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Analysis in Displacement Of Liquid Chromatography Changing Density And Viscosity As A Function Of Temperature And Pressure For Malathion

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ABSTRACT

In agriculture different pesticides are used, one of them is the Malathion, due to his big capacity as an insecticide. However, the properties of this compound depend on the temperature (T), the pressure (P) and the purity. Because of this, it is required that the compound has a good industrial preparation, besides a high purity in order to obtain high performance in the crops. Preparative chromatography is used in the purification process of pesticides. It is a separation technique that leverages the chemical affinity property, to isolate the different components of a sample, through the retention time in the chromatography column. Therefore, it is necessary the analysis of the temperature and the pressure in the model of displacement of liquid chromatography in order to determine the displacement of Malathion inside a column in function of time. With the model can be set a configuration of the properties of T and P, in which the resolution of the separation is increased. This paper presents the results of the analysis of the mathematical model and simulation of a column of liquid chromatography (LC) for the aforementioned variables, applied in the purification of Malathion. The model that has better results in the prediction of the behavior of the insecticide Malathion is the PSRK. It was found that with higher temperature and pressure a better separation of the compound was made. Using the ideal column, a 0.4 of length was required for tao of 1.

KEY WORDS

Liquid chromatography, Malathion, Chromatographic column, Pesticide, Insecticide

INTRODUCTION

Chromatography is the process by which the separation of different components of a mixture was performed, by means of differentiation in the chemical properties, which results in a specific separation method [1,2,3,4]. This separation is carried out in two phases of the system, the mobile phase which contains the sample and the stationary phase, which is mainly composed of alumina and silica. Through the second phase the dissolved sample flows. Chemical interactions between the sample and the phases determine the degree of migration and separation of the components contained. Different types of chromatography differs in the states of the phases. In the case of the liquid chromatography, the stationary phase is solid and the mobile is liquid [5,6,7].

Liquid chromatography is widely used for separation and purification of some mixtures from industry, the main mixtures to be purified are some natural compounds, enzymes, proteins, some pesticides, among others [2,4,7].

Due to the lack of specific experiments for each compound, increases the implementation costs at the industrial level, thereby the develop of the models for this technique it is necessary. Wicke in 1939, brought up the ideal model for liquid chromatography, which was improved by Wilson a year later [12,13]. These models were developed to predict the behavior in chromatography using a single compound, based on the Langmuir isotherm. Also they have begun to propose specialized models for different substances. Gu Tingyue in 1995 proposed a model based on mass balances, energy balances and dimensionless numbers as the Biot and Peclet,

applied to a liquid chromatography column (Buitrago Salazar, Ramos Sandoval, & Amaya Hurtado, 2015; Tingyue, n.d.). Because of the importance of the technique, Buitrago S. *et al* in 2015 developed a model for liquid chromatography pesticides.

Malathion is an organophosphate compound, which is widely used in agriculture as an insecticide. The organophosphorus compounds are characterized by being an inhibitor of acetylcholinesterase (AChE), reason why they are mainly used in crops of avocado, artichoke , mushroom, among others, which are often attacked by plagues of flies (*SciaridaePhoridae, Cecydomidae sp.).* When ingested in humans can cause cardiovascular collapse in some muscles, muscle cramps, tachycardia, hypertension, etc. [9]. Many of the organophosphorus compounds are classified as moderately toxic by the Environmental Protection Agency of the United States (US-EPA) [8].

Therefore, it is given the need to improve current methods, with which can decrease the amount of impurities present in the pesticides used in agriculture, in addition to reducing the cost of equipment used for that purpose, choosing the temperature and pressure suitable for the column, taking into account changes in the physicochemical properties of the compound.

MATERIALS AND METHODS

Mathematical model:

According to the work done by Buitrago Salazar *et al* in 2015 [3], to predict the movement of a solute through liquid chromatography varying the physical conditions of the column. Were planted the material balances for the particle (Eq. 1) and the fluid passing through the column (Eq. 2).

$$-\frac{1}{Pe_L}\frac{\delta^2 c_b}{\delta z^2}+\frac{\delta c_b}{\delta z}+\frac{\delta c_b}{\delta \tau}+\xi * \left(c_b - c_{p,r=1}\right)=0 \quad (1)$$

$$\frac{\delta}{\delta \tau}\left[\left(1-\epsilon_p\right)c_p^* + \epsilon_p c_p\right] - \eta\left[\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta c_p}{\delta r}\right)\right]=0 \quad (2)$$

