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Correlation between Molecular Sizes of Pure Compounds: Application in Surface Tension Prediction Based on Scaled Particle Theory

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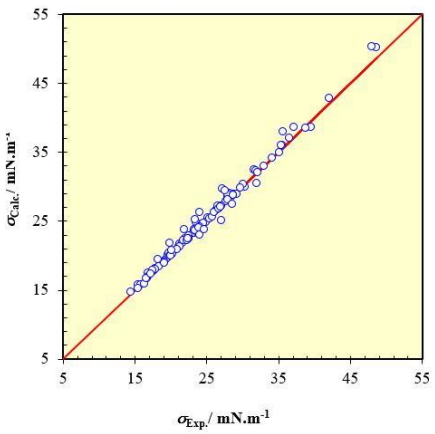
ABSTRACT

In this research study, molecular diameter for various pure compounds were estimated using seven methods, in which three diameters are based on scaled particle theory (SPT) and the others are obtained from actual molecular volumes assuming hard sphere shape for molecules by using Bondi, Edward and Van der Veen methods. The seventh one was obtained from a relationship between molecular volume and parachor. Correlation among seven types of molecular sizes for pure components is reported. Calculated diameters were used to prediction surface tension of 108 pure compounds based on SPT. The results demonstrated that the hard sphere diameter which was obtained from reported correlations can be used to estimate the pure substances surface tension with good accuracy. The absolute average deviation percent for surface tension prediction of pure fluids with different correlations is 1.3%, 11.26%, 11.52%, 32.42%, 14.62% 12.16% and 1.95%.

GRAPHICAL ABSTRACT



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Introduction

Studying the thermodynamic and transport properties of liquids and liquid mixtures is useful for many purposes, one of which is to obtain information on the molecular interactions among the components of the mixtures [1-2]. The thermodynamic and transport properties of liquids and liquid mixtures1 have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, and fluid flow [3]. As a fundamental parameter, surface tension is the single most accessible parameter that describes the thermodynamic state and contains implicit information on the internal structure of a liquid interface [4]. Apart from this theoretical interest, a detailed understanding of the behaviour of a vapor-liquid interface, such as enrichment of one component in a liquid surface, is important for modelling a distillation process [5]. Surface tension is important in many scientific areas, including heat transfer, mass transfer, gas absorption, distillation, liquid extraction, condensation, fluid flow, material sciences, environmental sciences, process simulation, and molecular dynamics [6-11], playing a significant role in several industries such as foods, paints, detergents, pharmaceuticals, agro-chemicals and petroleum engineering [12-17]. In addition, the surface tension of liquids must often be considered in designing rational chemical process equipment involving interphase heat and mass transfer [18-19].

Several methods have been developed to estimate the surface tension of pure fluids including parachor method [20], corresponding states model [21-22], the gradient theory [23], the perturbation theory [24]; the density functional theory [25] and group contribution method [26]. In this work, scaled particle theory (SPT) was employed to estimate the surface tension of polar and non-polar pure fluids. For estimating surface tension of pure fluids from SPT, knowing hard sphere diameter is necessary. We represent seven methods for calculating hard sphere diameter and report correlation among them. Based on calculated hard sphere diameter, surface tension of 108 pure substances is predicted with SPT. The first work on scaled particle theory (SPT) was published at 1959. In that study several exact conditions were derived and the dependence of surface tension on curvature was also given. It was reported that the macroscopic consideration on surface tension can sometimes be successfully extrapolated to molecular dimensions [27]. Additional papers applied SPT to one and two-dimensional systems [28]. SPT has been applied with considerable success to various studies, i.e., surface tension of pure fluids [29-30], partition coefficient in phase Equilibria [31], volatility in extractive distillation [32], solubility of gases in liquids [33-34], micellization of surfactants [35-37], glass transition of liquids [38], and estimation of thermodynamic properties [39-40]. The success of the theory encouraged workers to extend the formalism to real fluids [41], surface tension prediction for mixtures [42], critical temperature prediction [43] and determine the Lennard-Jones energy parameter [44].

SPT was extended and an approximate for the work of creating a spherical cavity in a real fluid was determined. This expression was used to derive an equation for evaluation of surface tension of pure substances [45]. The calculated surface tension by SPT is very sensitive to hard sphere diameter and a small change in hard sphere diameter cause a significant change in calculated surface tension. Therefore, for calculating surface tension with acceptable results it is necessary to have hard sphere diameter with high accuracy.

Theory

Following equation was derived for calculating surface tension of pure substance based on SPT [45]:

$$\sigma = \frac{kT}{4\pi a^2}\left\{\frac{12y}{1+y} + 18\left(\frac{y}{1+y}\right)^2\right\} - \frac{pa}{2} \quad (1)$$

where σ is the surface tension of pure substance, k is the Boltzmann's constant and p, T are the pressure and temperature, respectively. a is the hard sphere diameter and y is the packing fraction given by $y = \pi\rho a^3/6$ and ρ is the number density.

