



Limiting diffusion coefficients of sodium octanoate, and octanoic acid in aqueous solutions without and with α -cyclodextrin



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ABSTRACT

The Taylor dispersion technique has been used for measuring limiting binary mutual diffusion coefficients of octanoic acid and sodium octanoate at $T = 298.15 \text{ K}$ (D^0), respectively, using water as carrier solution, and different injections solutions from $(0.75 \text{ to } 100) \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. These D^0 values, together with the Stokes–Einstein equation, were used to determine the equivalent hydrodynamic radii, R_h , at infinitesimal concentration of these species (octanoic acid and sodium octanoate). In addition, the limiting diffusion coefficients of the molecular (D_m^0) and dissociated (D_d^0) forms of the octanoic acid were estimated.

We have also investigated the diffusion properties for a system containing octanoic acid, α -cyclodextrin (α -CD) and water. From these results, we have estimated the percentages of free (C_7COOH) and associated forms of octanoic acid (α -CD/ C_7COOH) and the equilibrium constant, K , for a supramolecular host–guest complex between octanoic acid and α -CD.

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1. Introduction

Medium-chain fatty acids (e.g., the octanoic acid) are found in about 7% in coconut oil [1] and at around $1 \text{ g} \cdot \text{L}^{-1}$ in milk [2] as a medium chain triacylglycerol (MCT), and they are also used as MCTs as food additives, or as biomass-derived bio-oil [3]. Taking advantage of octanoic acid being benign to human health, it was tested as a directional solvent for desalination, having showed a low solubility in water and a low salts dissolution capability [4].

Meanwhile, the presence of octanoic acid in human diet has recently aroused some concerns related with its side effects; specifically, the level of these medium chain fatty acids are normally elevated in patients subject to Ketogenic diet – an effective treatment with regards to treating pharmaco-resistant epilepsy [5], and there are also some reports on hepatic issues related to the presence of these substances in the human diet [6].

Cyclodextrins (CDs) are cyclic amphiphilic oligosaccharides, known to form host–guest inclusion complexes with many different types of compounds [7–9], as a consequence of the hydrophobic character of their internal cavity. The interactions of fatty acids with cyclodextrins has been used for their removal from vegetable oils [10], as a probe for the determination of olive oil acidity from the evaluation of the amount of fatty acids present in the olive oil

[10] and to prevent the oxidation of unsaturated fatty acids [11]. In the case of alkyl chain-based guests, the stability of host–guest compounds depends, among others, on the CD's cavity size and, in general, is higher for α -CD than for the other two natural CDs (β - and γ -CD) [12]. This is, in general, due to a more exothermic binding process involving the α -CD, justified by the best fitting between the size cavity of CD and the volume of alkyl chain length and, consequently, a stronger host–guest hydrophobic interaction [13].

Taylor dispersion technique has been extensively used in studies of multicomponent systems, either as binary, ternary or, more recently, quaternary ones [14–17].

However, this technique has not been often used for the characterization of amphiphilic systems. In what follows, we present limiting mutual diffusion coefficients of binary solutions formed by sodium octanoate and octanoic acid, respectively, and limiting diffusion coefficients of aqueous systems containing octanoic acid/ α -cyclodextrin.

2. Experimental

2.1. Materials

Octanoic acid, sodium octanoate and α -cyclodextrin were supplied from Sigma–Aldrich and were used as received (table 1). The solutions for the diffusion measurements were prepared in

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TABLE 1
Sample description.

Chemical name	Source	Mass fraction purity
α -Cyclodextrin	Sigma Aldrich	$\geq 0.98^a$ (Water mass fraction of (10.14%) ^b)
Sodium octanoate	Sigma Aldrich	>0.99
Octanoic acid	Sigma Aldrich	>0.98

^a The mass fraction purity is on the water-free basis.

^b The water content was determined by isothermal titration calorimetry [18].

calibrated volumetric flasks using bi-distilled water at $T = 298.15$ K in our laboratory. The solutions were freshly prepared and de-aerated for about 30 min before each set of runs. The concentrations of α -cyclodextrin were corrected for the water content 10.14% (w_T/w_T) for α -cyclodextrin, determined by isothermal titration calorimetry according to the reference [18].

2.2. Diffusion measurements

The Taylor dispersion method for measuring diffusion coefficients is based on the dispersion of a very small amount of solution injected into a laminar carrier stream of solvent or solution of different composition flowing through a long capillary tube (with length and radius of $(3.2799 \pm 0.0001) \cdot 10^3$ cm and (0.05570 ± 0.00003) cm, respectively) [16–19]. At the start of each run, a 6-port Teflon injection valve (Rheodyne, model 5020) was used to introduce 0.063 cm³ of solution into the laminar carrier stream of slightly different composition. A flow rate of 0.23 cm³ · min⁻¹ (corresponding to 3.5 rotations per minute of the peristaltic pump head) has been used, and was controlled by a metering pump (Gilson model Miniplus 3) to give retention times of about $8 \cdot 10^3$ s. The dispersion tube and the injection valve were kept at $T = (298.15 \pm 0.01)$ K in an air thermostat.

Dispersion of the injected samples was monitored using a differential refractometer (Waters model 2410) at the outlet of the dispersion tube. Detector voltages, $V(t)$, were measured at accurately timed 5 s intervals with a digital voltmeter (Agilent 34401 A) having an IEEE-488 interface. Binary diffusion coefficients were evaluated by fitting the detector voltages to the dispersion equation

$$V(t) = V_0 + V_1 t + V_{\max}(t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2 t]. \quad (1)$$

The additional fitting parameters were the mean sample retention time t_R , peak height V_{\max} , baseline voltage V_0 , and baseline slope V_1 .

