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Measurement and Correlation of Surface Tension for Single Aqueous Electrolyte Solutions

Masoud Sadeghi · Vahid Taghikhani ·
Cyrus Ghotbi

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Abstract In this study, the values of the surface tension for a number of single aqueous electrolyte solutions were measured at various temperatures and electrolyte concentrations using the well-known and computer-aided pendant-drop method. In order to conduct the experimental measurements, a high-pressure IFT-700 apparatus, equipped with a view cell and a data acquisition system, was used. The systems studied in this study were aqueous solutions of KCl, NaCl, $CaCl_2$, and Na_2SO_4. The pooled standard deviation and the confidence limit of the surface-tension data for a 95 % confidence level were determined to be $0.17\,\text{mN} \cdot \text{m}^{-1}$ and $\bar{\sigma} \pm 0.19$, respectively. It should be noted that while the surface tension for electrolyte solutions increases as the electrolyte concentration increases, it decreases with an increase in temperature as expected. Finally, data reduction was carried out using an empirical equation to show the effect of temperature, electrolyte concentration, and the nature of ionic species on the surface tension for the systems studied.

Keywords Electrolyte solutions · IFT apparatus · Pendant-drop method · Surface tension

List of Symbols

a, b, m, n, o, p	Empirical parameters in Eq. 1
T	Absolute temperature, K
c	Electrolyte concentration in mass%
s_r	Relative standard deviation
N_p	Number of experimental data points
i	Number of constants in Eq. 1

M. Sadeghi · V. Taghikhani · C. Ghotbi (✉)
Department of Chemical and Petroleum Engineering, Sharif University of Technology,
Azadi Ave., Tehran, Iran
e-mail: ghotbi@sharif.edu

Greek Letters

σ	Surface tension, $\mathrm{mN \cdot m^{-1}}$

Subscripts

w	Water
r	Relative

Superscripts

expt	Experimental
calcd	Calculated

1 Introduction

The surface tension of aqueous electrolyte solutions has great influence on mass and heat transfer across a liquid–vapor interface. A knowledge of the surface tension is of central importance in many applications including separation processes, environmental engineering, and the oil and gas industry [1–4]. To meet these requirements, it is indispensable to develop accurate estimation methods. The development of different methods to estimate the surface tension for electrolyte solutions needs the corresponding experimental data for the surface tension of electrolyte solutions over a wide range of concentration and temperature. Due to the lack of such data, it is necessary to generate experimental data for different single and mixed aqueous electrolyte solutions at different conditions.

While the surface tension of non-electrolyte solutions have been extensively investigated [1–4], experimental and theoretical studies of the surface tension for electrolyte solutions have been rarely conducted [5]. Oka [6] derived a quantitative limiting model of surface tension for strong electrolyte solutions by considering the ions to be homogeneously distributed in the solutions. Ali et al. [7] recently reported data for the surface tension of different single uni–uni valence potassium salts and studied the effect of temperature on the entropy and enthalpy at the vapor–liquid interface. Matubayasi et al. [8] reported the effect of temperature on the surface tension of aqueous solutions of chloride salts of sodium, magnesium, and lanthanum.

Experimental methods for measurement of the surface tension are generally divided into static and dynamic methods. In static methods, an equilibrium condition is attained while dynamic surfaces are studied in the latter [9]. The capillary-rise method, drop-weight method, maximum bubble-pressure method, ring method, and pendant-drop method are the examples of static methods [9–14]. All of the methods can be used to measure the surface tension at ambient temperature and pressure, but except for the pendant-drop method, they cannot be used to determine the surface tension in a wide range of temperature and pressure. This method can be coupled with computer-aided image processing to simply measure the surface tension [15].

In this study, the surface tension for KCl, NaCl, $CaCl_2$, and Na_2SO_4 aqueous electrolyte solutions was measured at various temperatures using the pendant-drop method with the high-pressure IFT-700 apparatus. To reduce the data, an empirical equation was used to show the effect of both temperature and electrolyte concentrations on the surface tension for the systems studied.