With the following boundary conditions (BC):

$$z=0 \qquad \frac{\delta C_b}{\delta z}=Pe_L\left[c_b-\frac{c_f(\tau)}{c_0}\right] \quad (3)$$

$$z=L \qquad \frac{\delta C_b}{\delta z}=0 \quad (4)$$

$$R=0 \qquad \frac{\delta C_p}{\delta r}=0 \quad (5)$$

$$r=1 \qquad \frac{\delta C_p}{\delta r}=Bi(c_b-c_{p,r=1}) \quad (6)$$

The parameters and the model solution was made according to the points made in the article (Buitrago Salazar *et al*., 2015). The parameters involved directly by the change in temperature (T) and pressure (P) are molecular diffusion (D_m), viscosity (v) and density (ρ) of Malathion.

These parameters directly affect the atomic volume (V_m), the effective intraparticle diffusivity (D_p) and the mass transfer coefficient (K).

Parameter variation:

Due to in the literature there are no experimental data of change in viscosity and density as a function of temperature for the insecticide Malathion, it was decided to use models of predicting physicochemical properties as NRTL, PSRK, Peng Robinson model and STEAM-TA. The main qualities of each method and his equation are below.

The NRTL model (Non-Random Two-Liquid) is used to calculate activity coefficients of different chemicals and be able to correlate with different physicochemical properties, it is widely used in highly non-ideal systems, equilibriums of liquid-liquid vapor-liquid. The model is governed by Equation 7.

$$ln\ \gamma_i=\frac{\sum_j x_j\tau_{ji}G_{ji}}{\sum_k x_k G_{ki}}+\sum_j\frac{\sum_j x_j G_{ij}}{\sum_k x_k G_{kj}}\left(\tau_{ij}-\frac{\sum_m x_m\tau_{mj}G_{mj}}{\sum_k x_k G_{kj}}\right)_{for\ T_{lower}\le T\le T_{upper}} \quad (7)$$

The PSRK model (Prediction SRK) uses the equation of state of Redlich-Kwong-Soave for pures compounds. It is widely used in hydrocarbon processing applications, such as gas processing, refinery and petrochemical processes. The model is governed by equations 8 to 10.

$$P=\frac{RT}{V_m-b}-\frac{a}{V_m(V_m+b)} \quad ; \quad a=a_0+a_1 \quad (8)$$

$$a_0=\sum_{i=1}^{n}\sum_{j=1}^{n}x_i x_j\sqrt{a_i a_j}\left(1-k_{ij}\right) \quad (9)$$

$$a_1 = \sum_{i=1}^{n} x_i \left(\sum_{j=1}^{n} x_j \left((a_i a_j)^{\frac{1}{2}} \; l_{ji} \right)^{\frac{1}{3}} \right)^3 \quad 10$$

The Peng-Robinson equation of state, is widely used in hydrocarbon processing applications, such as gas processing, refinery and petrochemical processes. Their results are widely compared to the PSRK model. The model is governed by equations 11 to 13.

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m+b)+b(V_m-b)} \quad 11$$

$$a_0 = \sum_i \; \sum_j \; x_i x_j (a_i a_j)^{0,5} (1 - k_{ij}) \quad 12$$

$$b = \sum_i x_i b_i \quad 13$$

The model STEAM-TA is used to predict properties of water and similar compounds, which are based on the ASME property tables of 1967. The prediction of properties is performed with this model to indicate the similarity of the test compound with the water.

Calculation of displacement:

It was performed through the aforementioned procedure, taking data of an ideal column (

Table 1), with which the initial values are obtained for each variation of temperature and pressure.

Table 1: Initial values for calculating the parameters in column 1.

Parameter	Value	Units
MW	10000	g/mol
Q	1,0000	mL/min
L	10,000	cm
d_c	1,0000	cm
R_p	0,0113	cm
ϵ_b	0,4000	
τ_{tor}	4,0000	
d_p	300,00	Å
ϵ_p	0,5000	

The matrix was solved by changing the temperature 4 times (25°, 40°, 60° and 80°C), according to the data found in obtaining parameters through the different methods for calculating the properties of density and viscosity.

To calculate the error in the equalization of the equations to zero, the mean, median and standard deviation was calculated. This procedure was conducted for each columns studied to verify the performance of Malathion versus time.

