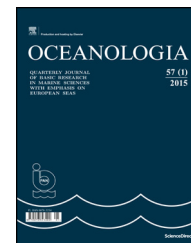


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/oceano](http://www.elsevier.com/locate/oceano)

ORIGINAL RESEARCH ARTICLE

# Thermoelastic surface properties of seawater in coastal areas of the Baltic Sea

Katarzyna Boniewicz-Szmyt<sup>a,\*</sup>, Stanisław J. Pogorzelski<sup>b</sup><sup>a</sup> Department of Physics, Gdynia Maritime University, Gdynia, Poland<sup>b</sup> Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

Received 13 August 2015; accepted 17 August 2015

Available online 3 September 2015

## KEYWORDS

Baltic Sea;  
Surface tension;  
Crude oil-seawater interface;  
Thermodynamic parameters;  
Surface viscoelasticity

**Summary** Correlations and data for the thermoelastic surface properties of seawater were determined by means of surface tension-temperature and surface pressure-area isotherm measurements performed in Baltic Sea coastal waters (Gulf of Gdańsk, Poland). Thermodynamic surface parameters examined include: surface free energy- $\gamma$ , entropy, enthalpy, surface specific heat of air-seawater (AW), air-crude oil (AO) and crude oil-seawater (OW) interfaces, and the surface elasticity was quantified in terms of complex viscoelasticity modules with relaxation times of the transition processes. The spatial and temporal evolution of the parameters differed significantly from the literature data for seawater since the effect of surface active substances of natural and municipal origin was likely to be present in these coastal waters. The seawater surface turned out to have the viscoelastic 2D character as well as other interfacial systems AO and OW where three crude oils in contact with the seawater were studied for comparison. The dilational elasticity modules were found to follow the sequence  $E_{AW} > E_{OW} > E_{AO}$ . Composite oil lens-covered seawater exhibited a significant drop of  $E$  from  $E_{AW}$  (crude oil free surface) even for low oil coverage fraction  $F_0$ .

The obtained surface and interfacial tension-temperature dependences allowed to correct the spreading coefficient ( $S = \gamma_{AW} - \gamma_{AO} - \gamma_{OW}$ ) to the desired temperature range, for example. The latter parameter with the sea surface elasticity data allows one to test the modified model of crude oil spreading proposed by the authors (Boniewicz-Szmyt and Pogorzelski, 2008), for spreading kinetics phenomenon at the surface-tension regime.

© 2015 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier Sp. z o.o. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

\* Corresponding author at: Department of Physics, Gdynia Maritime University, Morska 81-87, 81-225 Gdynia, Poland. Tel.: +48 585232250. E-mail addresses: [kbon@am.gdynia.pl](mailto:kbon@am.gdynia.pl) (K. Boniewicz-Szmyt), [fizsp@ug.edu.pl](mailto:fizsp@ug.edu.pl) (S.J. Pogorzelski).  
Peer review under the responsibility of Institute of Oceanology of the Polish Academy of Sciences.



Production and hosting by Elsevier

<http://dx.doi.org/10.1016/j.oceano.2015.08.003>

0078-3234/© 2015 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier Sp. z o.o. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

The knowledge of seawater surface thermal and elastic properties is important in several surface tension-mediated processes like: wind waves generation and damping, gas bubbles formation, sea foam and oil emulsion stability, spreading and kinetics of contamination expansion, for instance. Literatures contain many data for the properties of seawater, but only a few sources provide full coverage for all of these properties. The data are mainly based on experimental measurements carried out in and before the 1970s, and usually span a limited temperature and salinity range. Most of the data require interpolation and extrapolation to conditions of interest, and not all desirable properties are given, particularly transport and surface elastic properties affecting to a great extent physical and dynamical oceanographical processes mediated by interfaces. The International Association for the Properties of Steam (IAPS) has approved an international table of values for the surface tension (ST) of water in equilibrium with its vapor over the entire liquid range (Vargaftik et al., 1983). However, seawater is a particular water phase which SF can significantly differ from the recent reference dependences (Sharqawy et al., 2010), particularly in coastal waters enriched in surface-active contaminants (Pogorzelski and Kogut, 2003). As a first approximation, most physical properties of seawater are similar to those of pure water, which can be described by functions of temperature. The general trend for liquid surface tension is that it decreases with an increase of temperature. Solutes can have different effects on surface tension depending on their structure. Inorganic salts, which are the type of salts in seawater, increase the surface tension of the solution. Organic contamination in seawater may also have a considerable effect on the surface tension, particularly when surfactants, capable of forming surface layers of surface elasticity  $E$ , are involved. Any relative area change  $\Delta A/A$  of the interfacial system of dilational elasticity modulus  $E$  leads to the surface tension drop from the initial value  $\gamma_{AW}$  to  $\gamma_{AW} - E(\Delta A/A)$ , as demonstrated in Boniewicz-Szmyt and Pogorzelski (2008), where kinetics model of crude oil spreading at sea was corrected. Since the spreading phenomenon depends on the spreading coefficient  $S = \gamma_{AW} - \gamma_{AO} - \gamma_{OW}$ , the remaining interfacial tensions A/O, O/W and their temperature dependences, for the exemplary crude oils in contact with seawater, were evaluated during the course of this study. Moreover, the commonly met at sea composite surface consisting of lens-shaped crude oil areas covering a fraction  $F_0$  was also considered.

