

## Estimation of surface tension of pure liquids

D. H. L. PRASAD\*

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012.

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### Abstract

Based on the theorem of corresponding states, surface tension of liquids is expressed as

$$\gamma = [0.4 + 0.009 R_M + 0.00108 (4\pi N\mu^2/9kT_c)] \times P_c^{2/3} T_c^{1/3} (1 - T_R)^{11/9}.$$

The equation predicts surface tension of pure polar as well as non-polar liquids better than other generalised methods.

Key words : Surface tension, corresponding states, polar and non-polar liquids.

### 1. Introduction

Values of surface tension of liquids are needed in connection with several chemical engineering calculations such as those for interfacial area, plate-spacing, slot-opening, entrainment rate and liquid-holdup in problems relating to two-phase flow, nucleate-boiling heat transfer and the design of distillation columns. A good estimation method is very useful for design purposes in the absence of experimental data. In view of the applications in other fields as well, estimation of surface tension remained a topic of interest for over a century.

The theoretical aspects of surface tension have been discussed in several books on surface chemistry (for example Adamson<sup>1</sup>). Surface tension results due to the various forces acting on the molecules and is expressed as dynes/cm. From the theoretical and experimental knowledge, it can be stated that the surface tension of pure liquids in equilibrium with their own vapours (or with air) decreases with increase in pressure and temperature and becomes zero at the critical point.

\* Present address : Properties Group, Design and Engineering Division, Regional Research Laboratory, Hyderabad 500 009.

## 2. Methods of estimation of surface tension

Even before the time of Van der Waals<sup>2</sup>, attempts have been made to correlate surface tension of liquids in terms of other known or easily determinable properties. As a result, several methods for the estimation of surface tension have been proposed. Important ones among them have been mentioned here and their merits and limitations discussed. Detailed account is given by Partington<sup>3</sup> and Reid *et al.*<sup>4</sup>. Van der Waals equation<sup>2</sup>

$$\gamma = KT_c^{1/3} P_c^{2/3} (1 - T_R)^{n_\gamma} \quad (1)$$

with  $K$  and  $n_\gamma$  as universal constants is the basis for the correlations based on the theorem of corresponding states. While eqn. (1) does not give accurate results, methods extending the concept give results of engineering accuracy.

Macleod<sup>5</sup> found a relation between surface tension  $\gamma$ , density of liquid  $\rho_L$  and density of vapour  $\rho_V$  in the form

$$\gamma^{1/4} = [P](\rho_L - \rho_V) \quad (2)$$

Sugden<sup>6</sup> termed  $[P]$  the parachor and found that the parachor can be calculated by the group contribution method. Equation (2) predicts surface tension reasonably well (with an error of about 5%) if experimental values of liquid and vapour density are available at the conditions of interest. Variations of the method in terms of all the variables of eqn. (2) are possible. Lennard-Jones potential parameters have been used to correlate  $[P]$ 's.<sup>8</sup> Liquid and vapour densities can be determined from one of the preferred corresponding states correlations<sup>9-11</sup>.

Wright<sup>12</sup> proposed a variation of Sugden's method while the relationships with viscosity have been used on some occasions<sup>13,14</sup>.

Most of the methods discussed so far, and others proposed<sup>15-21</sup>, are disadvantageous as they require some physical properties such as viscosity, liquid density and/or vapour density, refractive index, etc., at the conditions of interest, in addition to the other parameters needed to use the correlations. Corresponding states methods based on Van der Waals equations overcome this difficulty and are superior as estimation methods.

Brook and Bird<sup>22</sup> developed the ideas given in Van der Waals paper for non-polar liquids and proposed

$$\gamma = P_c^{2/3} T_c^{1/3} (0.133 a_c - 0.281) (1 - T_R)^{11/9} \quad (3)$$

where the constant  $K$  in eqn. (1) is expressed as function of the third parameter defined by Riedel<sup>23</sup>, as

$$a_c = (d \ln P/d \ln T) \text{ at } T = T_c.$$

Hakim *et al.*<sup>24</sup> used Pitzer's acentric factor<sup>24</sup> and proposed the correlation

$$\gamma = P_c^{2/3} T_c^{1/3} Q_r [(1 - T_R)/0.4]^m \quad (4)$$

where

$$Q_p = 0.1574 + 0.359 \omega - 1.769 x - 13.69 x^2 - 0.51 \omega^2 + 1.298 \omega x$$

$$m = 1.21 + 0.5385 \omega - 14.61 x - 32.07 x^2 - 1.656 \omega^2 + 22.03 \omega x$$

$$\omega = -1.0 - \log P_R \text{ at } T_R = 0.7$$

$$x = \log (P_{RT}/P_{Rn}) \text{ at } T_R = 0.6$$

in which  $P_{Rn}$  is the reduced vapour pressure of normal fluid.

The twelve constants appearing in the relations for  $Q_p$  and  $m$  of the correlation were obtained from the experimental data of 16 polar liquids some of which are only slightly polar. The values of surface tension calculated using eqn. (4) are sensitive to the values of  $\omega$  and  $x$  which in turn depend heavily on the nature of the vapour pressure curve in the region  $T_R = 0.6$  to  $0.7$ .

### 3. Present work

An easily determinable property satisfying the requirements of characterising all classes of substances, as pointed out earlier<sup>25</sup>, molar polarization at the critical temperature,  $P_{MC}$ , defined as

$$P_{MC} = R_M + (4\pi N\mu^2/9 kT_c) \quad (5)$$

where

$R_M$  is the molar refraction, cc/mole

$N$  is the Avogadro's number, molecules/mole

$\mu$  is the dipole moment, debye units

$k$  is the Boltzmann constant

$T_c$  is the critical temperature, °K

has been chosen to explore the possibility of arriving at a good correlation for surface tension of liquids. The general form of eqn. (1) is retained, and effectively, this work can be considered as an attempt to relate  $K$  of eqn. (1) to easily determinable properties.