RESULTS AND DISCUSSION

The parameters that are directly affected by the variation of the temperature (T) and pressure (P) are the molecular diffusion (D_m), the viscosity (v) and the density (ρ) of Malathion (

Table 2). These values are affected by the temperature at the molecular level. Whereupon the changes in displacement will be affected. Due to the density is the ratio between the mass and volume of a substance, the volume change due to the change in the atomic volume (V_m), which will be increased directly with the change in temperature and hence his displacement inside the column. The change in viscosity, which is thick and sticky consistency of a substance, affect the interactions between the mobile phase and the stationary phase of the column. These parameters affect the effective diffusivity intraparticle (D_p) and the mass transfer coefficient (K).

Table 2: Variation of parameters through temperature.

Variable	Temperature [°C]			
	25	40	60	80
Density (ρ) [g/mL]	1,22018	1,22018	1,22018	1,22018
Viscosity (μ) [Pa sec]	0,00015	0,000148	0,00013	0,00012
Atomic volume (Vm) [m^3/kgmol]	0,27074	0,27074	0,27074	0,27074
Molecular diffusivity (Dm) [cm^2/sec]	2,966E-09	3,362E-09	3,924E-09	4,344E-09
Intraparticle effective diffusivity (Dp) [cm^2/sec]	6,899E-10	7,820E-10	9,127E-10	1,010E-09
Mass transfer coefficient (k)	1,955E-05	2,125E-05	2,356E-05	2,521E-05

Biot	637,6806	611,5868	580,8788	561,5144

In the atomic volume, there wasn't variation observed, because this parameter depends only on the density of the substance. Is observed how the variation of these parameters was directly proportional to the temperature for the other parameters except the Biot number, this number had a direct relationship, due to the molecular interactions that occur between the solute, the stationary phase and the mobile phase. At higher temperature physically exist a higher molecular diffusivity, which Malathion passed through the chromatographic column faster. It should be noted, that the Biot number for mass transfer indicates the facility of the molecular diffusion inside the column, so that the overall spread in the system will tend to decrease, however, the change was not significant. Buitrago Salazar *et al* in 2015 observed significate changes of 10 and up to 100 orders of magnitude.

Parameter variation:

The variation in viscosity versus temperature (

Fig. 1) and pressure (

Fig. 2) was performed with the different models mentioned for the insecticide Malathion. NRTL and Peng Robinson models result in a straight line, due to the calculation of the properties through these models, did not take into account the temperature as a factor of change. Which reason these models are insufficient to calculate the change in viscosity depending on the parameters analyzed.

The Steam-ta model also gives a straight line above 310 Kelvin, however for values above shows a peak. These results were not consistent, so it was decided to discard this method. Besides, this method is used to predict the properties of water. The method PSRK generated an adequate variation that was physically expected, an inverse relationship between temperature and viscosity. For calculating the displacement of Malathion through the column were decided to work with the PSRK model to calculate viscosity.

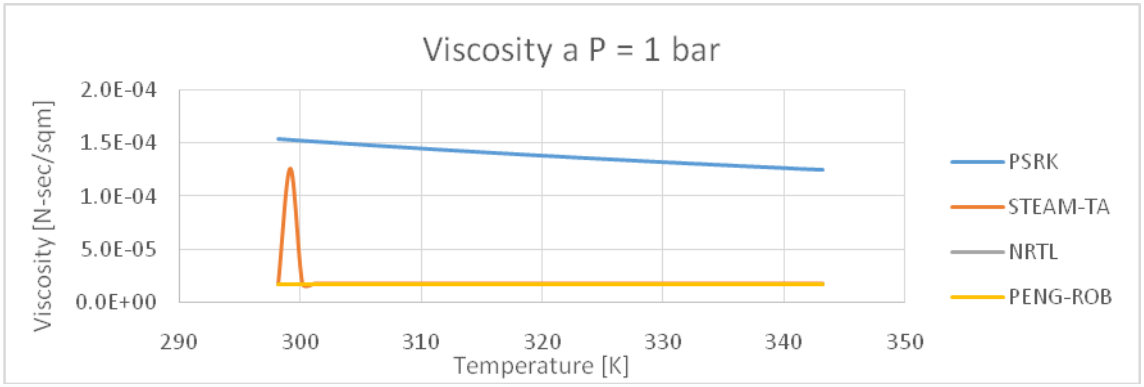

Fig. 1: Change in viscosity versus temperature for different prediction models.

Due to the lack of experimental parameters, the model PSRK, falls short predict the change in viscosity of Malathion in function of pressure.

