Supercritical water as reaction media.
Physical properties at supercritical conditions an overview.

J. García, O. Pérez, F.Fdez-Polanco, M.J. Cocero[*]
University of Valladolid – Chemical Engineering Department
Prado de la Magdalena s/n, 47011 – Valladolid (Spain)
[*]mjcocero@iq.uva.es   Fax: +34 983423013

ABSTRACT

Supercritical water is favorable medium to carry out diverse reactions, specially focusing on "green chemistry" and environmental applications. The intermolecular structure of water due to hydrogen bond, in these conditions, varies and causes changes in its properties and the properties of its solutions. In order to be able to study the behavior of these solutions, to design hydrolysis and oxidation processes, corrosion of equipment as well as the design of new experiments, is necessary to know some physical properties or water in supercritical state.

The review was made to know which are the equations of correlation and interpolation more suitable and accuracy to obtain different properties of supercritical fluids, applied to supercritical water. In this paper a brief discussion, correlation equation and limits of application for the dielectric constant, viscosity and ionic product are presented.

KEYWORDS

Supercritical water, EOS, correlation equation, physical properties, hydrogen bond.

1. INTRODUCTION

Nowadays, green chemistry presents alternative processes and products aimed at substituting toxic and hazardous traditional materials by environmental friendly compounds. Various types of reactions could be carried out in supercritical water as reaction media. Among this types, oxidation reactions are used to the complete destruction of organic wastes [1-3], hydrolysis to recycle materials from other processes [4,5], synthesis to obtain chemical compounds avoiding dangerous products such as phosgene, for example in dymethylcarbonate synthesis [6-9] and other heterogeneous catalysis [10].

A great variety of supercritical fluid laboratory processes are available, so industrial usage is growing up. In order to design and up-scale new supercritical processes the knowledge of physical properties is necessary. Correlation equations for experimental data are useful to predict behavior and to find new possibilities.

Water possesses a high critical point (374 ℃ and 221 bar) because of the strong interactions between the molecules due to hydrogen bond. Hydrogen bond appears when the hydrogen atom is joined to a small atom with a high electro-negativity. At supercritical conditions, the order of hydrogen bond is reduced considerably and so the physical properties of water change drastically at this conditions and it can be used as reaction media.

Touba and Mansorii [11] studied hydrogen bonding referring to the formation of chemical aggregates or polymers, considering the following reaction:

$$(H_2O)_i + (H_2O)_1 \xleftarrow{\quad K_i(T) \quad} (H_2O)_{i+1} \qquad i = 1,2,...,\infty \tag{1}$$
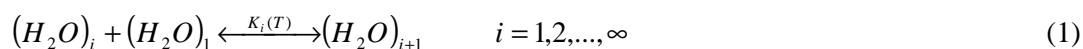
where $K_i(T)$ is the equilibrium constant at temperature T. They develop modified equations of state considering the associating water species. Touba considers that at room conditions, a molecule of water possesses hydrogen bonds with a hundred of molecules making a hydrogen bond lattice. At supercritical conditions, although the bonds lattice is destroyed, the hydrogen bonding persists among a pair of water molecules.

Neutronic dispersion, and vibrational and electronic spectroscopies are used to study the structure of the hydrogen bond of water and aqueous solutions. Neutronic dispersion was used at room and subcooling conditions [12,13] and spectroscopic methods were used under supercritical conditions. Proton Nuclear Magnetic Resonance (NMR) [14], Infrared Spectroscopy (IR) [15] and Raman Spectroscopy [16] had been applied to probe the density effect on the water structure. Nakahara et al. [17] measured the chemical shift by NMR of hydrogen bonding to temperatures between 300 and 400 ℃, estimating the number of hydrogen bonds to different densities, with distances limits of bond of 2.3 and 2.4 Å.

Experimental data and correlation equations for physical properties at supercritical conditions are reviewed for density, viscosity, dielectric constant, ionic product, thermal conductivity and inorganic salts solubility in the whole work and in the poster. In this paper dielectric constant, viscosity and ionic product are presented briefly as an example.

2. DIELECTRIC CONSTANT

The dielectric constant of a substance is a measure of the relative effectiveness of that substance as an electrical insulator. It is related to the interaction grade among the molecules

of a fluid, the dipole moment and the polar orientation; that property diminishes strongly with the increment of temperature and decrease of density in supercritical region.

