Correlation of Surface Tension of Mono-Solvents at Various Temperatures

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Abstract: Surface tension is among the most important factors in chemical and pharmaceutical processes. Modeling the surface tension of solvents at different temperatures helps to optimize the type of solvent and temperature. The surface tension of solvents at different temperatures with their solvation parameters was used in this study to develop a model based on the van’t Hoff equation by multiple linear regression. Abraham solvation parameters, Hansen solubility parameters, and Catalan parameters are among the most discriminating descriptors. The overall MPD of the model was 3.48%, with a minimum and maximum MPD of 0.04% and 11.62%, respectively. The model proposed in this study could be useful for predicting the surface tension of mono-solvents at different temperatures.

Keywords: surface tension; solvation parameters; model; predict

1. Introduction

Surface activity is one of the main physico-chemical properties of liquids. Surface and/or interfacial tension represents the surface and/or interfacial activity of a liquid. Surface tension data is required in many industrial applications, including wettability, dispersibility, and deflocculation of the solid particles in liquids; emulsification of immiscible liquids in emulsion and microemulsion formulations; detergency in sanitary; adsorption of gases and solutes from solutions; solubilization of insoluble drugs in liquid dosage forms; biological activity of drugs and drug absorption from mucosa [1]. Surface tension affects the transformation of heat and mass in solutions which influences many chemical processes [2]. It is a vital step in drug formulation. For example, granulation is a method to improve the falling ability of a powder by adding a binder to the active pharmaceutical ingredient. A crucial step in optimizing granulation performance is wetting the substrate with the binder and spreading the binder over the substrate. Surface tension also acts as an important parameter in controlling the coating process. Suspensions are a dosage form with many pros and cons compared to other dosage forms. One of the disadvantages is related to its instability and cake formation, which could be modified by surface tension control. A comprehensive review of the applications of surface tension in the pharmaceutical sciences was provided in an earlier review paper [3]. Many biological reactions occur at the surface but not in solution. For proper absorption of a drug and efficient function on its active site, it needs to be dissolved properly in the gastric fluids. Surface tension plays a vital role in the function of the respiratory system. A mixture of surface active agents, such as dipalmitoyl lecithin, causes a reduction in the surface tension of alveoli fluid. Increasing the surface tension of alveoli lining fluid results in respiratory distress syndrome and atelectasis, which are two major respiratory disorders. The most important roles of surface tension in clinical sciences have been summarized in a review work [4].
Surface tension reflects the intermolecular interactions and forces between a liquid molecule and the air and depends on many different variables, including viscosity, the existence of ionized compounds in the solution, and temperature [5].

There are various methods for measuring surface tension, including the Du Noüy ring method, Wilhelmy plate method, and spinning drop method, but they all require a lot of cost and energy, and they require an expert to perform the laboratory work. Numerical methods to predict the surface tension of mixed solvents have been proposed, but there are few studies on computational modeling for surface tension prediction of mono-solvents at different temperatures [5].

The aim of this study is to propose a mathematical model for calculating the surface tension of mono-solvents at various temperatures by combining an adopted van’t Hoff model with the solvation parameters, including Abraham solvation parameters, Hansen solubility parameters, and Catalan parameters. The applicability of the proposed model is evaluated by using the published surface tension data of several different mono-solvents at various temperatures.

### 2. Computational Methods

The surface tension of a liquid is decreased by an increase in temperature. An adapted version of the van’t Hoff equation is used to represent the temperature effects on the surface tension data ($\sigma_i, T$). The van’t Hoff type model is:

$$\log \sigma_i, T = \alpha_i + \beta_i \frac{T}{T}$$  \hspace{1cm} (1)

in which $\alpha_i$ and $\beta_i$ are the model constants [6]. It has been shown that $\alpha_i$ and $\beta_i$ terms could represent the effects of the physico-chemical properties (PCP) of a given solvent at various temperatures. It is possible to include Abraham solvation parameters ($AP_i$) [7], Hansen solubility parameters ($HP_i$) [8], and Catalan parameters ($CP_i$) [9] to represent the effects of solvent’s PCPs on surface tension. To do this, we combined these PCPs with the van’t Hoff type model as:

$$\log \sigma_i, T = \left( \alpha_0 + \sum_{i=1}^{5} \alpha_i \cdot AP_i + \sum_{i=1}^{3} \alpha_i \cdot HP_i + \sum_{i=1}^{4} \alpha_i \cdot CP_i \right) + \left( \beta_0 + \sum_{i=1}^{5} \beta_i \cdot AP_i + \sum_{i=1}^{3} \beta_i \cdot HP_i + \sum_{i=1}^{4} \beta_i \cdot CP_i \right)$$ \hspace{1cm} (2)

where $\alpha$ and $\beta$ terms are the model constants.