A certain fraction of dissolved organic matter (DOM) in the sea has surface-active (SA) properties and makes up a very reactive part of the organic matter (Druffel and Bauer, 2000). According to their SA properties, these substances accumulate at marine interfaces thereby influencing gas, mass, momentum and energy transfer between the thus modified interfaces. The composition of sea surface films is largely undefined, although significant enrichments of many specific classes of compounds in the surface microlayer have been demonstrated (for review, see Hunter and Liss, 1981). Natural sea films most resemble layers composed of proteins, polysaccharides, humic-type materials and long chain aliphatic acid esters (Van Vleet and Williams, 1983). In particular, the Polish coastal zone of the southern Baltic Sea is a

recipient of riverine waters and remains under severe anthropogenic pressure that leads to formation films of undefined composition with a complex interfacial architecture. The exhibited natural film parameters variability with the environmental factors (film temperature, ionic strength, pH of the aqueous subphase, wind speed, time scale of relaxation processes taking place in a multicomponent natural film) have been already discussed in detail elsewhere (Mazurek et al., 2008).

The aim of the paper was twofold: (1) to determine the apparent sea surface thermodynamic functions (entropy, enthalpy, surface tension, surface specific heat), and their temperature variability also in the contact with model crude oils; (2) to quantify the surface-active substances effect on the dilational viscoelasticity of the seawater surface in shallow coastal areas of the Baltic Sea and on the interfacial systems: crude oil/seawater and air/crude oil affecting composite air/crude oil/seawater surface elasticity. The collected data will be further used in the corrected model of crude oil spreading at sea proposed by the authors (Boniewicz-Szmyt and Pogorzelski, 2008), for model evaluations.

## 2. Surface thermodynamics and viscoelasticity – theory

### 2.1. Thermodynamic functions

In the studies of ST of liquids, one needs data for calibration of instruments at different temperatures. The variation of  $\gamma$  for water with temperature  $t$  [°C] is given as follows by various investigators, as reviewed in Vargaftik et al. (1983).

By Harkins (1952):

$$\gamma_{\text{water}} = 75.680 - 0.138t - 0.05356t^2 + 0.0647t^3. \quad (1)$$

The high accuracy is important in such data, since we use these for calibration purposes. More recent and reliable data by Cini et al. (1972) indicate that

$$\gamma_{\text{water}} = 75.668 - 0.139t - 0.2885 \times 10^{-3}t^2. \quad (2)$$

The International Association for the Properties of Steam (IAPS) has approved an international table of values for the surface tension of water in equilibrium with its vapor over the entire liquid range (Vargaftik et al., 1983). However, seawater is a particular water phase which SF can differ significantly from the recent reference dependences (Sharqawy et al., 2010), particularly in coastal waters enriched in surface-active contaminants and solid dust particles (Pogorzelski and Kogut, 2003). The surface entropy and total enthalpy (per unit area) can be derived from ST versus  $T$  dependence (Adamson and Gast, 1997).

The surface entropy,  $S_s$ , corresponding to the above relation is

$$S_s = \frac{-d\gamma}{dT} \quad (3)$$

and the corresponding expression for surface enthalpy,  $H_s$ , is

$$H_s = \gamma - T \left( \frac{d\gamma}{dT} \right). \quad (4)$$

Since ST is a type of Helmholtz free energy, the expression for surface entropy is  $S_s = -d\gamma/dT$ . Hence, an amount of heat ( $H_s$ )

Download English Version:

<https://daneshyari.com/en/article/2069704>

Download Persian Version:

<https://daneshyari.com/article/2069704>

[Daneshyari.com](https://daneshyari.com)