2 Experiments

2.1 Apparatus

To measure the surface tension of electrolyte solutions at various temperatures, an IFT-700 apparatus was used. A schematic diagram of the IFT-700 is shown in Fig. 1. As seen from this figure, the apparatus was equipped with two different liquid tanks with two separate hand pumps and a gas injection line to set the view cell at desirable pressures. The temperature of the view cell can be set using an automatic heater up to 180 °C. In order to prevent the effect of external vibration on the geometry of the pendant-drop, an isolation table was used. The whole system was kept in an isolated room to make sure that there are no environmental changes to affect the final results. The apparatus is equipped with a camera and is connected to a computer. After connecting to the computer, the surface tension of the solution is calculated according to an algorithm shown by Song and Springer [15].

2.2 Surface-Tension Measurements

A desirable amount of electrolyte solution was introduced in tank TL1 as shown in Fig. 1. While the valve A was open, valves B and C remained closed. It should be stated that since the experiments were carried out at an ambient pressure, no additional pressure was added to the cell using the hand pump. In order to push out the air inside the capillary tube, valve C was kept open and the capillary tube was filled with the electrolyte solution using the hand pump. As soon as the first droplet of the

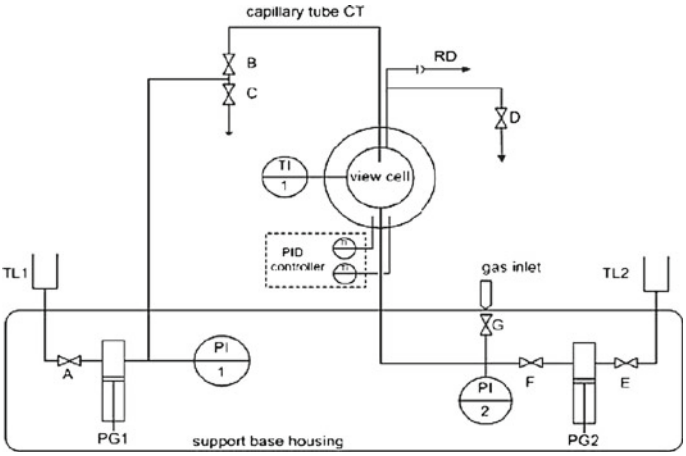

Fig. 1 Schematic diagram for IFT-700 used to measure the surface tension for electrolyte solutions

liquid appeared from the capillary tube, valve C was closed and the temperature of the view cell was set using the cell heater. Finally, to form an appropriate pendant drop, valve B was slightly opened. Having formed the pendant drop, the geometry of the droplet formed was analyzed using a computer interface program. The results for the surface tension at different electrolyte concentrations and at various temperatures were recorded. The measurements were made after maintaining the system at a selected temperature for a reasonable amount of time to make sure that an equilibrium condition was attained. Also, it is worth noting that before conducting the experiments, the apparatus was calibrated using pure distilled water over the temperature ranges studied for the electrolyte solutions. To check the repeatability of the experimental data, the experiments at each condition were repeated thrice and the results presented are the averages of replicas.

2.3 Chemicals

KCl, NaCl, $CaCl_2$, and Na_2SO_4 were supplied by Merck with nominal purities >99 %, and pure deionized water was used. All of the materials were used without further purification.

3 Results and Discussion

To calibrate the apparatus, the surface tension of deionized distilled water was measured at different temperatures. Each experiment was repeated thrice daily and also for three consecutive days. Table 1 shows the measured mean surface-tension values for deionized distilled water at different temperatures. As shown in Table 1, the measured surface-tension values are in good agreement with those reported in the literature [16]. Table 2 presents the results for the surface tension of three aqueous electrolyte solutions, i.e., NaCl, $CaCl_2$, and Na_2SO_4 solutions at four different temperatures and at a specified electrolyte concentration. It is observed that an increase in temperature results in a decrease in the surface tension. As a matter of fact, an increase in temperature can reduce the energy that is required to stretch the surface of a liquid, i.e., the surface tension. Although there is no large difference among the absolute values of the surface tension measured for each system, at a specified temperature the surface tension depends on the nature of the system. Tables 3, 4, and 5 present the results for the surface tension of KCl, NaCl, $CaCl_2$, and Na_2SO_4 electrolyte solutions at various temperatures and at electrolyte concentrations of 10 mass%, 14 mass%, and 18 mass%, respectively. In Tables 3, 4, and 5, the numbers 1–4 represent the KCl, NaCl, $CaCl_2$, and Na_2SO_4 electrolytes, respectively. Again it can be seen that an increase in temperature results in a decrease in the surface tension. Also it is observed that the surface tension for electrolyte solutions increases with electrolyte concentration. This observation can be plausibly justified by the fact that an increase in the electrolyte concentration will increase the electrostatic attraction between species existing in solution and this, in turn, will increase the cohesive energy between molecules and ionic species. Thus, an increase in such energy will increase the surface tension or the amount of energy required to stretch the surface of a liquid. The variation of the surface

