Antoine and extended Antoine models), a group contribution method (Ceriani-Gani-Lu method) and a corresponding states principle approach (Reynes and Thodos model with eight different combinations of critical properties and normal boiling temperatures). RMSD and correlation coefficient R^2 are used to compare the methods. Experimental data are in good agreement with all predicted data.

Acknowledgements

The authors gratefully acknowledge the financial support of the European Commission through the European Regional Development Fund and of the Romanian state budget, under the grant agreement POC P-37-449 (acronym ASPiRE).

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