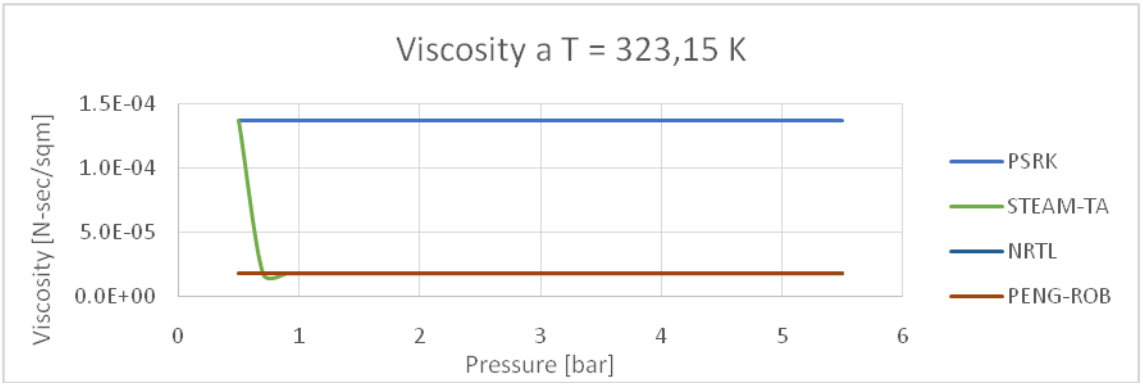

Fig. 2: Change of viscosity as a function of pressure for different prediction models.

However, determining the density variation as a function of temperature (Fig. 3) of the insecticide Malathion, no significant variations in the values were found, this was mainly due to that they were not all the experimental parameters necessary for prediction in the models used.

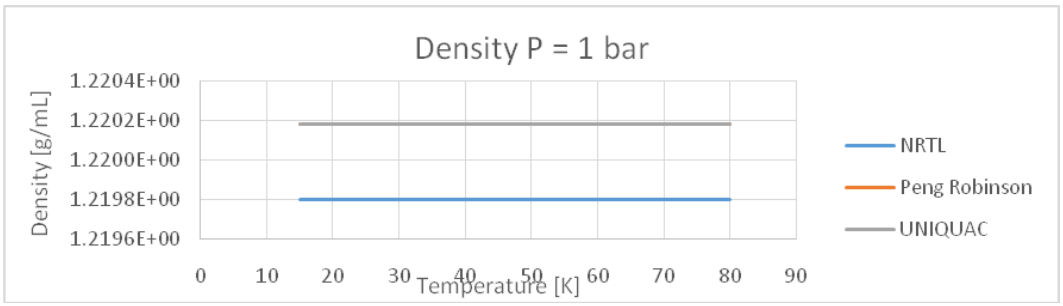

Fig. 3: Change in density function of temperature for different prediction models.

The prediction in the density as a function of pressure was not performed due to lack of the necessary parameters for the same. Reason why the models fall short to achieve an approximation. Also as mentioned above, change with temperature it was not significant, which these models cannot calculate the actual variation of the density of Malathion. Therefore it was decided to use the value found by the NRTL and Peng robinson model in the test of temperature.

Mathematical model:

The mathematical model was solved by following the steps proposed by Buitrago Salazar *et al* [3]. To verify the system solution through the proposed method was determined the average, the median, and the standard deviation (

Table 3) for each column. These values were calculated using the data obtained from each point of the matrix, in total 240 points..

Table 3: Error in the model solution.

Parameter	T = 25°C	T = 40°C	T = 60°C	T = 80°C
Average	-0,0380	-0,0911	-0,0888	-0,0947
Median	4,448,E-05	0,000,E+00	1,912,E-06	0,000,E+00
Standard deviation	1,7984	1,5768	1,5811	1,5662

The average data for the three columns was very close to the desired value of zero, which is confirmed by the standard deviation, which shows the dispersion of the data, and display the contents in the solution peaks, these peaks indicate errors located in the solution. However in this case the deviation was low, whereby the 240 equations for the solution of the method tend to reach his desired value, giving credence to the results.

The system of equations (Equation 1 and 2) for each column respectively was resolved, with these solutions the displacement of the maximum concentration of the pesticide through column length (Fig. 4) was determined. For this perfect column, it is recommended to work at high temperatures, as shown in the Fig. 4. At low temperatures different concentration Malathion peaks along the column were observed, so their separation was not efficient, however, as the temperature increases, was found a thinner peak in length to about 0.4 column, so this would be the ideal length of the column. With this, decreases in a 60% the required length of a column and thus will be a noticeable reduction in costs. The section between 0.03 and 0.28 in length, are given several concentration peaks that were mixed, which indicates that at this point so far was making the separation of the analyzed compound.

