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IAPWS Certified Research Need - ICRN
ICRN 13

Surface Tension of Aqueous Solutions

The IAPWS Working Group - Power Cycle Chemistry has examined the published work in the area of surface tension of aqueous solutions, which is of direct relevance to the reliability of electric power plants.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. Specifically experimental studies are needed to quantify the effects of surface tension effects on nucleation for aqueous salt solutions and ammonia water mixtures in the temperature range 25 C to 150 C.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will act as a liaison between research groups.

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ICRN Summary

Surface tension is a property of great interest to the power industry because of its effect on different physical processes of practical relevance, for instance in steam nucleation and heat exchange.
The steam nucleation process, occurring in the last stages of the low pressure cylinder, has increased in importance because of its recognized contribution in reducing steam turbine efficiency. The efficiency losses associated with condensation are significantly large (Baumann rule):

$$\eta_{\text{wet}} = \eta_{\text{dry}} * (1 - 0{,}5\alpha Y)$$

η_{wet} = stage efficiency with “humid” steam
η_{dry} = stage efficiency with “dry” steam
α = correlation factor ($\cong 1$)
Y = steam humidity

This situation arises from the combined effect of the following losses:

a.	*thermodynamic*	the obtainable (useful) turbine work is reduced, compared with the equilibrium expansion, because of the steam undercooling;
b.	*mechanical*	interaction between the humidity formed (droplet structure and dimensions) and the turbine stage blades and also the two phases (vapor and liquid);
c.	*fluid dynamic*	condensation shocks contribute to flow instabilities (energy dissipation and larger droplet sizes), variation of droplet paths (increased mechanical losses) and generally 3D heterogeneity of the fluid (non optimal blade design).

The total losses have been estimated (320 MW once-through supercritical unit) around 13 kJ/kg, equivalent to 0,7 % lower efficiency: 75% associated with fluid dynamics and 25% with thermodynamic effects.

Moreover, the deposition of salts on turbine surfaces influences corrosion and the droplet sizes effects erosion: in general any condensation processes occurring in industrial equipment are affected to some extent.

The “flow pattern” actually occurring in heat exchangers is of the largest practical importance, even larger when the role of the heat exchange is stressed, as in the Kalina cycle. In this advanced cycle an increase in efficiency is expected because of the possibility of minimizing the energy dissipation associated to the constant temperature water evaporation (as in the standard Rankine cycle) by using the binary mixture (H_2O-NH_3) it is possible to follow more closely the required temperature profile. This implies a particular heat exchange design, which might be achived by a series of heat exchangers appropriately designed. The lack of property data for this novel fluid makes it difficult to design a cycle with all the expected benefits. For instance the surface tension of the H_2O-NH_3 system, over a large range of temperature and pressure is required.

Static and dynamic surface tension.

When a surface is formed, or it changes in shape or volume, a surface tension related work has to be considered. However the process has its own dynamics, as every process has, the surface tension may vary with time because of process kinetics. This dependence could, for example, be related to the rate of change of surface area ($m^2\ s^{-1}$), and may be positive or negative in value. In steam nucleation the area production rate depends on the nucleation rate, *J*, estimated as 10^{-6} m^2 s^{-1} (when $J = 10^{10}$ s^{-1}) or 10^4 m^2 s^{-1} (when $J = 10^{12}$ s^{-1}).

The static surface tension value applies to a thermodynamic equilibrium condition (system at steady state), while the dynamic surface tension value refers to a kinetic condition (transient system). The dynamic surface tension values may be related to the migration rate (diffusion) of surfactants from the bulk to the surface. This aspect should be carefully investigated to assess the relative importance for using dynamic or static values for practical applications.

Surface tension and nucleation.

Nucleation, according to the well established Becker-Doering model, is expressed by the following relationship:

$$J = \beta * Z * \mathrm{e}^{-\frac{\Delta G}{kT}}$$

$$\Delta G = -\frac{4}{3}\pi r^{*3}\frac{\rho_l}{M_M}N_A k_B T_V \ln\frac{p}{f_{H2O}} + 4\pi r^{*2}\sigma$$

$$Z = \frac{Mm}{2\pi r^{*2} N_{AV}\rho_l} * \sqrt{\frac{\sigma}{kT}}$$

β = impingement factor, from the kinetic theory of gases

The surface tension (σ) actually affects both the Zeldovich and the free energy terms: through the free energy term it exponentially affects the process.