Solutions of different composition were injected into water and therefore represented the differential value of D at water.

3. Results and discussion

3.1. Binary systems

3.1.1. Limiting diffusion coefficients for sodium octanoate

Table 2 gives the average values of diffusion coefficients, D , for each sodium octanoate (C_7COONa) solution tested. Each D value has been obtained from at least 4 profiles generated by different injecting samples, in water. The uncertainty of these values is not greater than (1 to 3)%, as has been previously reported [16,19,20]. It can be observed that the diffusion coefficients decrease slightly with an increase of the sodium octanoate concentration. Besides, the dependence of D on c follows a linear equation (see table 2) and, consequently, the limiting diffusion coefficient, D^0 , can be estimated and is equal to $0.858 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

By using the Nernst-Hartley equation [21],

TABLE 2

Mutual diffusion coefficients, D , of sodium octanoate (C_7COONa) and octanoic (caprylic) acid (C_7COOH) as a function of concentration, c , as obtained from the Taylor technique by using water as carrier stream, and the respective standard deviations of the mean, S_D , at $T = 298.15$ K and at $p = 101.3$ kPa.

C_7COONa		C_7COOH	
$c/$ (mol · dm ⁻³)	$D \pm S_D/$ (10 ⁻⁹ m ² · s ⁻¹)	$c/$ (10 ⁻³ mol · dm ⁻³)	$D \pm S_D/$ (10 ⁻⁹ m ² · s ⁻¹)
0.025	0.856 ± 0.010	0.75	1.189 ± 0.004
0.050	0.854 ± 0.004	1.00	1.077 ± 0.005
0.075	0.852 ± 0.003	1.50	0.950 ± 0.003
0.085	0.851 ± 0.004	2.00	0.872 ± 0.004
0.100	0.850 ± 0.001	2.50	0.849 ± 0.002
	^b $D^0 = 0.858$ (±0.001)		^c $D_m^0 = 0.697$ (±0.007)

^a Averaged result for $n = 4$ experiments.

^b Extrapolated value of D^0 obtained from the fitting of a straight line equation to D values as a function of concentration, c : $D/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1}) = 0.8579 (\pm 0.0002) - 0.079 (\pm 0.002)c$, ($R^2 = 0.9976$).

^c Extrapolated value at higher concentrations, where the degree of dissociation is zero ($\alpha = 0$), obtained from the equation $D/(10^{-9} \text{ m}^2 \cdot \text{s}^{-1}) = 0.697 (\pm 0.007) + 3.7 \cdot 10^{-4} (\pm 1 \cdot 10^{-5}) \cdot c^{-1}$, ($R^2 = 0.997$). Standard uncertainties u are $u_c(c) = 0.03$; $u(T) = 0.01$ K and $u(p) = 2.03$ kPa.

$$D^0 = \frac{RT}{F^2} \frac{|Z_c| + |Z_a|}{|Z_c \times Z_a|} \frac{\lambda_c^0 \lambda_a^0}{\lambda_c^0 + \lambda_a^0}, \quad (2)$$

where D^0 value is the diffusion coefficient for the sodium octanoate at infinitesimal concentration (table 2), Z_c and Z_a , and λ_c^0 and λ_a^0 represent the algebraic valences and the equivalent conductances at infinitesimal concentration of Na^+ and octanoate anion, respectively, and taking the limiting ionic conductivity of sodium ion as equal to $50.51 \cdot 10^{-4} \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ [21], we have estimated λ_a^0 , being equal to $23.65 \cdot 10^{-4} \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$. This latter value shows a deviation of ca. 5% from the limiting ionic conductivity of the octanoate ion computed from self-diffusion coefficient for octanoate ($D^0 = 0.600 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$); i.e., $\lambda_a^0 = 22.53 \cdot 10^{-4} \text{ m}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$ [22].

Our data show that the mutual diffusion coefficient of this system at infinitesimal concentration ($D^0 = 0.858 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) is significantly larger (1.43 times) than that above limiting diffusion coefficient. This increase in the λ_a^0 value can be justified by the electrostatic dragging effect of sodium ions on octanoate ions [23].

3.1.2. Limiting diffusion coefficients for octanoic acid

The mean values of the mutual diffusion coefficients, D , for octanoic acid for different concentrations of the injected solutions in water are also reported in table 2. These D values were obtained by using the same procedure as described above.

Being the octanoic acid a weak acid ($\text{p}K_a = 4.89$ [24]) the limiting diffusion coefficient of the molecular form (i.e., fully associated), D_m^0 , can be estimated from a plot of $D = f(c^{-1})$. In our case such dependence follows a linear relationship (see footnote in table 2) and, consequently, the D_m^0 can be estimated by extrapolation, when the degree of dissociation approaches zero ($\alpha \rightarrow 0$), and is equal to $0.697 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, at $T = 298.15$ K.

The diffusion coefficient of fully ionized octanoic acid, D_{\pm}^0 , is obtained from the Nernst-Hartley equation (equation (2)), taking the limiting ionic equivalent conductances equal to $\lambda_c^0 = 349.81 \cdot 10^{-4} \Omega^{-1} \cdot \text{m}^2 \cdot \text{s}^{-1}$ [21] and $\lambda_a^0 = 23.65 \cdot 10^{-4} \text{ m}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1}$, and is equal to $1.180 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

From the differences between D_m^0 and D_{\pm}^0 , (D_m^0 is significantly lower than that of the corresponding D_{\pm}^0), we conclude that the dissociation influences the rate of diffusion of this weak electrolyte. That is, increasing the number of free solute species (the dissociation increases the chemical potential gradient that drives the solute through the solvent), and since the movement of two separate ions

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