Thirty-two solvents with their numerical surface tension ($\sigma_i, T$) values at different temperatures were obtained from the literature (Table 1) [10–33]. The tabulated numerical values pertain to a homogeneous liquid system at the specified temperature in equilibrium with its own vapor pressure. The solvents considered in the study contain a wide range of functional groups, and they cannot be classified as belonging to a single type of chemical compound. For each solvent, Abraham solvation parameters [7,24,35], Catalan parameters [9], and Hansen solubility parameters [8] were gathered from different sources. Details of the parameters with their references are listed in Tables 2–4. Parameters for each solvent were divided by temperature to differentiate between the descriptor’s numerical values at different temperatures. Repeated data were excluded from the final analyses, and for the data with close reported surface tension data, the average numerical value of surface tension was used for further analysis.
Table 1. Experimental ($\sigma_{LT}^{Exp}$) and calculated ($\sigma_{LT}^{Calc}$) surface tension values of the studied mono-solvents at different temperatures (T), the mean percentage deviation (MPD), and the references for $\sigma_{LT}^{Exp}$ data.

| Solvent             | T (K) | $\sigma_{LT}^{Exp}$ | $\sigma_{LT}^{Calc}$ | MPD  | Ref.          |
|---------------------|-------|----------------------|-----------------------|-------|--------------|
| 1,4-dioxane         | 288   | 33.98                | 32.40                 | 4.74  | [10]         |
| 1,4-dioxane         | 293   | 33.58                | 31.70                 | 5.51  | [10]         |
| 1,4-dioxane         | 298   | 32.69                | 31.10                 | 4.80  | [10]         |
| 1,4-dioxane         | 303   | 32.15                | 30.50                 | 5.01  | [10]         |
| 1,4-dioxane         | 308   | 31.42                | 30.00                 | 4.52  | [10]         |
| 1,4-dioxane         | 303   | 24.68                | 24.80                 | 0.28  | [11]         |
| 1,4-dioxane         | 293   | 24.21                | 24.20                 | 0.04  | [11]         |
| 1,4-dioxane         | 298   | 24.10                | 23.70                 | 1.70  | [11,12]      |
| 1,4-dioxane         | 303   | 22.79                | 22.70                 | 0.26  | [11]         |
| 1,4-dioxane         | 308   | 26.08                | 26.40                 | 1.23  | [11]         |
| 1,4-dioxane         | 293   | 25.61                | 25.90                 | 1.09  | [11]         |
| 1,4-dioxane         | 298   | 25.43                | 25.40                 | 0.08  | [11,12]      |
| 1,4-dioxane         | 303   | 24.74                | 25.00                 | 0.89  | [11]         |
| 1,4-dioxane         | 308   | 24.19                | 24.30                 | 1.41  | [11]         |
| 1,4-dioxane         | 288   | 27.41                | 26.80                 | 2.12  | [11]         |
| 1,4-dioxane         | 293   | 26.94                | 26.30                 | 2.26  | [11]         |
| 1,4-dioxane         | 298   | 26.90                | 25.90                 | 3.90  | [11,12]      |
| 1,4-dioxane         | 303   | 26.07                | 25.40                 | 2.57  | [11]         |
| 1,4-dioxane         | 308   | 25.52                | 25.00                 | 2.16  | [11]         |
