

Solubilities of Anthraquinones in Pressurized Solvents

M.F. Barrera Vázquez^(1,2), A.E. Andreatta^(1,3), R.E. Martini^(1,2), S.B. Bottini⁽⁴⁾

⁽¹⁾ *IDTQ- Grupo Vinculado PLAPIQUI – CONICET*

⁽²⁾ *UNC. Facultad de Ciencias Exactas Físicas y Naturales. Av. Vélez Sarsfield 1611, Ciudad Universitaria.*

⁽³⁾ *UTN. Facultad Regional San Francisco. Av de la Universidad 501, San Francisco, Córdoba, Argentina.*

⁽⁴⁾ *PLAPIQUI (UNS-CONICET). Cno. La Carrindanga Km 7. Bahía Blanca
E-mail: mfbarreravazquez@plapiqui.edu.ar*

INTRODUCTION

Anthraquinones (AQs) are an important category of secondary metabolites present in various vegetable species [1]. They are highly bioactive compounds, potentially useful for therapeutic applications, as antiviral, anti-bacterial and anti-cancer agents [2-5]. Extraction processes using pressurized hot water and supercritical fluids offer an environmentally friendly alternative to traditional extracting and purifying methods applied to anthraquinone-containing plants [6,7]. Knowledge on high-pressure phase equilibria of AQs + solvent mixtures is required to evaluate the potentiality of these processes. The need is for both, experimental data and thermodynamic models that are able to predict phase boundaries at different process conditions. In this work, the solubility of 1,4-dihydroxy-9,10-anthraquinone (quinizarin) in pressurized hot water have been measured, using a simple and reliable dynamic method. For the binary quinizarin + H₂O, the measurements covered a range of 333-463 K and pressures closed to 3, 6 and 9 MPa. The group-contribution with association equation of state GCA-EOS [8] was used to calculate solid-liquid equilibria of binary mixtures of AQs with pressurized hot water.

MATERIALS & METHODS

The equipment consists in a stainless steel high-pressure extractor cell with 10mL internal volume, a HPLC pump, a coiled preheater and a downstream back pressure regulator (BPR). The extraction cell is equipped with a heating system using aluminum heating jackets with two electrical resistances and provided with a temperature regulator. To maintain the temperature set is installed within a thermally insulated box. The pressure in the extractor is measured with a pressure gauge. To begin the solubility measurements, 0.5 g of quinizarine are loaded inside the cell and then the system is closed. Later, the operating temperatures of the preheater and cell are set. The BPR is used to set the pressure at the operating value. The following operating conditions were studied: temperatures equal to 333-463 K; pressures of 3, 6 and 9 MPa. The water flow rate used in these experiments was 0.75 mL/min. This flow rate was slow enough to ensure that equilibrium was obtained. The concentrations of the quinizarine were analyzed using a spectrophotometer at absorbance 480.18 nm.

A group-contribution with association equation of state GCA-EOS [8] was applied to represent phase equilibrium data. For this purpose, a new functional groups, (AC=O) was defined to represent the anthraquinones. Parameters for these news functional groups were determined by fitting pure component and solubility experimental data.

RESULTS & DISCUSSION

Aqueous solubility of the quinizarin as a function of temperature is shown in Fig 1, at different pressures. As it can be observed, the solubility increases as temperature increases, as expect.

This increment is more important above 413K. The pressure increment produces a decrease in solubility of quinizarin, as it was observed for other authors for polycyclic aromatic compounds [9, 10]. The experimental solubility data for the AQ were correlated using the model GCA-EOS. In consequence to it, a new functional group (C=O) is defined in way of representing this class of compound aromatic. Parameters for these new functional groups were determined by fitting pure component and binary experimental data. The parameterization carried out in this work provided a satisfactory correlation of experimental data as shown in Fig. 1.

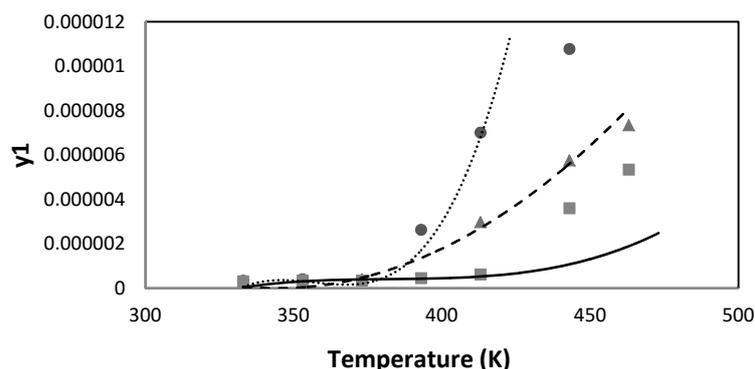


Figure 1. Comparison of solubility calculated using equation GCA-EOS (lines) and experimental data (symbols) of the quinizarin in H₂O at 3 MPa (●), 6 MPa (▲) and 9 MPa (■).

CONCLUSIONS

In this work is shown the solubility data of quinizarin in hot pressurized water at different pressure and temperature conditions. GCA-EoS equation, with the definition of the aromatic ketone functional group (C=O), is able to give a good representation of the experimental conditions solid-liquid mixture of quinizarin in water.

REFERENCES

- [1] R. Wijnsma, R. Verpoorte. 1986. In: W. Herz, H. Grisebach, G.W. Kirby, Ch. Tamm (Eds.), *Prog. Chem. Org. Nat. Prod.*, vol. 49, Springer-Verlag, Wien, pp. 79–149.
- [2] Nuñez Montoya S.C.N., Agnese A.M., Pérez C., Tiraboschi I.N., Cabrera J.L. 2003. *Phytomedicine* 10, 569-574.
- [3] Comini L.R., Nuñez Montoya S.C., Paéz P.L., Argüello G.A., Albasa I., Cabrera J.L. 2011. *J. of Photochemistry and Photobiology B: Biology* 102, 108-114.
- [4] Comini L.R., Fernandez I.M., Rumie Vittar N.B., Nuñez Montoya S.C., Cabrera J.L., Rivarola V.A. 2011, *Phytomedicine* 18, 1093-1095.
- [5] Königheim B. S., Beranek M., Comini L. R., Aguilar J.J., Marioni J., Cabrera J.L., Contigiani M. S. and Nuñez Montoya S.C. 2012. *Natural Products Communications* 6, 1-3.
- [6] Barrera Vázquez M.F., Comini L.R., Milanesio J.M., Nuñez Montoya S.C., Cabrera J.L., Bottini S., Martini R.E. 2015, *J. of Supercritical Fluids* 101, 170–175
- [7] Shotipruk A., Kiatsongserm J., Pavasant P., Goto M., Sasaki M. 2004. *Biotechnol. Prog.* 20, 1872-1875.
- [8] Skjold-Joergensen, S. 1988. *Industrial & Engineering Chemistry Research*, 27 (1), 110-118.
- [9] Miller D.J., and Hawthorne S.B. 1998. *J. Chem. Eng. Data* 43, 1043-1047.
- [10] Rössling, G. L., Franck, E. U. 1983. Solubility of Anthracene in Dense Gases and Liquids to 200 °C and 2000 Bar. *Ber. Bunsen-Ges. Phys. Chem.* 87, 882-890.