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Measurement of the diffusion coefficient of a model food dye (malvidin 3,5-diglucoside) in a high pressure CO_2 + methanol system by the chromatographic peak-broadening technique

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Abstract

The accurate determination of the diffusion coefficients of solutes in supercritical solvents is a prerequisite for the modeling and design of extraction processes. At present, reported data on the diffusion of polar solutes in the system CO_2 + methanol at high pressure is scarce. In the work described here, malvidin 3,5-diglucoside was chosen as a representative example of anthocyanin compounds (natural food dyes). The diffusion coefficient of this compound was determined using a chromatographic peak-broadening technique. The effect of the amount of methanol in the solvent has been analyzed and the results show that a decrease in the diffusion coefficient occurs as the amount of methanol increases. This behavior has been attributed to the formation of solute–methanol clusters. Finally, the results obtained have also been correlated with temperature, solvent density and viscosity, with the best fit found in the correlation with density.

Keywords: Diffusion coefficient; Anthocyanins; Cosolvent; Chromatographic peak-broadening; Near critical fluid

1. Introduction

The use of the supercritical fluid extraction technique in the food industry is now commonplace due to the number of studies that have appeared in the last decade [1,2]. The application of this technique to the production of food additives—such as aromas, antioxidants, and dyes—is highly competitive in comparison to conventional methods owing to the excellent properties shown by supercritical fluids [3]. In the modeling and subsequent design of industrial processes [4], it is necessary to ascertain the values of the mass transfer parameters of the system. In the work described here, we determined and correlated the diffusion coefficient of malvidin 3,5-diglucoside in the system CO_2–methanol in the near critical region. This substance was chosen as

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a representative example of the anthocyanin compounds, which are responsible for the coloration of a diverse range of plants that are commonly used as sources of food dyes.

A wide range of techniques have been reported in the literature for the determination of the binary diffusion coefficient in supercritical fluids [5]. The most commonly used method is undoubtedly the chromatographic peak-broadening technique, which is also called Taylor's dispersion technique. This method is based on the work carried out by Taylor [6,7] and later extended by Aris [8]. The application of this technique to the determination of the diffusion coefficient of solutes in CO_2 at high pressure has been demonstrated in a large number of studies [9]. However, the application of this technique to the system CO_2–cosolvent has not been developed to the same extent. There are only a few reports that describe the study of the diffusion coefficient of solutes, including acridine, benzene, phenanthrene, benzoic acid, in the system CO_2–cosolvent [10–12].

Many of these reports describe the formation of associations or clusters of the different solutes with the cosolvent. The result of this phenomenon is a decrease in the diffusion coefficient with cosolvent concentration. This effect was also observed in the work described here and the results are compared with the value of the diffusion coefficient in liquid methanol at atmospheric pressure.

2. The chromatographic peak-broadening technique

This method is based on the work of Taylor [6,7] and Aris [8] on the dispersion of a solute in laminate flow through a tube. An impulse sign of a solute becomes wider in the form of a peak as the solute travels along the tube, a phenomenon caused by the action of diffusion in the axial direction (Fig. 1).

The mathematical expression obtained by Taylor and Aris, which was later used by Funazukuri et al. in the estimation of the diffusion coefficient of solutes in supercritical fluids [13,14], is as follows:

$$C = A\theta^{-1/2}\exp\left[\frac{-(1-\theta)^2}{4\theta D_{\varepsilon\phi}/uL}\right] \tag{1}$$

This equation represents the variation of the tracer response concentration C, in a peak that moves at speed u in a right tube of length L and radius r. A is a constant, θ is dimensionless time (t/τ), where τ is the half residence time (defined as L/u) and D_{ef} is the axial dispersion coefficient given by the following expression:

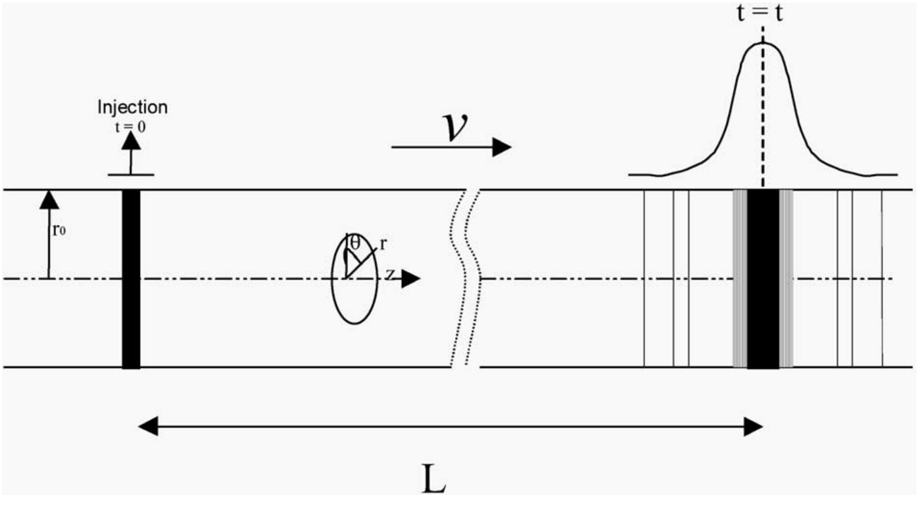

Fig. 1. Broadening of a peak in a tube due to the axial diffusion.

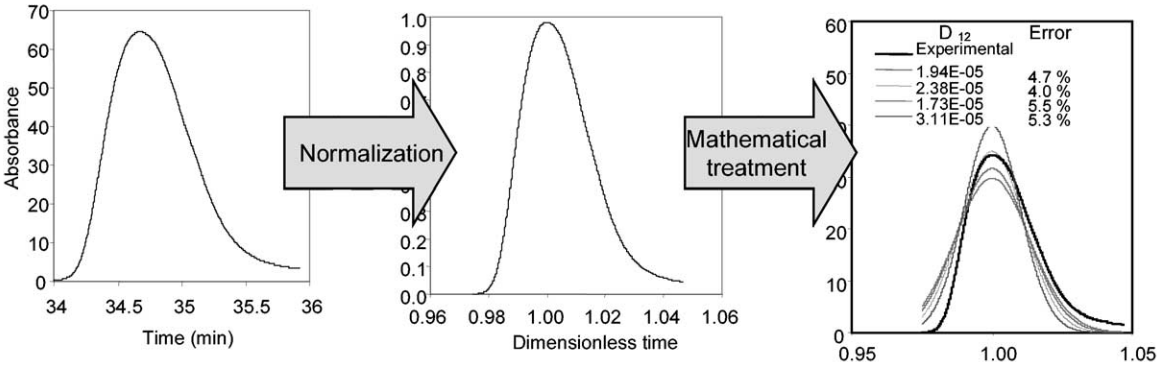

Fig. 2. Description of the treatment of the diffusion coefficient data.

$$D_{\mathrm{ef}} = \frac{r^2 u^2}{48 D_{12}} \quad \text{when} \quad \frac{L}{2u} \gg \frac{r^2}{(3.8)^2 D_{12}} \tag{2}$$

where D_{12} is the diffusion coefficient.

For an appropriate analysis of the data it is necessary to obtain a symmetrical peak with Gaussian form. The curve obtained can be considered as Gaussian when $D_{\mathrm{ef}}/uL < 0.01$ [15]. In the study of the symmetry requirements it is necessary to define an asymmetry factor, such as the relationship between the two concentrations to the tenth part of the maximum value of the height of the peak. Peaks that have an asymmetry factor greater than 1.3 should not be considered.

Eq. (1) has been defined only for the case of right tubes. However, in the development of the diffusion experiments it is necessary to use columns of great length (generally more than 10 m). In these cases, the columns must be coiled so that they can be placed in a bath to maintain a constant temperature. Given this situation, the following condition must be established so that the previous equations are valid:

$$\mathrm{De}\,\mathrm{Sc}^{0.5} < 10 \tag{3}$$

where De and Sc are the Dean and Schmidt numbers, respectively, defined as:

$$\mathrm{De} = \frac{\rho u d_{\mathrm{tubo}}}{\mu} \sqrt{\frac{d_{\mathrm{tube}}}{d_{\mathrm{coil}}}} \quad \text{and} \quad \mathrm{Sc} = \frac{\mu}{\rho D_{12}} \tag{4}$$

where ρ is the solvent density, μ is the solvent viscosity, d_{tube} is the tube diameter and d_{coil} is the diameter of the coil.

For the comparison of different experimental data carried out at different concentrations, Eq. (1) can be normalized as follows:

$$C^* = \frac{C}{(1/\tau)\int_0^{\infty} C \cdot \mathrm{d}t} = \frac{1}{2(\pi\theta D_{\mathrm{ef}}/uL)^{1/2}} \exp\left[\frac{-(1-\theta)^2}{4\theta D_{\mathrm{ef}}/uL}\right] \tag{5}$$

where C^* is the normalized tracer response concentration.