Experimental values of surface tension of ten substances (acetone, benzonitrile, ethyl-mercaptan, *n*-propyl-alcohol, propionic acid, *n*-hexane, *n*-octane, toluene, carbon-tetrachloride and cyclopentane) representing polar as well as non-polar substances are converted to the reduced units by calculating the values of  $(\gamma/P_c^{2/3} T_c^{1/3})$  and  $T_R$ . The reduced surface tension of each substance is plotted as a function of  $(1 - T_R)^{11/9}$  to verify the temperature dependence. The slopes of the straight lines through the points on these graphs give the values of  $K$  for each substance. Temperature dependence is found

Table I

Summary of comparison of calculated values of surface tension with experimental data

Substance*	No. of points	% average absolute deviation**		
		Present method	Brock and Bird method	Macelod and Sugden method
Acetic acid (29, 30)	4	8.2	52.6	4.5
Acetone (29, 30)	6	2.5	5.1	2.9
Aniline (29, 30)	6	4.5	6.4	5.2
Benzene (29, 30)	7	8.7	2.3	4.3
Benzonitrile (29)	3	0.3	2.2	3.2
Bromobenzene (29)	3	4.7	0.3	0.9
<i>n</i> -Butane (29)	3	3.8	1.1	9.2
<i>n</i> -Butylalcohol (30)	3	7.6	36.3	2.8
Carbondisulphide (29, 30)	5	3.0	2.9	4.5
Carbontetrachloride (29, 30)	8	1.5	4.4	1.2
Chlorobenzene (29, 30)	6	2.0	1.0	1.5
2,3-Dimethylbutane (29)	2	2.6	0.4	0.8
Ethylacetate (29, 30)	8	12.4	1.4	2.9
Ethylbenzoate (29)	5	10.3	13.2	5.0
Ethylmercaptan (29)	2	2.0	2.3	7.9
<i>n</i> -Heptane (29, 30)	7	0.6	2.0	1.8
<i>n</i> -Hexane (30)	3	3.4	0.3	0.1
Isobutyric acid (29)	5	8.9	54.0	2.4
Methylalcohol (29, 30)	6	16.8	92.2	13.7
Methylformate (5, 28)	6	10.0	7.0	9.0
<i>n</i> -Octane (30)	3	0.3	0.2	0.1
Phenol (29, 30)	5	2.1	25.8	7.8
<i>n</i> -Propylalcohol (28, 29)	5	5.2	52.2	2.0
<i>n</i> -Propylbenzene (29)	5	2.0	0.9	2.5
Toluene (30)	3	3.1	2.0	2.1
2, 2,3-Trimethylpentane (31)	1	9.0	2.3	3.0
Overall	120	5.6	15.3	4.0

\* Numbers in parentheses indicate references to experimental data.

\*\* Per cent average absolute deviation =

$$\frac{\sum_{i=1}^N \left[ \frac{(\text{Exptl. value} - \text{Calc. value})}{\text{Exptl. value}} \right]}{N} \times 100$$

where  $N$  is the number of data points,

to be well represented by  $(1 - T_R)^{11/9}$ , as the surface tension values could be predicted from the graphs with an error of less than or equal to 1%.

Values of  $K$  could be related to the constituents of molar polarization at the critical temperature—the non-polar contribution ( $R_M$ ) and polar contribution ( $4\pi N \mu^2/9 kT_c$ ). The resulting equation for surface tension is:

$$\gamma = [0.4 + 0.009 R_M + 0.00108 (4\pi N \mu^2/9 kT_c)] \times P_c^{2/3} T_c^{2/3} (1 - T_R)^{11/9} \quad (6)$$

#### 4. Results and discussion

Values of surface tension of several pure liquids calculated using eqn. (6), the Brock and Bird method and the Macleod and Sugden method are compared with the experimental data. In view of the difficulties in obtaining accurate values of  $\omega$  and  $\alpha$ , the Hakim *et al* method has not been tested for this group of substances. Comparisons summarised in Table I show that the present method is decidedly superior to the other generalized method of Brock and Bird and is of accuracy comparable to that of Macleod and Sugden method which requires liquid and vapour density data at the conditions of interest. Table II summarizes the comparison of the calculations for polar substances using the present method, Hakim and co-workers method and Brock and Bird method. Experimental data used for this are those from refs. 28 and 32 (which are also the input data used in the development of the Hakim and co-workers

Table II

#### Summary of comparison of surface tension of some polar substances

Substance	No. of points compared	Per cent average absolute deviation		
		Present method	Hakim and coworkers method	Brock and Bird method
Acetone	11	1.9	5.6	6.4
Ammonia	11	17.6	4.6	8.2
1-Butanol	10	6.7	16.5	32.1
Ethanol	18	10.8	26.8	74.7
Methanol	13	15.8	21.4	81.4
Methyl chloride	3	1.1	2.3	0.1
1-Propanol	11	5.3	16.7	55.1
2-Propanol	8	3.7	12.3	54.1
Sulphur dioxide	6	15.8	4.2	31.4
Water	71	5.4	24.1	42.3
Overall	162	7.7	18.9	43.9

correlation). On an overall basis the present method gives considerably superior results compared to the other methods and is therefore recommended as a good estimation method for surface tension in the absence of reliable experimental data.

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