| 1-pentanol          | 293   | 25.69                | 25.50                 | 1.09  | [13,14]      |
| 1-pentanol          | 298   | 25.00                | 25.00                 | 0.12  | [12,14]      |
| 1-pentanol          | 318   | 23.67                | 23.30                 | 1.44  | [13,14]      |
| 1-propanol          | 293   | 23.69                | 24.20                 | 2.11  | [13,14]      |
| 1-propanol          | 298   | 23.34                | 23.70                 | 1.37  | [12,14]      |
| 1-propanol          | 303   | 22.89                | 23.20                 | 1.22  | [14]         |
| 1-propanol          | 308   | 22.51                | 22.70                 | 0.84  | [14]         |
| 1-propanol          | 313   | 22.11                | 22.30                 | 0.68  | [14]         |
| 1-propanol          | 318   | 21.69                | 21.80                 | 0.69  | [13,14]      |
| 1-propanol          | 323   | 21.31                | 21.40                 | 0.56  | [14]         |
| 2-butanol           | 293   | 23.01                | 23.70                 | 2.78  | [13]         |
| 2-butanol           | 298   | 24.70                | 22.80                 | 7.61  | [15]         |
| 2-butanol           | 293   | 24.70                | 22.80                 | 7.61  | [15]         |
| 2-butanol           | 298   | 24.00                | 22.20                 | 7.38  | [15]         |
| 2-methyl–1-propanol | 298   | 22.34                | 23.40                 | 4.52  | [16]         |
| 2-pentanol          | 293   | 23.70                | 24.20                 | 2.24  | [13]         |
| 2-pentanol          | 298   | 23.28                | 23.70                 | 1.89  | [13]         |
| 2-pentanol          | 315   | 21.60                | 22.20                 | 2.69  | [13]         |
| 2-propanol          | 293   | 21.74                | 22.10                 | 1.66  | [14]         |
| 2-propanol          | 298   | 21.03                | 21.60                 | 2.57  | [14]         |
| 2-propanol          | 303   | 20.72                | 21.10                 | 1.64  | [14]         |
| 2-propanol          | 308   | 20.23                | 20.60                 | 1.73  | [14]         |
| 2-propanol          | 313   | 19.71                | 20.10                 | 2.13  | [14]         |
| 2-propanol          | 318   | 19.21                | 19.70                 | 2.55  | [14]         |
| 2-propanol          | 323   | 18.69                | 19.30                 | 3.26  | [14]         |
| acetone             | 273   | 25.17                | 25.50                 | 1.47  | [17]         |
| acetone             | 287   | 24.70                | 23.40                 | 5.22  | [17]         |
| acetone             | 288   | 23.37                | 23.30                 | 0.39  | [17]         |
| acetone             | 293   | 23.03                | 22.60                 | 1.78  | [18]         |
| acetone             | 298   | 22.50                | 22.00                 | 2.22  | [18]         |
| acetone             | 303   | 21.80                | 21.40                 | 1.79  | [17]         |
| acetone             | 308   | 21.20                | 20.90                 | 1.60  | [17]         |
| acetone             | 313   | 20.80                | 20.30                 | 2.21  | [18]         |
| acetone             | 318   | 19.78                | 19.90                 | 0.35  | [17]         |
Table 1. Cont.