The experimental procedure described by Funazukuri et al. [13,14] consists of the introduction of an impulse of the sample into a capillary column and the measurement of the concentration of the material on exiting the column. The experimental curve obtained is compared with the theoretical one calculated using Eq. (5) for different values of the relationship D_{ef}/uL. The value of this relationship that provides the closest agreement between the experimental and theoretically calculated values is taken as valid. Once the value of D_{ef} is known, it is possible to calculate the diffusion coefficient D_{12} using Eq. (2). Fig. 2 shows a schematic representation of the treatment that the data undergo in each experiment.

3. Experimental apparatus and procedure

The diffusion coefficients of anthocyanins in the systems carbon dioxide + methanol and methanol alone were determined using a modified series 602 supercritical chromatograph from ‘LEE SCIENTIFIC’. The modifications consisted of replacing the original pump of the equipment with two syringe pumps supplied by ‘ISCO’ (Lincoln, Nebraska). This change was required for the determination of the diffusion coefficient of the solute in the carbon dioxide and methanol system.

Fig. 3 shows a schematic view of the equipment used in this study. The main items are the two syringe pumps—models 100DX (for methanol) and 260D (for CO_2); a valve for the sample injections (‘Rheodyne’ serial number 7725i) equipped with an external loop of 20 ml volume; a coiled column for the diffusion of the solutes (30 m length, 0.25 mm internal diameter and 20 cm coil diameter); an oven to maintain the diffusion column at constant temperature—the oven had a maximum temperature of 450 °C; a variable wavelength UV detector (DIONEX model ‘UV detector’) with two cells of 60 and 200 ml, respectively, that were able to support a maximum pressure of 500 bar and operate at ambient temperature; and finally, a thermostated restrictor (ISCO) situated at the exit of the UV detector to regulate the flow rate. The body of the valve and the tip of the restrictor were maintained at 80 °C during all experiments.

We designed a set of experiments in which the composition of the solvent system (carbon dioxide + methanol or methanol alone), temperature, and pressure were varied as indicated in Table 1. All the experiments were repeated five times. It is necessary to bear in mind that the pump controller introduces the cosolvent into the system as a volumetric fraction at the working pressure and 25 °C. For this reason, it is necessary to calculate

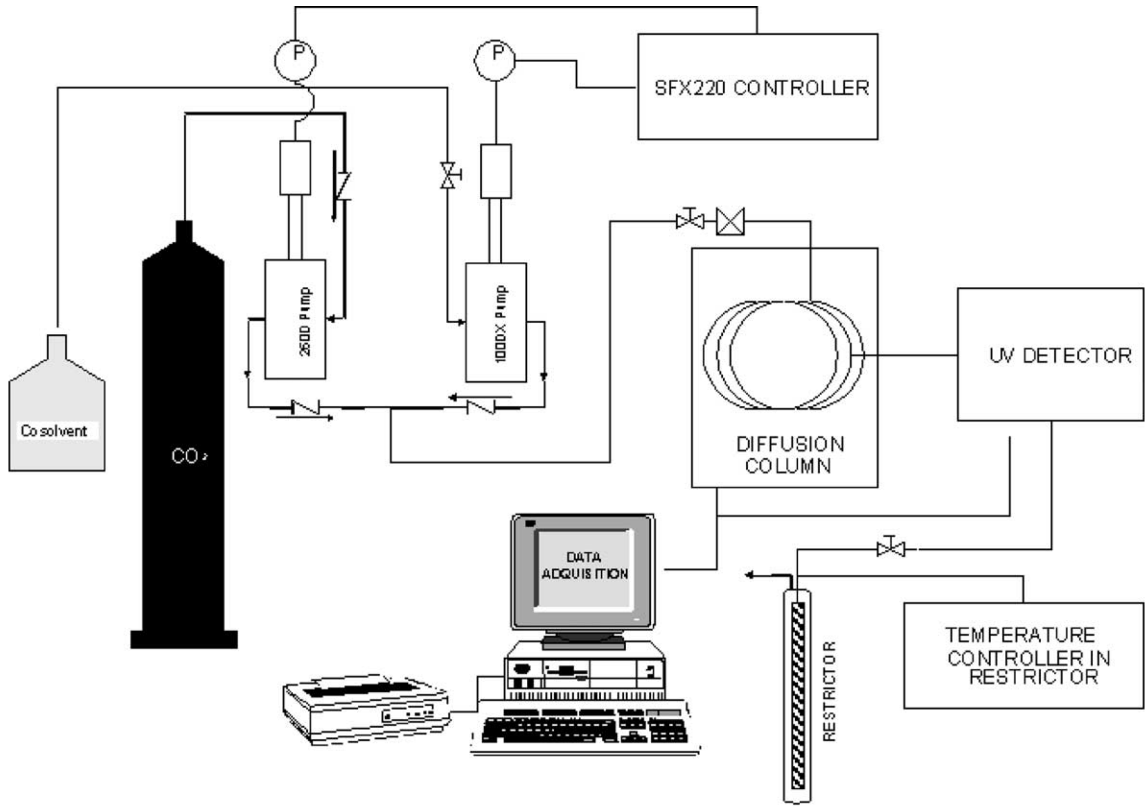

Fig. 3. Equipment used for the determination of the diffusion coefficient.