At room conditions, liquid water has a high dielectric constant, round 80, not only due to the dipoles of individual molecules, but also to molecules association due to hydrogen bonding. At supercritical conditions, water changes its structure and most of the intermolecular associations are broken, causing the decrease of constant and changing polar interactions into dipole – dipole interactions [18, 19].

In 1920 appears the first experimental data [20] obtained at high pressures and low temperatures. Now data up to 600 ºC and 2 GPa are available [21-27].

One of the last correlations recommended by IAPWS [28] has been formulated by Fernandez et al. in 1997 [29]. This interpolation equation is based on Harris-Alder equation, computing the dielectric constant as a function of temperature and density. This equation is valid for temperatures down to 323 K and pressures up to 600 MPa.

Experimental data from Lukashov (1975, 1981) and predicted values with Uematsyu-Frank equation [30] and Fernandez equation are presented in table 1 as an example.

Table 1:

T (K)	ρ (kg/m³)	A	B	g	ε (eq. Fdez et al.)	ε (Lukashov, 81)	ε (Lukashov, 75)	ε (eq. U-F)
673	100	1.75	0.02059	1.14133	1.757	1.79	1.75	1.639
	200	4.14	0.04117	1.35304	2.97	2.92	2.90	2.8706
	300	7.32	0.06176	1.59434	4.725	4.65	4.46	4.666
773	100	1.52	0.02059	1.13787	1.658	1.68	1.61	1.5541
	200	3.55	0.04117	1.33384	2.69	2.656	2.46	2.6159
	300	6.22	0.06176	1.55562	4.15	4.060	3.81	4.1732
873	100	1.34	0.02059	1.13757	1.58	1.45	1.45	1.5023
	200	3.12	0.04117	1.32403	2.485	2.13	2.13	2.4814

3. IONIC PRODUCT

Ionization capacity of water is represented with the equilibrium reaction:

$$H_2O_{(aq)} + H_2O_{(aq)} \xleftrightarrow{\quad K_w(T) \quad} H_3O^+_{(aq)} + OH^-_{(aq)} \tag{2}$$
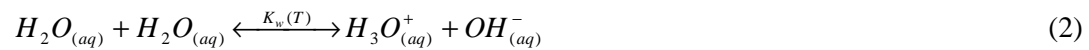
where $K_w(T)$ is the ionization constant as a function of temperature (T). At ambient conditions, the value of K_w is 10^{-14} changing to 10^{-23} at supercritical conditions. As an example, the value of pH changes 5.6 at 250 ºC to 8 at the critical point [31].

The first experimental determinations of ionization constant (K_w) to high temperatures were carried out by Noyes et al. and published in 1907 [31] and 1910 [32]. The measurements of this constant in supercritical region were carried out by Hamann et al. [33] to 13.3 GPa and 800 ºC, using technical of explosion; Holzapfel and Franck [34] to 10 GPa and 1000 ºC, applying instantaneous static pressurization; Quist [35] in ranges of 100 at 400 MPa and 300 to 800 ºC, by electric conductance. Values for ionic product at 25.0 Mpa are presented in figure 1.

Figure 1 : Ionic product at 25.0 MPar
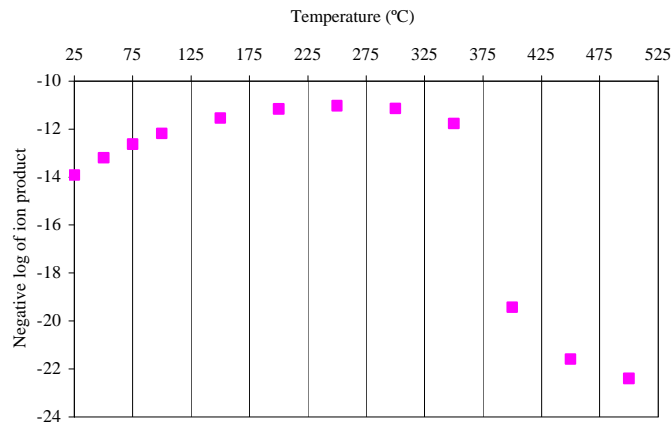
Marshall and Franck equation (1981), recommended by IAPWS, is presented in poster. This equation computes $\log(K_w)$ as a function of temperature and density for pressures up to 1 GPa and temperatures up to 1000 ºC with a precission of $\pm 0.3 \log(K_w)$.