| Solvent            | T (K) | $\sigma_{LT}^{Exp}$ | $\sigma_{LT}^{Calc}$ | MPD   | Ref. |
|--------------------|-------|----------------------|----------------------|-------|------|
| acetone            | 323   | 19.51                | 19.40                | 0.62  | [18] |
| acetone            | 328   | 18.60                | 19.00                | 1.88  | [17] |
| acetonitrile       | 298   | 28.41                | 28.40                | 0.21  | [19] |
| acetonitrile       | 303   | 28.03                | 27.50                | 2.07  | [19] |
| acetonitrile       | 308   | 27.40                | 26.60                | 2.88  | [19] |
| acetonitrile       | 313   | 26.76                | 25.80                | 3.55  | [19] |
| acetonitrile       | 318   | 26.13                | 25.10                | 4.06  | [19] |
| benzene            | 293   | 28.85                | 32.20                | 11.61 | [20] |
| benzene            | 303   | 27.55                | 30.80                | 11.62 | [20] |
| butyl acetate      | 298   | 24.88                | 22.80                | 8.32  | [21] |
| cyclohexane        | 288   | 25.34                | 24.30                | 4.18  | [22] |
| cyclohexane        | 293   | 25.00                | 23.40                | 6.28  | [23] |
| cyclohexane        | 298   | 24.20                | 22.60                | 6.49  | [23] |
| cyclohexane        | 303   | 23.85                | 21.90                | 8.22  | [23] |
| cyclohexane        | 308   | 23.02                | 21.20                | 7.91  | [22,23] |
| cyclohexane        | 313   | 21.84                | 19.90                | 8.70  | [22,23] |
| cyclohexane        | 318   | 20.71                | 18.80                | 9.13  | [22,23] |
| dimethylsulfoxide  | 288   | 43.68                | 45.40                | 3.94  | [24] |
| dimethylsulfoxide  | 298   | 42.18                | 43.90                | 4.10  | [24] |
| dimethylsulfoxide  | 308   | 41.11                | 42.60                | 3.55  | [24] |
| dimethylsulfoxide  | 318   | 39.99                | 41.40                | 3.40  | [24] |
| dimethylsulfoxide  | 328   | 38.72                | 40.20                | 3.93  | [24] |
| ethanol            | 288   | 22.68                | 24.70                | 8.86  | [14,25] |
| ethanol            | 293   | 22.28                | 24.10                | 8.17  | [25] |
| ethanol            | 298   | 21.78                | 23.60                | 8.13  | [12,25] |
| ethanol            | 303   | 21.40                | 23.00                | 7.62  | [25] |
| ethanol            | 308   | 21.04                | 22.50                | 7.13  | [25] |
| ethanol            | 313   | 20.66                | 22.10                | 6.82  | [25] |
| ethanol            | 318   | 20.36                | 21.60                | 6.24  | [25] |
| ethanol            | 323   | 19.91                | 21.20                | 6.53  | [25] |
| ethyl acetate      | 298   | 23.93                | 21.90                | 8.32  | [20] |
| ethylene glycol    | 283   | 49.76                | 46.70                | 6.25  | [26,27] |
| ethylene glycol    | 293   | 49.02                | 45.60                | 7.04  | [26,27] |
| ethylene glycol    | 298   | 48.24                | 45.10                | 6.59  | [26,27] |
| ethylene glycol    | 303   | 47.67                | 44.60                | 6.48  | [26,27] |
| ethylene glycol    | 308   | 47.50                | 44.10                | 7.14  | [26,27] |
| ethylene glycol    | 313   | 47.58                | 43.70                | 8.22  | [26,27] |
| ethylene glycol    | 318   | 46.40                | 43.30                | 6.79  | [26,27] |
| ethylene glycol    | 323   | 46.68                | 42.80                | 8.23  | [26,27] |
| heptane            | 288   | 20.73                | 22.20                | 6.90  | [11,22] |
| heptane            | 293   | 20.40                | 21.30                | 4.56  | [11,28] |
| heptane            | 298   | 19.64                | 20.60                | 4.74  | [11,22] |
| heptane            | 303   | 19.34                | 19.90                | 2.69  | [11,22] |
| heptane            | 308   | 18.80                | 19.20                | 2.07  | [11,22] |
| heptane            | 313   | 18.46                | 18.60                | 0.60  | [28] |
| heptane            | 318   | 17.76                | 18.00                | 1.24  | [22] |
| heptane            | 323   | 17.42                | 17.40                | 0.06  | [28] |
| heptane            | 328   | 16.68                | 16.90                | 1.44  | [22] |
| heptane            | 333   | 16.46                | 16.40                | 0.18  | [28] |
| heptane            | 343   | 15.32                | 15.50                | 1.44  | [28] |
| methanol           | 293   | 22.80                | 22.80                | 0.18  | [14] |
| methanol           | 298   | 22.27                | 22.30                | 0.09  | [14] |
| methanol           | 303   | 21.79                | 21.70                | 0.46  | [14] |
| methanol           | 308   | 21.52                | 21.20                | 1.67  | [14] |
| methanol           | 313   | 21.13                | 20.70                | 2.22  | [14] |
| methanol           | 318   | 20.61                | 20.20                | 2.04  | [14] |
Table 1. Cont.

