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Separation of some light monocarboxylic acids from water in binary solutions in a reverse osmosis pilot plant

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Abstract

The separation of formic (C_1), acetic (C_2), propionic (C_3), and n-valeric (C_5) acids in binary water solutions has been studied using a reverse osmosis (RO) membrane pilot plant operating at different temperatures and pressures (usually 21°C and 1.72 MPa). The RO membrane, which is composite, polyamide and spiral-wound, having a surface area of 2.6 m^2, was fed by a solution of 0.5 M of C_1, C_2 and C_3 acids and 0.146 M of C_5. The pilot plant was used to simulate a cascade series of RO modules by recycling the permeate flux at the end of each semi-batch run. The influence on the retention coefficient, R, of molecular weight and molar volume, pK_a of the different acids was determined. For acetic acid the influence of temperature (T) and transmembrane pressure (ΔP) was also studied, obtaining an inverse and direct good linear correlation for R vs. T and R vs. ΔP, respectively. The results are particularly interesting for acetic acid–water separation, which is an open question in industrial applications.

Keywords: Reverse osmosis; Carboxylic; Acetic; Acid; Separation

1. Introduction

Light carboxylic acids (LCA), i.e., C_1–C_5, are widely used in industrial processes, particularly acetic acid. Formic acid (C_1) is used in tanning processes and as a reducing agent. Acetic acid (C_2) has the largest production among the LCA mentioned above; it is used in the production of cellulose esters, terephthalic acid, dimethyl terephthlatate and as a solvent; acetylation reactions via acetic anhydride produce acetic acid. Propionic acid (C_3) is found in butter and milk; some esters are used to prepare perfumes. It is formed in great quantity from carbohydrates by fermentation with *Propionibacterium*. n-butyric acid (C_4) as glyceride is present in milk fat; notwithstanding its bad smell, its esters (ethyl and isoanyl) are used in artificial flavors. Valeric acids (C_5) have five isomers and some of these are

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found in nature in some plant roots (*Valeriana officinalis, Angelica archangelica*); the acids are used to synthesize natural products.

The use of LCA in different industries often requires purifying aqueous outcoming streams containing such compounds in order to reduce waste contamination or to recover partially the acids. Such problems are still an open question from an industrial point of view, especially for acetic acid. An attempt in this direction has been made by the authors using an esterification reaction [1].

As discussed below, published papers on the separation of LCA from water using RO [5–10,15], or nanofiltration [11], are devoted to much diluted solutions, usually in the range of 0.01–0.05 mol l^{-1} (0.17 or 0.85 mol l^{-1} [11]) using laboratory apparatuses with small surface area membranes. Our aim is therefore to operate with a higher concentration of acids (for C_1, C_2, and C_3: 0.5 mol l^{-1}; for C_5: 0.146 mol l^{-1}) using a high surface area RO membrane (2.6 m^2) in a pilot plant. Such a plant, operating usually at 1.72 MPa, can simulate a cascade module plant by recycling the permeate solution at the end of each batch run. The retention parameter, R, together with the values of other parameters, was recorded both during each batch run and from one run to the next.

2. Experimental

2.1. Products

LCAs are all Fluka products. The main characteristics of these products (including C_4 acid not used in our experiments) are reported in Tables 1A and 1B. The differences between the molar volume for the liquid and the isolated molecule, shown in Table 1A, give an indication of the degree of association of the molecule in pure liquid.

2.2. Laboratory plant

Fig. 1 shows the pilot plant scheme (MeTe Srl, Olgiate Olona, VA, Italy). The main components

Table 1A
Main characteristics of light carboxylic acids (C_1–C_5)

Name	Molecular weight (MW), g mol^{-1}	Molar volume (V_m), cm^3 mol^{-1}		μ dipolar moment, Deby		Melting point, °C	Normal boiling point, °C	pK_a (25°C) [4]
		a	b	[2]	[3]			
Formic	46.025	37.7	30.5	1.5	1.41	8.4	100.5	3.75
Acetic	60.052	57.2	41.1	1.3	1.7	16.7	118.2	4.76
Propionic	74.080	74.6	47.4	1.5	1.46	-22	141.1	4.87
n-Butirric	88.1007	91.99	65.8	1.5	1.3[d]	- 7.9	163.5	4.82
n-Valeric	102.34	143.8	90.9	1.0[c]		-34.5	186.3	4.84
Water	18.015	18.0	12.0	1.8	1.854	0	100	

[a] V_m calculated from density at $T = 20°C$.
[b] Calculated from electronic density of an isolated molecule. A value of 0.001e Å^{-3} of the electronic density was assumed as the contour of the molecule.
[c] This datum is referred to as iso-valeric acid.
[d] This datum is referred to as iso-butirric acid.