4. VISCOSITY

Viscosity of a fluid represents the facility of movement of the molecules with respect to others; this depends on the attractive forces that maintain the bonds to them. Taking the Newton's law for viscosity it is represented:

$$\boldsymbol{t}_{xy} = -\boldsymbol{m} \cdot \frac{dv_x}{dy} \qquad (3)$$

where: τ_{xy} = flow density of movement, μ = viscosity, $\dfrac{dv_x}{dy}$ = velocity gradient

The viscosity of supercritical water has been determined by capilarity methods [36-42] and by an oscillating disk [43-45].

The Sengers and Kamgar-Parsi (1984) [46] prediction equation, recommended by International Association for Properties of Water and (IAPWS, 1996) [47], is presented in poster. This equation computes viscosity as a function of reduced temperature ($\overline{T}$) and density ($\overline{r}$) in the form:

$$\overline{m} = \overline{m}_0\left(\overline{T}\right) * \overline{m}_1\left(\overline{T}, \overline{r}\right) * \overline{m}_2\left(\overline{T}, \overline{r}\right) \tag{4}$$

where:

$\overline{m}_0\left(\overline{T}\right)$: viscosity of vapor in limit of ideal gas

$\overline{m}_1\left(\overline{T}, \overline{r}\right)$: Incremental factor for temperature and density

$\overline{m}_2\left(\overline{T}, \overline{r}\right) = 1$ in most cases, it could be calculated with an experimental equation.

This equation could be applied for pressures up to 500 MPa and temperatures up to 900 ºC in some conditions.

The experimental values from the Release on Viscosity of Ordinary Water Substance, IAPWS, 1997, [48] are compared with that obtained with Sengers K-P equation.

5. BIBLIOGRAPHY

[1] KRAJNC M., LEVEC J., Applied Catalysis, 13, 1997, 15-25
[2] RICE S.F., STEEPER R.R., J. Hazardous Materials, 59, 1998, 1-14
[3] COCERO M.J., ALONSO E., SANZ M.T. AND FDZ-POLANCO F., J. Supercrit. Fluids, Vol. 24 Issue 1, 2002, p. 37
[4] ADSCHIRI, T., 6th Worl Congress on Chemical Engineering, Melbourne 2001.
[5] ARAI, Y., SAKO T. and TAKEBAYASJI Y., Springer, Eds. 2002
[6] ZHAO T.,HAN Y., SUN Y., Fuel Process. Tech., 62, 2000, 187-194
[7] HU J., CAO Y., YANG P., DENG J-F, FAN K-N.*, J. Molec. Catalysis, 185, 2002, 1-9
[8] ONOY., CT, 35, 1997, 339-347
[9] CAMY S., PIC J.S., BADENS E., CONDORET J.S., J. Supercrit. Fluids, 0, 2002, 159-166
[10] SAVAGE P.E., Catalysis Today, 62, 2000, 1-7
[11] TOUBA H., MANSOORI G.A., Fluid Phase Equil., vol. 150-151, 1998, p. 459
[12] BELLISSENT-FUNEL, M.-C., NATO ASI Series C on "Hydrogen Bonded Liquids", J.C. Dore and J. Texeira (eds.), 329, 1991, p. 117
[13] BELLISSENT-FUNEL, M.-C., BOSIO, L., J. Chem. Phys., 102, 1995, p. 3727
[14] MATUBAYASI, N., WAKAI, C., NAKAHARA, M., J. Chem. Phys., 110, 1999, p. 8000
[15] FRANCK, E.U.; ROTH, K. Discuss. Faraday Soc., 43, 1967, p. 108
[16] WALRAFEN, G.E., CHU, Y.C., PIERMARINI, G.J., J. Phys. Chem., 100, 1996, p. 10363
[17] NAKAHARA, M., MATUBAYASI, N., WAKAI, C., TSUJINO, Y., J. Mol. Liquids, 90, 2001, p. 75
[18] FRANCK, E.U., Chem. Thermodynamics, 19, 1987, p. 225
[19] MODELL, M.; THOMASON, T., Hazardous Waste, 1, 1984, p. 453