| Solvent                    | T (K) | \(\sigma_{i,T}^{\text{Exp}}\) | \(\sigma_{i,T}^{\text{Calc}}\) | MPD  | Ref. |
|----------------------------|-------|--------------------------------|--------------------------------|------|------|
| methanol                   | 323   | 19.86                          | 19.80                          | 0.55 | [14] |
| methyl acetate             | 298   | 24.79                          | 22.90                          | 7.62 | [29] |
| N,N-dimethylformamide      | 288   | 36.96                          | 36.40                          | 1.41 | [22] |
| N,N-dimethylformamide      | 298   | 35.83                          | 35.30                          | 1.40 | [22] |
| N,N-dimethylformamide      | 308   | 34.65                          | 34.30                          | 0.95 | [22] |
| N,N-dimethylformamide      | 318   | 33.37                          | 33.40                          | 0.12 | [22] |
| N,N-dimethylformamide      | 328   | 32.03                          | 32.60                          | 1.69 | [22] |
| N,N-dimethylformamide      | 239   | 41.13                          | 44.30                          | 7.80 | [22] |
| N,N-dimethylformamide      | 278   | 42.60                          | 40.80                          | 4.18 | [22] |
| N,N-dimethylformamide      | 288   | 41.35                          | 40.10                          | 3.00 | [22] |
| N,N-dimethylformamide      | 298   | 40.25                          | 39.50                          | 1.99 | [22] |
| N,N-dimethylformamide      | 303   | 40.38                          | 39.10                          | 3.12 | [30] |
| N,N-dimethylformamide      | 308   | 39.10                          | 38.80                          | 0.66 | [22] |
| N,N-dimethylformamide      | 313   | 39.99                          | 38.50                          | 3.63 | [30] |
| N,N-dimethylformamide      | 318   | 37.91                          | 38.30                          | 0.98 | [22] |
| N,N-dimethylformamide      | 328   | 36.80                          | 37.80                          | 2.61 | [22] |
| N,N-dimethylformamide      | 333   | 35.90                          | 35.70                          | 4.46 | [30] |
| N,N-dimethylformamide      | 338   | 35.66                          | 35.30                          | 4.54 | [22] |
| propylene glycol           | 298   | 35.80                          | 36.30                          | 1.51 | [31] |
| propylene glycol           | 303   | 35.70                          | 35.80                          | 0.34 | [31] |
| propylene glycol           | 313   | 35.00                          | 34.90                          | 0.40 | [31] |
| propylene glycol           | 323   | 34.10                          | 34.00                          | 0.35 | [31] |
| toluene                    | 288   | 28.93                          | 31.90                          | 10.40| [22] |
| toluene                    | 298   | 27.76                          | 30.50                          | 9.69 | [22] |
| toluene                    | 308   | 26.60                          | 29.10                          | 9.47 | [22] |
| toluene                    | 318   | 25.46                          | 27.90                          | 9.66 | [22] |
| toluene                    | 328   | 24.29                          | 26.80                          | 10.50| [22] |
| water                      | 283   | 74.27                          | 77.60                          | 4.42 | [32] |
| water                      | 293   | 72.72                          | 74.80                          | 2.83 | [32] |
| water                      | 298   | 71.92                          | 73.50                          | 2.18 | [16,32,33]|
| water                      | 303   | 71.18                          | 72.30                          | 1.53 | [32,33]|
| water                      | 308   | 70.35                          | 71.10                          | 1.08 | [32,33]|
| water                      | 311   | 69.91                          | 70.40                          | 0.76 | [32] |
| water                      | 313   | 69.49                          | 70.00                          | 0.73 | [32] |
| water                      | 318   | 68.67                          | 69.00                          | 0.41 | [32,33]|
| water                      | 323   | 67.78                          | 67.90                          | 0.24 | [32,33]|
| water                      | 328   | 66.60                          | 67.00                          | 0.57 | [32,33]|