Table 1
Variables studied in the determination of the diffusion coefficient of anthocyanins in the near critical region

Solvent	CO_2 + methanol	Methanol
Temperature (°C)	40, 50 and 60	40, 50 and 60
Pressure (bar)	100, 200, 300 and 400	Atmospheric
Methanol (%)	5, 10 and 20	100

Values of the molar fraction of methanol in the solvent at the working conditions

Pressure (bar)	5% vol. Methanol	10% vol. Methanol	20% vol. Methanol
100	5.93	11.75	23.06
200	5.64	11.21	22.12
300	5.40	10.75	21.32
400	5.21	10.39	20.69

the value of the molar fraction of solvent for each pressure due to the changes in the density of CO_2 and methanol with this variable. The value obtained in each case is also shown in Table 1.

3.1. Flow-rate selection

According to Funazukuri et al. [14], the dispersion that a tracer experiences along a sufficiently long tube should conform to a series of restrictions related to the form of the coiled tube. Below a certain flow rate, the value of the dispersion and diffusion coefficients are equal. Therefore, it is necessary to determine the flow rate limit in order to allow the value of the diffusion coefficient to be estimated.

For this reason we carried out a series of experiments under the following intermediate working conditions: 300 bar of pressure, temperatures of 40 and 60 °C, and 10% methanol. The results obtained in terms of dispersion versus solvent velocity inside the tube are shown in Fig. 4 for the experiments that conform to the symmetry requirements described above.

From the results obtained it can be deduced that the best solvent velocity inside the tube for the experiments is in the range 1–3 cm/s. Below the first limit, the tests show a large degree of error, whereas above the second limit, the dispersion moves away from the value of the diffusion coefficient. The real value of the diffusion coefficient coincides with the extrapolation of the data to a solvent velocity of zero.

4. Experimental results and discussion

The experimental results obtained for the diffusion coefficients under the selected operating conditions are shown in Table 2. The data that did not adhere to the symmetry requirements described in the method are not included.

4.1. Effect of cosolvent

Fig. 5 shows the experimental data for diffusion coefficient versus the percentage of methanol in the solvent for the different operating temperatures studied. The data obtained from the run at atmospheric pressure for methanol are included as a reference.

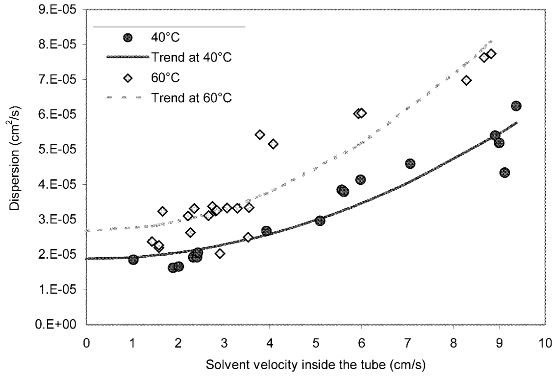

Fig. 4. Obtained results and trends of the dispersion data at 40 and 60 °C.

Table 2
Mean of the experimental results of diffusion coefficients of anthocyanins in CO_2 and methanol with their accuracy at the 95.0% confidence level

% Cosolvent	Temperature (°C)	Pressure (bar)	Diffusion coefficient $(cm^2/s) \times 10^5$
5	40	100	–
		200	3.22 ± 1.02
		300	3.70 ± 0.85
		400	3.15 ± 0.22
	50	100	–
		200	3.67 ± 0.38
		300	4.32 ± 3.01
		400	3.44 ± 0.23
	60	100	–
		200	4.32 ± 0.75
		300	4.53 ± 0.91
		400	4.44 ± 0.52
10	40	100	2.56 ± 0.11
		200	2.14 ± 0.45
		300	1.88 ± 0.16
		400	2.28 ± 0.17
	50	100	2.93 ± 0.87
		200	2.91 ± 0.41
		300	2.39 ± 0.04
		400	2.21 ± 0.49
	60	100	–
		200	3.92 ± 0.27
		300	2.67 ± 0.19
		400	2.49 ± 0.67
20	40	100	1.87 ± 0.82
		200	1.88 ± 0.55
		300	1.59 ± 0.56
		400	1.57 ± 0.81
	50	100	2.93 ± 0.58
		200	2.07 ± 1.34
		300	1.79 ± 0.14
		400	1.62 ± 2.50
	60	100	–
		200	2.26 ± 0.07
		300	–
		400	–
Experimental results in liquid methanol at atmospheric pressure			
	40		0.37 ± 0.01
	50		0.46 ± 0.06
	60		0.48 ± 0.09