[20] FALCKENBERG, G., Ann Phys., 61, 1920, p. 145

[21] KYROPOULOS, S., Z. Phys., 40, 1926, p. 507

[22] LEES, W. L., Thesis, Harvard Univ., Cambrigde, Massachusetts, 1949

[23] FOGO, J. K., BENSON, S.W., COPELAND, C.S., J. Chem. Phys., 22, 1954, p. 209

[24] KOSLOV, M.G., BOGOMALOV, Y.A., MICHUROV, Y.P., SEROV, E.P., KURONOV, N.M., SMIRNOV, O.K., KEMEL'MAN, M.N., Teploenergetika, 14, 1967, p. 10

[25] HEGER, K., Dissertation, University of Karlsruhe, Karlsruhe, Germany, 1969

[26] LUKASHOV, Y.M., GOLUBEV, B.P., RIPOL-SARAGOSY, F.B., Teploenergetika, 22, 1975, p.6

[27] LUKASHOV, Y.M., Ph. D. dissertation, Moscow Power Institute, 1981

[28] RELEASE ON THE STATIC DIELECTRIC CONSTANT OF ORDINARY WATER SUBSTANCE FOR TEMPERATURES FROM 238 K TO 873 K AND PRESSURES UP TO 1000 MPa, http://www.iapws.org/relguide/dielec.pdf, 1997

[29] FERNÁNDEZ, D.P., GOODWIN, A.R.H., LEMMON, E.W., LEVELT SENGERS. J.M.H., WILLIAMS, R.C., J. Phys. Chem. Ref. Data, 26, **1997**, p. 1125

[30] UEMATSU, M., FRANCK, E.U., J. Phys. Chem. Ref. Data, 9, **1980**, p. 1291

[31] NOYES, A.A., Series of Experimental Investigations, A.A. Noyes, W.D. Coolidge, A.C. Melcher, H.C. Cooper, Y. Kato, R.B. Sosman, G.W. Eastman, C.W. Kaholt, W. Böttger (eds.), The Carnegie Institution of Washington, Washington, DC, **1907**, p. 239

[32] NOYES, A.A., KATO, Y., SOSMAN, R.B., J. Am. Chem. Soc., 32, **1910**, 159

[33] HAMANN, S.D., LINTON, M., Trans. Faraday Soc., 65, **1969**, p. 2186

[34] HOLZAPFEL, W.B., FRANCK, E.U., Ber. Bunsenges. Phys. Chem., 70, **1966**, p. 1105

[35] QUIST, A.S., J. Phys. Chem., 74, **1970**, p. 3396

[36] WHITELAW, J.H., J. Mech. Eng. Sci., 2, **1960**, p. 288

[37] MAYINGER, F., Int. J. Heat Mass Transfer, 5, **1962**, p. 807

[38] TANAKA, K., SASAKI, M., HATTORI, H., KOBAYASHI, Y., HAISHIMA, K., SATO, K., TASHIRO, M., Trans. JSME, 12, **1965**, p. 1847

[39] NAGASHIMA, A., TANISHITA, I., Bull. JSME, 12, **1969**, p. 1467

[40] RIVKIN, S.L., LEVIN, A.Y., IZRAILEVSKI, L.B., Thermal Eng., 17, **1970**, p. 127

[41] RIVKIN, S.L., LEVIN, A.Y., IZRAILEVSKI, L.B., Teplo I Massoperenos, 7, **1972**, p. 61

[42] RIVKIN, S.L., LEVIN, A.Y., IZRAILEVSKI, L.B., KHARITONOV, K.F., Thermal Eng., 20, **1973**, p. 14

[43] DUDZIAK, K.H., FRANCK, E.U., Ber. Bunsenges. Phys. Chem., 70, **1966**, p. 1120

[44] TIMROT, D.L., SEREDNITSKAYA, M.A., BESPALOV, M.S., Thermal Eng., 20, **1973**, p. 106

[45] OLTERMANN, G., Thesis, Thechnische Universität Hannover, **1977**

[46] SENGERS, J.V., WATSON, J.T.R., BASU, R.S., KAMGAR-PARSI, B., HENDRICKS, R.C., J. Phys. Chem. Ref. Data, 13, **1984**, p. 893

[47] RELEASE ON THE IAPWS FORMULATION 1995 FOR THE THERMODYNAMIC PROPERTIES OF ORDINARY WATER SUBSTANCE FOR GENERAL AND SCIENTIFIC USE, http://www.iapws.org/relguide/IAPWS95.pdf, **1996**

[48] RELEASE ON THE VISCOSITY OF ORDINARY WATER SUBSTANCE, http://www.iapws.org/relguide/visc.pdf, **1997**