Table 2. Applied solvation parameters of studied solvents for modeling.

| Descriptor | Definition |
|------------|------------|
| \(c\)      | The intercept value in Abraham’s solvation model |
| \(e\)      | Excess molar refraction |
| \(s\)      | Polarity/polarizability |
| \(a\)      | Hydrogen-bond acidity |
| \(b\)      | Hydrogen-bond basicity |
| \(v\)      | McGowan volume characteristic |

\(\delta_D\) \(\delta_P\) \(\delta_H\) The energy from dispersion forces between molecules The energy from dipolar intermolecular force between molecules The energy from hydrogen bonds between molecules

Catalan parameters \(\[9\]\)

| \(S_{DP}\) | Solvent dipolarity |
| \(S_P\)    | Solvent polarizability |
| \(S_A\)    | Solvent acidity |
| \(S_B\)    | Solvent basicity |
Table 3. Numerical values of the Abraham solvent parameters.

| Solvent                      | c    | e    | s    | a    | b    | v    |
|------------------------------|------|------|------|------|------|------|
| 1-butanol                    | 0.17 | 0.40 | −1.01| 0.06 | −3.96| 4.04 |
| 1-hexanol                    | 0.12 | 0.49 | −1.16| 0.05 | −3.98| 4.13 |
| 1-octanol                    | −0.03| 0.49 | −1.04| −0.02| −4.24| 4.22 |
| 1-pentanol                   | 0.15 | 0.54 | −1.23| 0.14 | −3.86| 4.08 |
| 1-propanol                   | 0.14 | 0.41 | −1.03| 0.25 | −3.77| 3.99 |
| 1,4-dioxane                  | 0.10 | 0.35 | −0.08| −0.56| −4.83| 4.17 |
| 2-butanol                    | 0.19 | 0.35 | −1.13| 0.02 | −3.57| 3.97 |
| 2-butanolone                 | 0.25 | 0.26 | −0.08| −0.77| −4.86| 4.15 |
| 2-methyl–1-propanol          | 0.13 | 0.25 | −0.98| 0.16 | −3.88| 4.11 |
| 2-pentanol                   | 0.12 | 0.46 | −1.33| 0.21 | −3.75| 4.20 |
| 2-propanol                   | 0.10 | 0.34 | −1.05| 0.41 | −3.83| 4.03 |
| acetone                      | 0.31 | 0.31 | −0.12| −0.61| −4.75| 3.94 |
| acetonitrile                 | 0.41 | 0.08 | 0.33 | −1.57| −4.39| 3.36 |
| benzene                      | 0.14 | 0.46 | −0.59| −3.10| −4.63| 4.49 |
| butyl acetate                | 0.25 | 0.36 | −0.50| −0.87| −4.97| 4.28 |
| cyclohexane                  | 0.16 | 0.78 | −1.68| −3.74| −4.93| 4.58 |
| dimethylsulfoxide            | −0.19| 0.33 | 0.79 | −1.26| −4.54| 3.36 |
| ethanol                      | 0.22 | 0.47 | −1.04| 0.33 | −3.60| 3.86 |
| ethyl acetate                | 0.33 | 0.37 | −0.45| −0.70| −4.90| 4.15 |
| ethylene glycol              | −0.27| 0.58 | −0.51| 0.72 | −2.62| 2.73 |
| heptane                      | 0.33 | 0.67 | −2.06| −3.32| −4.73| 4.54 |
| methanol                     | 0.28 | 0.33 | −0.71| 0.24 | −3.32| 3.55 |
| methyl acetate               | 0.35 | 0.22 | −0.15| −1.04| −4.53| 3.97 |
| N-methyl–2-pyrrolidone       | 0.15 | 0.53 | 0.23 | 0.84 | −4.79| 3.67 |
| N,N-dimethylformamide        | −0.31| −0.06| 0.34 | 0.36 | −4.87| 4.49 |
| propylene glycol             | −0.15| 0.75 | −0.97| 0.68 | −3.13| 3.25 |
| toluene                      | 0.14 | 0.53 | −0.72| −3.01| −4.82| 4.55 |
| water                        | −0.99| 0.58 | 2.55 | 3.81 | 4.84 | −0.87|

Multiple linear regression was used in this study to develop a model to calculate the surface tension of different solvents at various temperatures based on the parameters mentioned in Table 1. Surface tension was set as the dependent variable, and solubility parameters as independent variables. Descriptors with p-value >0.1 were excluded from the model. The p-value shows the statistical significance of the coefficients of each independent variable assessed employing the t-test.

The results of the correlations with the proposed model were compared with those of the previously reported model by Freitas et al. [36], which calculates the surface tension of liquids at 20 °C ($\sigma_{20}^\circ C$):

$$\sigma_{20}^\circ C = 14.9 + 4.35A_i^{Exp} - 1.3B_i^{Exp} + 11.3S_i^{Exp} + 10.9E_i + 3.0V_i + 0.8N_C$$

(3)

and a model based on Abraham solute parameters [37] to compute the surface tensions at various temperatures ($\sigma_{T}^\circ$):

$$\log \sigma_T^\circ = 1.245E_i + 0.344A_i + 0.542V_i$$

$$+ \frac{1}{2}(384.020 - 305.012E_i + 22.350S_i - 101.827A_i + 16.608B_i - 152.522V_i)$$

(4)

where $A_i^{Exp}$, $B_i^{Exp}$, $S_i^{Exp}$, $E_i$ and $V_i$ are the Abraham solute parameters of the liquids. The numerical values of $A_i^{Exp}$, $B_i^{Exp}$ and $S_i^{Exp}$ were derived from experimental solubility data of the compounds dissolved in a number of organic solvents with known Abraham solvent parameters [37]. $E_i$ was calculated from refractive index data [38] and $V_i$ was computed using a group contribution method of McGowan and Abraham [39]. $N_C$ is the number of carbons in n-alkanes minus six, i.e., $N_C = 0$ for n-alkanes up to hexane and 1 for heptane [36]. As an informational note, the Abraham solute descriptors used in Equations (3) and (4) are
denoted by capitalized alphabetical characters. These solute descriptors could either be determined from experimental solubility data (denoted by $\text{Exp}$ as superscript in this work) or could be computed using available software [40]. Abraham solvent parameters, which will be used in later equations, will be denoted by lowercase alphabetical characters.