Other formulations have been developed for nucleation, all of these include the effect of the surface tension in a more complex way, this is in at least one exponential term.

Surface tension data for aqueous solutions.

Data are commonly available at normal temperature and pressure (T = 25 °C, P = 0,1 MPa) for a large number of substances and aqueous solutions. For the "water substance" enough data have been produced to derive a formulation covering the complete range of the liquid-vapour saturation line, from the triple point to the critical point. Very few data are available for multicomponent systems, particularly the aqueous systems, covering the temperature and pressure ranges of interest for power industry applications. A common approximation adopted to obtain the surface tension value at a given temperature consists of correcting the surface tension of the solution at the particular concentration using the temperature dependence of pure water.

Surface tension determination.

The determination of the surface tension can be accomplished with different techniques:

i. *Du Nouy Ring Method*: The traditional method used to measure surface or interfacial tension. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured.

ii. *Capillary Rise Method:* One of the oldest methods used for the surface tension measurement. The rise or the fall of liquids in capillary tubes and its applications to the measurement of surface tension may be treated quantitatively: the liquid colum acts as a manometer to register the pressure difference across the curved interface (meniscus).

iii. *Wilhelmy Plate Method*: An universal method especially suited to check surface tension over long time intervals. A vertical rectangular plate of known horizontal. perimeter is attached to a balance, and the force due to wetting is measured

iv. *Spinning Drop Method*: This technique is ideal for measuring low interfacial tensions. The diameter of a drop within a heavy phase is measured, while both are rotated.

v. *Pendant Drop Method:* Surface and interfacial tension can be measured by this technique,even at elevated temperatures and pressures. Geometry of a drop is a analyzed optically. Also the volume (mass) of the drop or the drop time (at an assigned flow rate) may be used for the surface tension determination

vi. *Bubble Pressure Method*: A measurement technique for determining surface tension at short surface ages. Maximum pressure of each bubble is measured

vii. *Drop Volume Method*: A method for determining interfacial tension as a function of interface age. Liquid of one density is pumped into a second liquid of a d different density and time between drops produced is measured.

viii. *Surface waves:* A method for determining the surface tension base on the speed of propagation of a surface wave of predetermined wavelength.

ix. *Oscillating Liquid Jets:* Liquid jets, emerging from a slightly elliptical tube, vibrate around their equilibrium cross section (circular cross section due to the surface tension). The application of the method is of interest when continuous measurements is necessary (high mass flow) or on media, which do not allow contact with measuring devices or capillary tubes.

The above techniques are applicable to liquids, and liquid/vapor systems. When solids are involved, different techniques are required.

Need for further developments.

Research is required to provide a better analysis of the surface tension effects on nucleation and the other process, particularly the following aspects should be specifically addressed:

i. dynamic versus static surface tension, for specific applications;

ii. effects of background gases (air) on the surface tension measurements, and other surface related parameters;

iii. surface tension measurement methods, for high temperature and pressures.

Systems of interests

Aqueous salt solutions and ammonia water mixtures (used in Kalina cycle) are of interest. There is an urgent need for new surface tension data and formulations for these mixtures in the temperature range 25 °C to 150 °C, along of the liquid-vapor phase boundaries. It should be noted that these phase boundaries need to be better defined on *PVT* diagrams.

The systems of interest for the power industry would cover essentially the aqueous solutions of the following substances:

i. NH_3
ii. organic amines (low relative molecular mass)
iii. organic acids (low relative molecular mass)
iv. HCl
v. NaCl
vi. H_2SO_4
vii. $NaHSO_4$
viii. Na_2SO_4
ix. NH_4Cl

x. $(NH_4)HSO_4$
xi. $(NH_4)_2SO_4$
xii. NaOH
xiii. etc.

In the following ranges:

a.	concentration	0 to saturation
b.	temperature	20 to 350 °C
c.	pressure	0,005 to 25 Mpa

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