From the graphs obtained we can deduce that the diffusion coefficients of anthocyanins in the solvent systems studied decrease as the quantity of methanol in the solvent increases. This behavior is similar to that described in the literature for compounds like benzoic acid, which experiences acid/base-type solute–methanol chemical associations [10]. These associations, or clusters, increase the effective size of the solute and, as a consequence, the diffusion coefficient decreases. In this case, the condensation of a methanol molecule with an anthocyanin molecule results in a structure of increased size, a situation that leads to a decrease in the diffusion coefficient.

Smith et al. [10] suggested the possibility of estimating the increase in volume of the methanol–solute cluster by simply studying the relationship between the diffusion coefficient at different cosolvent percentages. For example, when the percentage of methanol in the solvent is increased from 5 to 10%, the volume of the associated species doubles, and if the increase is from 5 to 20%, then the cluster volume triples. On the other hand, the increase in the volume of the cluster when liquid methanol is used as the solvent is approximately 35 times greater than the volume of the cluster found on using supercritical carbon dioxide with 5% of methanol.

Finally, the values of the diffusion coefficients of anthocyanin in the methanol/carbon dioxide system are lower than those found in the literature for benzoic acid, acridine and phenanthrene in the same system [10]. This behavior is due to the larger size of the anthocyanin molecule.

4.2. Effect of temperature

The diffusion coefficient data for anthocyanins versus temperature in liquid methanol at atmospheric pressure and in carbon dioxide with 5, 10 and 20% vol. of methanol, at different operating pressures, are plotted in Fig. 6. These graphs show that the diffusion coefficient increases with temperature. This fact is in full agreement with the conclusions reported in the literature for the diffusion coefficients of a range of substances in supercritical CO_2 [5,10,11,16–18].

This dependence with temperature is more marked in the experiments carried out with CO_2 and methanol at high pressure than in those carried out with liquid methanol at atmospheric pressure. This trend is attributed to the wide variations in density and viscosity with temperature in the region near to the critical point.

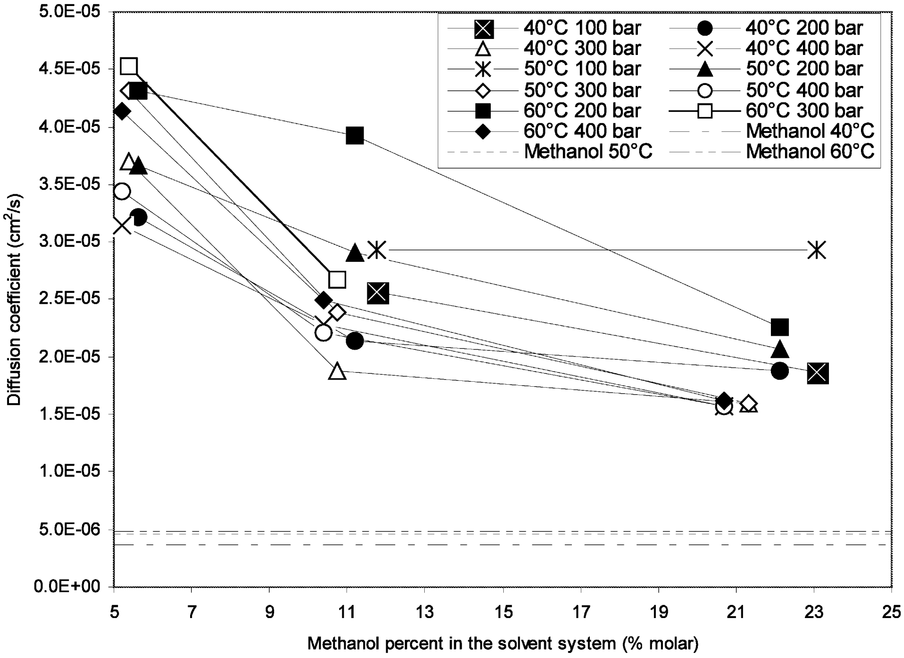

Fig. 5. Variation of the diffusion coefficient of anthocyanins in the methanol–CO_2 system vs. amount of methanol in the solvent.