Table 1 Experimental mean surface-tension data and reference surface-tension values [16] for pure water (1, 2, 3 refer to first, second, and third day data, and 'ref' refers to the reference value)

$T\,(^\circ\mathrm{C})$	$\overline{\sigma_1}\left(\mathrm{mN\cdot m^{-1}}\right)$	$\overline{\sigma_2}\left(\mathrm{mN\cdot m^{-1}}\right)$	$\overline{\sigma_3}\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_{\mathrm{ref}}\left(\mathrm{mN\cdot m^{-1}}\right)$
30	71.54	71.58	72.12	71.2
40	68.96	69.86	70.64	69.48
50	67.83	67.57	69.15	67.77
60	66.16	66.39	66.16	66.07
70	65.8	64.73	65.39	64.36

Table 2 Surface tension for 4 mass% aqueous solutions of NaCl (1), $\mathrm{CaCl_2}$ (2), and $\mathrm{Na_2SO_4}$ (3) at different temperatures

$T\,(^\circ\mathrm{C})$	$\sigma_1\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_2\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_3\left(\mathrm{mN\cdot m^{-1}}\right)$
30	71.44	72.74	71.53
40	70.66	70.84	70.70
50	68.25	69.62	68.80
60	67.31	67.62	67.27

Table 3 Surface tension for 10 mass% aqueous solutions of KCl (1), NaCl (2), $\mathrm{CaCl_2}$(3), and $\mathrm{Na_2SO_4}$(4) at different temperatures

$T\,(^\circ\mathrm{C})$	$\sigma_1\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_2\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_3\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_4\left(\mathrm{mN\cdot m^{-1}}\right)$
30	71.58	73.42	74.59	73.56
40	69.86	71.81	72.56	71.88
50	67.57	70.97	70.38	70.50
60	66.39	69.74	68.56	69.11

tension of potassium chloride with temperature at different electrolyte concentrations is shown in Fig. 2.

Table 6 compares the experimental surface-tension values of the 10 mass% NaCl electrolyte solution at different temperatures obtained in this study with those reported in the literature [17]. As can be deduced from Table 6, the experimental data obtained in this study for the surface tension of NaCl electrolyte solution are in good agreement with those reported in the literature [17].

A virial expansion series was used to fit the experimental data for surface tension as follows:

$$\sigma = \sigma_{\mathrm{w}} + a + bc + mT + ncT + oc^2 + pT^2 \qquad (1)$$

Table 4 Surface tension for 14 mass% aqueous solutions of KCl (1), NaCl (2), $CaCl_2$(3), and Na_2SO_4(4) at different temperatures

$T\,(^\circ\mathrm{C})$	$\sigma_1\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_2\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_3\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_4\left(\mathrm{mN\cdot m^{-1}}\right)$
30	72.12	76.09	76.08	74.02
40	70.64	74.60	73.65	72.82
50	69.15	72.47	71.52	71.65
60	66.16	71.83	70.63	69.93

Table 5 Surface tension for 18 mass% aqueous solutions of KCl (1), NaCl (2), $CaCl_2$(3), and Na_2SO_4 (4) at different temperatures

$T\,(^\circ\mathrm{C})$	$\sigma_1\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_2\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_3\left(\mathrm{mN\cdot m^{-1}}\right)$	$\sigma_4\left(\mathrm{mN\cdot m^{-1}}\right)$
30	76.78	77.04	77.53	76.28
40	75.23	74.73	74.89	74.97
50	74.65	73.38	73.25	73.22
60	71.44	71.44	71.87	71.40