The accuracy of the models was investigated by computing $\text{MPD}$ (mean percentage deviation) as follows:

$$\text{MPD} = \frac{100}{N} \sum \left( \frac{\sigma_{\text{Calc}} - \sigma_{\text{Exp}}}{\sigma_{\text{Exp}}} \right)$$

where $N$ is the number of data points used in the regression analyses.

### Table 4. Numerical values of the Hansen and Catalan parameters for the solvents investigated in this work.

| solvent           | $\delta_D$ | $\delta_P$ | $\delta_H$ | $SP$  | $SdP$ | $SA$  | $SB$  |
|-------------------|------------|------------|------------|-------|-------|-------|-------|
| 1-butanol         | 16.00      | 5.70       | 15.80      | 0.67  | 0.66  | 0.34  | 0.81  |
| 1-hexanol         | 15.90      | 5.80       | 12.50      | 0.70  | 0.55  | 0.32  | 0.88  |
| 1-octanol         | 17.00      | 3.30       | 11.90      | 0.71  | 0.45  | 0.30  | 0.92  |
| 1-pentanol        | 13.83      | 8.82       | 13.80      | 0.69  | 0.59  | 0.32  | 0.86  |
| 1-propanol        | 16.00      | 6.80       | 17.40      | 0.66  | 0.75  | 0.37  | 0.78  |
| 1,4-dioxane       | 19.00      | 1.80       | 7.40       | 0.74  | 0.31  | 0.00  | 0.44  |
| 2-butanol         | 13.38      | 9.53       | 14.08      | 0.66  | 0.71  | 0.22  | 0.89  |
| 2-butanone        | 16.00      | 9.00       | 5.10       | 0.67  | 0.87  | 0.00  | 0.52  |
| 2-methyl–1-propanol | 13.38    | 9.53       | 14.08      | 0.66  | 0.68  | 0.31  | 0.83  |
| 2-pentanol        | 13.65      | 8.87       | 12.95      | 0.67  | 0.67  | 0.20  | 0.92  |
| 2-propanol        | 12.97      | 10.35      | 15.68      | 0.63  | 0.81  | 0.28  | 0.83  |
| acetone           | 15.50      | 10.40      | 7.00       | 0.65  | 0.91  | 0.00  | 0.48  |
| acetonitrile      | 11.59      | 12.95      | 16.34      | 0.65  | 0.97  | 0.04  | 0.29  |
| benzene           | 18.40      | 0.00       | 2.00       | 0.79  | 0.27  | 0.00  | 0.12  |
| butyl acetate     | 14.49      | 7.74       | 6.53       | 0.67  | 0.54  | 0.00  | 0.53  |
| cyclohexane       | 16.80      | 0.00       | 0.20       | 0.68  | 0.00  | 0.00  | 0.07  |
| dimethylsulfoxide | 18.40      | 16.40      | 10.20      | 0.83  | 1.00  | 0.07  | 0.65  |
| ethanol           | 15.80      | 8.80       | 19.40      | 0.64  | 0.78  | 0.40  | 0.66  |
| ethyl acetate     | 15.80      | 5.30       | 7.20       | 0.66  | 0.60  | 0.00  | 0.54  |
| ethylene glycol   | 17.00      | 11.00      | 26.00      | 0.78  | 0.91  | 0.72  | 0.53  |
| heptane           | 15.30      | 0.00       | 0.00       | 0.64  | 0.00  | 0.00  | 0.08  |
| methanol          | 15.10      | 12.30      | 22.30      | 0.61  | 0.90  | 0.61  | 0.55  |
| methyl acetate    | 12.68      | 11.42      | 11.79      | 0.65  | 0.64  | 0.00  | 0.53  |
| N-methyl–2-pyrrolidone | 18.00 | 12.30      | 7.20       | 0.81  | 0.96  | 0.02  | 0.61  |
| N,N-dimethylformamide | 17.40 | 13.70      | 11.30      | 0.76  | 0.98  | 0.03  | 0.61  |
| propylene glycol  | 12.75      | 14.23      | 27.95      | 0.73  | 0.89  | 0.48  | 0.60  |
| toluene           | 18.00      | 1.40       | 2.00       | 0.78  | 0.28  | 0.00  | 0.13  |
| water             | 15.50      | 16.00      | 42.30      | 0.68  | 1.00  | 1.06  | 0.03  |