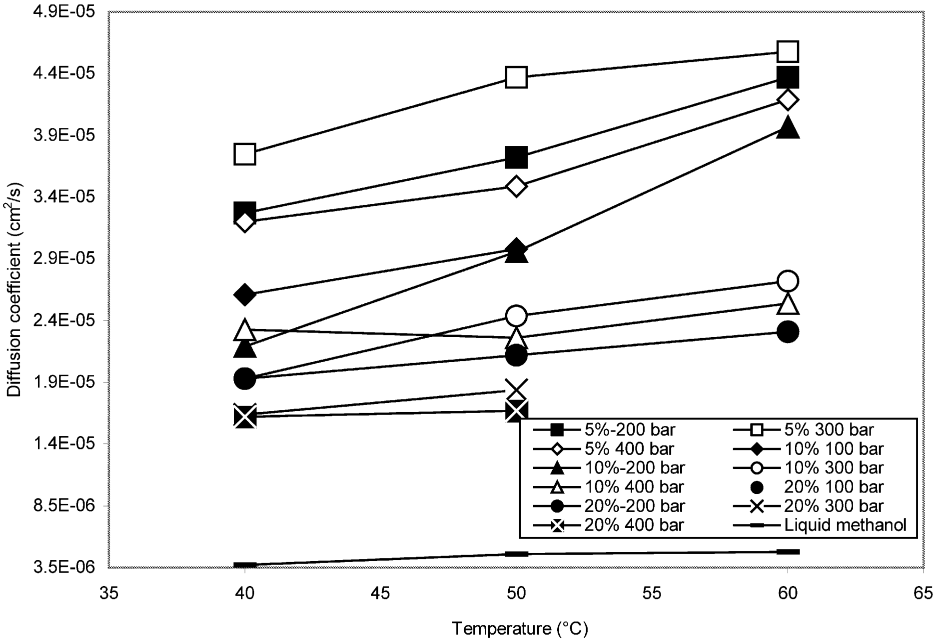

Fig. 6. Variation of the diffusion coefficient of anthocyanins in the methanol–CO_2 system vs. temperature.

5. Correlation of diffusion data

In this section, we will describe the fitting of the experimental diffusion coefficient data to different experimental equations proposed in the literature [5]. The correlations selected are empirical correlations that relate the diffusion coefficient with temperature, density, and viscosity. In all of these cases the accuracy of the fit is analyzed.

5.1. Correlation of diffusion coefficient-temperature (at constant pressure)

The diffusion coefficient in a supercritical fluid has a strong dependence on the temperature at constant pressure. This behavior is caused by the wide variations in the solvent density. The equations that relate the diffusion coefficient with temperature are of two types:

$$D_{12} = a + bT \qquad (6)$$

$$\ln D_{12} = a' + \frac{b'}{T} \qquad (7)$$

where D_{12} is the diffusion coefficient (cm²/s), T is the temperature (°C) and a, a', b and b' are fitting parameters.

The values of the parameters a and b from Eqs. (6) and (7) are shown in Table 3, and the average absolute deviation (AAD) of the experimental data at all the selected pressures are defined as follows:

$$\text{AAD } (\%) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{(D_{12})_{\text{exptl}} - (D_{12})_{\text{calcul}}}{(D_{12})_{\text{exptl}}} \right| \qquad (8)$$

where n is the number of values of the experimental diffusion coefficient. We eliminate the AAD of correlations from only two experimental data, The rest of the data always show a good fit when the AAD is lower than 4%. Both equations follow the same trend, although Eq. (7) leads to deviations that are somewhat larger than those obtained with Eq. (6). Finally, we correlated the experimental data for the diffusion coefficients of anthocyanins in liquid methanol to Eqs. (6) and (7). The parameters are presented in Table 3 along with the AAD data.