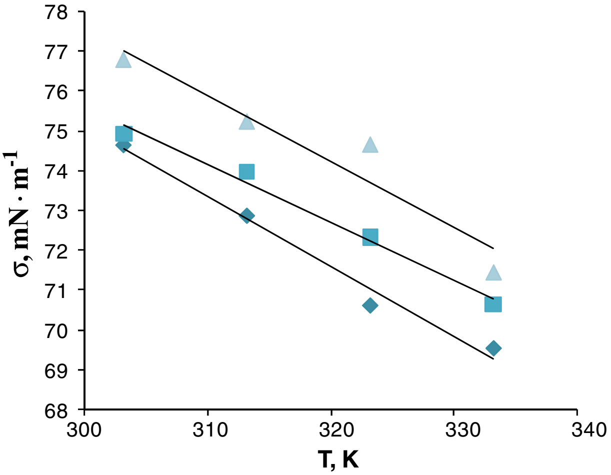

Fig. 2 Variation of the surface tension of a potassium chloride electrolyte solution with temperature at different concentrations: ◆; represents KCl 10 mass%, ■; KCl 14 mass%, and ▲; KCl 18 mass%

Table 6 Surface tension for 10 mass% aqueous NaCl solution (1 stands for this work, and 2 for reported literature surface tension values [17])

$T\,(^\circ\mathrm{C})$	$\overline{\sigma_1}\left(\mathrm{mN\cdot m^{-1}}\right)$	$\overline{\sigma_2}\left(\mathrm{mN\cdot m^{-1}}\right)$
30	73.42	73.25
40	71.81	71.50
50	70.97	70.00
60	69.74	–

Table 7 Regressed parameters along with the relative standard deviation for the proposed virial series in Eq. 1

Salt	a	b	m	n	o	p	s_r
$CaCl_2$	5.1208	−0.6185	−0.1756	0.0365	1.9646	0.0017	0.47
KCl	−3.2717	2.0251	0.1537	−0.0007	0.0306	−0.0016	0.60
NaCl	−1.9744	3.6460	−0.0254	−0.0128	−0.3033	0.0008	0.77
Na_2SO_4	−2.8938	2.4971	0.1162	−0.0069	0.8162	−0.0009	0.39

where

$$\sigma_w = 76.325 - 0.171T \tag{2}$$

In Eq. 1, σ_w is the surface tension for pure water at temperature T in °C and c is the concentration of the electrolyte in mass%. *a, b, m, n, o*, and *p* are fitting parameters which can be obtained using a non-linear regression of the proposed empirical equation to the experimental data for the surface tension at the temperature ranges studied in this work. The regressed parameters for each electrolyte system are presented in Table 7. Equation 2 shows the variation of the surface tension of pure water with temperature. Equation 2 was fitted according to the experimental data for the surface tension of pure water at different temperatures given by Vargaftik [16].

It is found that the proposed virial series can fit the experimental data with good accuracy. Also, the deviations of the results obtained from the model from the experimental data can be given by the following relative standard deviation as [18]:

$$S_r = \frac{100\left(\sum\left(\sigma^{\text{expt}} - \sigma^{\text{calcd}}\right)^2 \Big/ \left(N_p - i\right)\right)^{\frac{-1}{2}}}{\bar{\sigma}} \tag{3}$$

In Eq. 3, $s_r, \sigma, \bar{\sigma}, N_p$, and i represent, respectively, the relative standard deviation, surface tension, average surface tension, number of data points, and the number of constants in Eq. 1.

To determine the accuracy of the experimental data generated in this study, the pooled standard deviation and the confidence limit of the data for a 95 % confidence level were determined to be $0.17\,\text{mN}\cdot\text{m}^{-1}$ and $\bar{\sigma} \pm 0.19$, respectively. In all cases the surface tension is in mN per meter and T is in K.

4 Conclusion

The surface tension for a number of single electrolyte solutions was measured with a standard deviation of $0.17\,\text{mN}\cdot\text{m}^{-1}$, using the computer-aided pendant-drop method. The data were measured at various electrolyte concentrations and temperatures. The surface tension for electrolyte solutions decreases with increasing temperature, while it increases with an increase in electrolyte concentration. Finally, an accurate empirical equation was proposed to show the effect of the temperature, concentration, and nature of electrolyte on the surface tension of electrolyte solutions.

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