### 3. Results and Discussion

The collected surface tension data of the mono-solvents at various temperatures were correlated with three sets of solvation parameters, and the obtained model after excluding non-significant parameters ($p > 0.05$) is:

$$\log \sigma_T = \left( \frac{-1.713 - 0.037s + 0.118a + 0.0088b + 0.008\delta_D + 0.006d + 0.003\delta_H + 3.636SP - 0.0875dP - 0.089SB}{729.913 - 16.509c - 23.369e - 29.450a - 19.611v - 687.155SP - 35.211SA} \right)$$

The correlation coefficient of this equation is 0.992, the F value is 503, and the correlation is statistically significant with a $p$-value of $<0.0005$. The F value is the Fischer test value revealing the statistical significance of the overall correlation. The minimum and maximum
MPD values for the back-calculated surface tensions belong to 1-butanol at temperature 293 ($\text{MPD} = 0.04\%$) and benzene at temperature 303 ($\text{MPD} = 11.62\%$). The overall MPD of the correlated data points was 3.48% ($N = 146$). Equation (6) is valid for interpolation purposes in all temperatures and for extrapolation purposes in a narrow range of temperatures.

Previous studies have shown the importance of Abraham solvation parameters in calculating the surface tension of the mono-solvents [12]. A comparison between surface tension prediction for mono-solvents with our proposed model and Freitas study at 20 °C ($\sigma_{20}^\circ$) is shown in Figure 1. Moreover, the MPD for a previous model by our group was 11%. It can be clearly understood that considering the Catalan and Hansen parameters, the prediction ability of the model has been improved in comparison to previous models.

An important distinction between the current method and the earlier method of Freitas et al. is that Equation (3) used the solute descriptors of the organic solvents as input parameters. The current treatment uses the Abraham model equation coefficients for each solvent as the input parameters for Equation (2). Solvent coefficients, rather than solute descriptors, are likely the more appropriate parameter to use when dealing with properties such as surface tension. While both types of parameters can be used in describing molecular interactions, their numerical values are determined under a different set of experimental conditions. In the case of solute descriptors, the measurements are normally performed at low concentrations where the dissolved solute is completely surrounded by solvent molecules. Such measurements would not capture the effects of self-association. Solvent parameters, on the other hand, would include effects arising from self-association, as well as any special structural features resulting from “solvent stacking”. We recognize that the limited availability of solvent coefficients does make it appealing to use the more readily available solute parameters when developing predictive expressions. Experimental-based solute descriptors are known for more than 8000 different organic and organometallic compounds [40]. Abraham model solvent coefficients, on the other hand, have been determined for only 130 different organic molecules and a few binary aqueous-alcoholic mixtures [41].

In order to validate the model, each solvent was sorted based on the temperature and was divided into training and test sets one by one in order to have different solvents containing various physiochemical properties with different temperatures in both test and training sets. The temperature values of the used training data points are listed in the second column of Table 1 using bold font. The proposed model was trained using the training data points, and the rest of the data points were predicted by the trained model. The obtained overall MPD value was 4.01% ($N = 118$). The results confirm the validity of the model.

Figure 1. Comparison of MPD values for the calculated surface tension of studied solvents at 293 K by combination of van’t Hoff type model and the solvation parameters (Equation (6)) and the reported model by Freitas et al. (Equation (3)).
4. Conclusions

A van't Hoff type-mathematical expression was developed for predicting the surface tension of both water and 27 different organic mono-solvents as a function of temperature using only Abraham solvation parameters, Hansen solubility parameters, and Catalan parameters as input values. The derived mathematical expression described the experimental surface tension data within an overall MPD of the model was 3.48%. The minimum and maximum MPD between predicted and observed values were 0.04% and 11.62%, respectively. The predictive model reported in the current study could help researchers to estimate the surface tension of mono-solvents at different temperatures and identify possible outlier values in need of re-measurement. The availability of needed solvation parameters currently limits the applicability of the proposed model; however, progress is being made to estimate Abraham model solvent coefficients using functional group additivity and machine learning methods [42-44].

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