Table 3
Parameters of the correlations between diffusion coefficients and temperature-Eqs. (6) and (7)

Methanol (%)	Pressure (bar)	Parameters of Eq. (6)			Parameters of Eq. (7)		
		a ($\times 10^5$)	b ($\times 10^7$)	AAD (%)	a	b	AAD
5% vol.	100	–	–	–	–	–	–
	200	0.99	5.50	1.2	−9.49	−34.54	2.0
	300	2.10	4.15	2.2	−9.57	−24.81	1.5
	400	1.10	4.95	2.6	−9.59	−31.59	3.4
10% vol.	100	1.08	3.70	–	−9.90	−27.00	–
	200	−1.46	8.90	1.9	−8.97	−71.75	2.5
	300	0.34	3.95	2.2	−9.80	−42.56	1.3
	400	1.80	1.05	3.4	−10.48	−9.24	3.7
20% vol.	100	−2.37	10.6	–	−8.64	−89.81	–
	200	1.12	1.90	0.0	−10.34	−21.87	0.6
	300	0.79	2.00	–	−10.46	−23.70	–
	400	1.37	0.50	–	−10.90	−6.27	–
Liquid methanol	Atmospheric pressure	0.16	0.55	3.55	−11.68	−32.20	2.68

5.2. Correlation of diffusion coefficient–density

The possibility of establishing a correlation between all the experimental data and a single parameter allows the prediction of the diffusion coefficient using only one equation. In this sense, the application of empirical equations that relate the diffusion coefficient with the density and the viscosity of the solvent is of great utility.

As far as the density is concerned, the experimental diffusion coefficient data are plotted in Fig. 7 versus the solvent system density. The estimation of the density values was carried out with the program 'SF Solver™' (1991, ISCO, Inc. Lincoln, Ne), which is based on the modified Handinson–Brobst–Thomson method described by Reid et al. [19]. This method is adequate for the prediction of the compressed liquid density in the near critical region.

The results show different trends depending on the percentage of methanol in the solvent. The selected equation for the adjustment of the diffusion coefficient data and density is as follows:

$$\mathrm{Ln}\, D_{12} = a + b\rho \qquad (9)$$

where D_{12} is the diffusion coefficient (cm^2/s), ρ is the density (g/cm^3) and a and b are fitting parameters.

The parameters and the AAD of the data predicted with Eq. (9) are shown in Table 4. Finally, it is possible to establish linear correlations between the parameters a and b and the percentage of methanol in the solvent system in the following way (Table 4):

$$a = -10.125 + 0.1937 \cdot X \quad (r^2 = 0.991)$$

$$b = 0.0073 - 0.2553 \cdot X \quad (r^2 = 0.9999) \qquad (10)$$

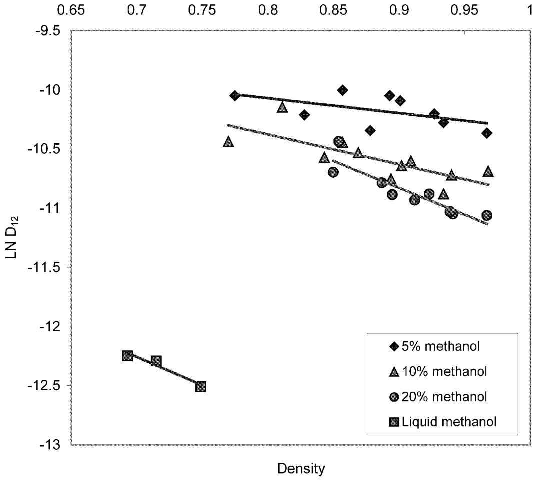

Fig. 7. Relation between the diffusion coefficient and density of the solvent system.

Table 4
Parameters of the correlation between the diffusion coefficient, density and viscosity described in Eqs. (9) and (12)

Solvent system	Eq. (9)			Eq. (12)		
	b	*a*	AAD	*b* ($\times 10^6$)	*a* ($\times 10^6$)	AAD
CO_2 + 5% methanol	–1.27	–9.05	8.3	1.64	21.1	9.3%
CO_2 + 10% methanol	–2.54	8.34	9.6	2.49	1.6	9.4%
CO_2 + 20% methanol	–5.10	–6.20	6.6	4.44	–13.0	7.4%
Liquid methanol	–4.80	–8.90	2.6	1.68	0.17	4.1%

Correlation of parameters *a* and *b*

Parameters	Eq. (9)			Eq. (12)		
	Slope	Intercept	r^2	Slope	Intercept	r^2
a	0.1937	−10.125	0.991	-2.16×10^{-6}	2.85×10^{-5}	0.93
b	−0.2553	0.0073	0.9999	1.88×10^{-7}	6.65×10^{-7}	0.999

Substituting Eq. (10) into Eq. (9) gives Eq. (11), which incorporates in a single equation the dependence of the diffusion coefficient of anthocyanins on the density of the solvent system and the volumetric percentage of methanol in the solvent system:

$$\mathrm{Ln}\, D_{12} = -10.125 + 0.1937 \cdot X + 0.0073 \cdot \rho - 0.2553 \cdot X \cdot \rho \qquad (11)$$

where X is the volumetric percentage of methanol in CO_2 and ρ is the density of the solvent system.