The

Fig. 5, shows the intraparticle concentration of Malathion for a tao of 1, no significant differences as the temperature varies. This is mainly due to the compound used for the stationary phase, because it is a compound which must remain physico chemically stable while the change in the temperature, whereas diffusion inside the particle will remain constant.

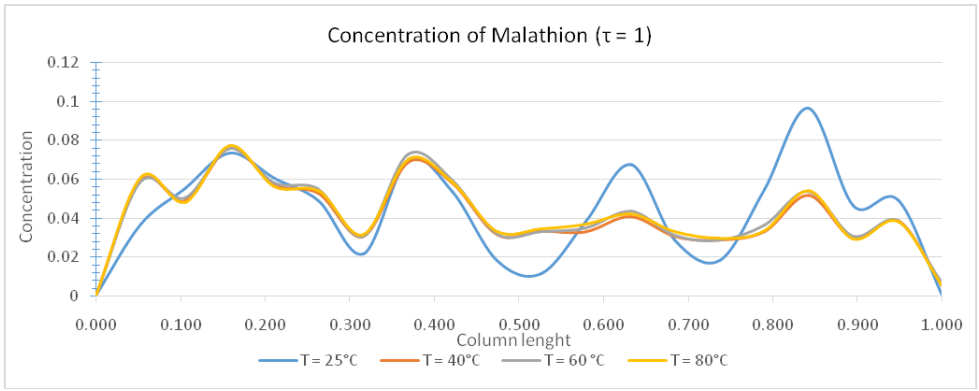

Fig. 4: Concentration of Malathion peaks for tao of 1 at different temperaturas.

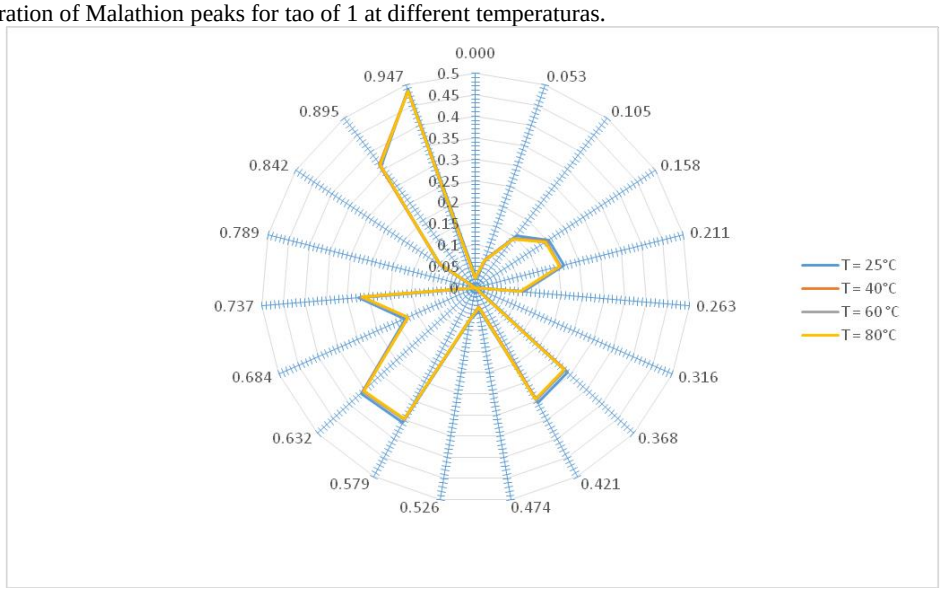

Fig. 5: Concentration of Malathion depending on the radius of the particle for tao of 1 at different temperatures.

These research was interesting and contribute to the knowledge, due to they contribute to the development of the technique of liquid chromatography separation. His best objective was made easier the industrial implementation, besides being a base for developing future models for predicting the displacement inside a column of liquid chromatography.

Conclusions:

Analysis of prediction models of physicochemical properties most used was performed. When they were analyzed for Malathion, it was found that it was required more experimentation in order to obtain the required parameters in each model. However the PSRK model, obtained a greater accuracy in predicting the properties.

The model based on the material balances of liquid chromatography system was solved. The system solution was verified by calculating the error in the development of the equations. The average solutions for the four cases were less than 0.1, so that the error accumulated through each grid point was low.

To use the ideal column in the separation of Malathion is recommended to work with high values of temperature to avoid dispersion of the compound through the entire column chromatography, and thereby obtain an extraction point. It was found that the column has a good separation using a length of about 0.4 for tao of 1. It was also determined that there was no variation in the concentration versus particle radius of the stationary phase, due to its physicochemical stability with temperature.

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