5.3. Correlation of diffusion coefficient–viscosity

The equations based on the Stokes–Einstein model [20] show an inverse dependence between the diffusion coefficient and the viscosity. This dependence means that the following correlation is required:

$$D_{12} = a + \frac{b}{\mu} \qquad (12)$$

where D_{12} is the diffusion coefficient (cm^2/s), μ is the viscosity (cP) and a and b are fitting parameters.

In Fig. 8, the diffusion coefficient data is plotted versus the inverse of the viscosity for the systems carbon dioxide plus 5, 10 and 20% of methanol at high pressure, as well as liquid methanol at atmospheric pressure. The trend line obtained is also shown. The values of the parameters *a* and *b* and the AAD data are shown in Table 4.

The viscosity of the solvent system was estimated by the Chung method described by Reid et al. [19] and is based on the value of the density of the solvent system estimated in the previous section. The estimated viscosities by the Chung method are shown in Table 5.

We proceeded to study the correlation between the diffusion coefficient and density and it was established that a linear regression exists between the parameters *a* and *b* in Eq. (12) as follows (Table 4):

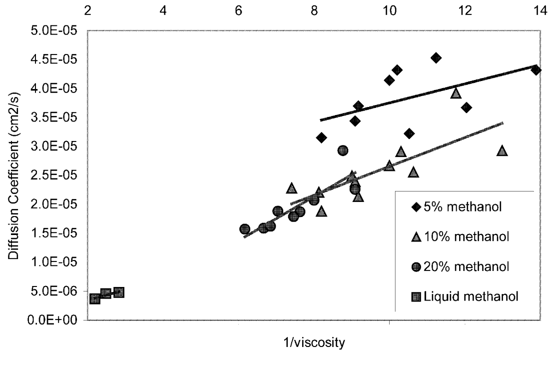

Fig. 8. Relation between the diffusion coefficient and viscosity of the solvent system.

Table 5
Estimated viscosities of the solvent system (CO_2+methanol) by the Chung method

Solvent system	Temperature (°C)	Pressure (bar)			
		100	200	300	400
CO_2+5% methanol	40	0.074	0.095	0.109	0.122
	50	0.052	0.083	0.098	0.110
	60	0.032	0.072	0.089	0.100
CO_2+10% methanol	40	0.094	0.109	0.122	0.135
	50	0.077	0.097	0.110	0.123
	60	0.056	0.085	0.100	0.111
CO_2+20% methanol	40	0.131	0.142	0.15	0.162
	50	0.114	0.125	0.134	0.146
	60	0.099	0.110	0.122	0.133

$$a = 2.85 \cdot 10^{-5} - 2.16 \cdot 10^{-5} \cdot X \quad (r^2 = 0.93)$$

$$b = 6.65 \cdot 10^{-7} - 1.88 \cdot 10^{-7} \cdot X \quad (r^2 = 0.999) \tag{13}$$

The substitution of parameters a and b into Eq. (12) allows the diffusion coefficient to be estimated using the following equation:

$$D_{12} = -2.85 \cdot 10^{-5} - 2.16 \cdot 10^{-6} \cdot X + \frac{6.65 \cdot 10^{-7}}{\mu} + 1.88 \cdot 10^{-7} \frac{X}{\mu} \tag{14}$$

where X is the volumetric percentage of methanol in CO_2 and μ is the viscosity of the solvent system (estimated by the Chung method).

6. Conclusions

The work described here presents data concerning the diffusion coefficient of malvidin 3,5-diglucoside in carbon dioxide with methanol as a cosolvent. The substance under investigation belongs to the anthocyanin family, members of which are commonly used as food dyes. Previous studies concerning transport properties in supercritical fluids with cosolvents are scarce. The data presented here, along with the data fitting performed in this study, are very useful in the design of extraction processes using these solvent systems.

The results obtained in this work show that the diffusion coefficient decreases as the percentage of methanol in the solvent increases. This behavior has been attributed to the formation of solute/methanol clusters, which give rise to an effective increase in the size of the resulting solute. This behavior, as well as the values obtained, is similar to that described in the literature.

Finally, an adjustment of the data obtained has been carried out in terms of the temperature, density and viscosity. The results obtained in this adjustment highlight the good fit found in the correlation between the diffusion coefficient, density and percentage methanol in the solvent system. This correlation also allows the coefficient to be estimated using only one equation with an AAD value of less than 10%.

Acknowledgements

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