For calculating surface tension of pure substances, it is necessary to have hard sphere diameter. Molecular diameter can be estimated by seven methods:

The first type of molecular diameter (a_W) can be determined from the Van der Waals molecular volume (V_W). V_W is regarded as the summation of individual volume of molecular fragments [46]:

$$\pi a_W^3/6 = V_W \quad (2)$$

The second type of molecular diameter (a_β) is obtained from experimental value of isothermal compressibility (β) using following equation derived from SPT [47]:

$$\beta = \left(\frac{\pi a_\beta^3}{6kT}\right)\left[\frac{(1-y_\beta)^4}{y_\beta(1+2y_\beta)^2}\right] \quad (3)$$

Where $y_\beta = \pi\rho a_\beta^3/6$.

The third type of molecular diameter (a_E) is determined from the actual molecular volume (V_E) that can be calculated by the method of Edwared in which V_E is equal the summation of individual volume of molecular fragments [48]:

$$\pi a_E^3/6 = V_E \quad (4)$$

The fourth type of molecular diameter (a_V) is determined from the correlation of V_W with the hard sphere diameter [49]. The proposed correlation is:

$$\left(\frac{\pi}{6}\right) N a_V^3 = -10 + 1.13V_W \quad (5)$$

With a_V (in cm) and V_W (in cm^3/mol) and N is Avogadro's number.

The fifth type of molecular diameter (a_P) is calculated from parachor data. Sugden defined parachor with the following equation [50]:

$$P = \sigma^{1/4} M/(\rho_l - \rho_v) \quad (6)$$

P is the parachor, M the molecular weight of the compound, and ρ_l and ρ_v are the densities of the liquid and vapour in equilibrium. It was found that P could be simply calculated from group additivity contributions. Although the dependence of surface tension on density predicted by Eq. (6) has been theoretically derived close to the critical point [51] the parachor has continued to be mainly regarded as an empirical quantity, with the large amount of data available clearly indicating a relationship with the molecular volume. Telang related the parachor to molecular dimensions by the following expression [52]:

$$a_P = 0.92\times10^{-8} P^{0.4}/T_c^{0.1} \quad (7)$$

Where a_P is the molecular diameter in cm, T_c is the critical temperature expressed in K. Eq. (7) has a reliability of $\pm 2.2\%$ for all compounds except those having – OH, $-C\equiv N$, – COOH, or $\rangle$C=O groups and one to three non-functional carbon atoms. For these latter the constant 0.92 becomes 0.96 [53].

The parachor of pure compounds was analysed from the point of view of SPT [54]. They used theories of liquids and derived a simple relationship between the molecular parachor and the hard sphere diameter:

$$P = 2.841\times10^{19} T^{1/4} f(y) a_S^{2.5} \quad (8)$$

Where a_S is the molecular diameter. $f(y)$ is defined with following equation:

$$f(y)=[\frac{y(2+y)^{1/4}}{y(1-y)^{1/2}}] \quad (9)$$

The sixth type of molecular diameter (a_S) can be calculated with Eqs. (8), (9) using literature data of parachor [53].

The seventh type of molecular diameter (a_σ) can be calculated with Eq. (1) using surface tension literature data for pure compounds [55-57].

Result and Discussion

We used equations (1), (2), (3), (4), (5), (7), (8) and (9) for calculating molecular diameters (a_W, a_β, a_E, a_V, a_P, a_S and a_σ) of various pure compounds. The parameters required for the calculation together with experimental surface tension are collected in Table 1 where the compounds are ordered according their type. The results of calculation are summarised in Table 2.

First, correlation between a_β, a_E was investigated as illustrated in Figure 1, where the values of a_β inside the bracket in Table 2 were used for the plot (For these compounds, experimental isothermal compressibility was available). As it is obvious from Figure 1, there is good linearity between a_β and a_E. It means that one can estimate a_β values from a_E using following equation due to the lack of experimental isothermal compressibility factor:

$$a_\beta = 1.146\, a_E - 1.1591 \quad (10)$$

Here, part of the a_β values was obtained from a_E using Eq. (10), since the experimentally available a_β data are not so numerous.

At the next step correlation among a_W, a_β, a_E, a_V, a_P, a_S, and a_σ was investigated as illustrated in Figures 2, 3, 4, 5, 6 and 7 , where the values of a_β inside the bracket in Table 2 were used for the plot. Regression line is given by Eqs. (11), (12), (13), (14), (15) and (16):

$$a_\sigma = 1.1329\, a_E - 1.1670 \quad (11)$$

$$a_\sigma = 0.9929\, a_\beta - 0.0337 \quad (12)$$

$$a_\sigma = 0.9923 a_V - 0.0329 \quad (13)$$

$$a_\sigma = 1.1148\, a_W - 1.0481 \quad (14)$$

$$a_\sigma = 1.3789\, a_P - 0.8133 \quad (15)$$

$$a_\sigma = 1.0108\, a_S - 0.0709 \quad (16)$$

Table 1. The parameters required for the calculation together with experimental surface tension for studied pure fluids.

No.	Compound	T_C (K)	ρ (gr.cm^{-3})	$\sigma_{exp.}$ (mN.m^{-1})	No.	Compound	T_C (K)	ρ (gr.cm^{-3})	$\sigma_{exp.}$ (mN.m^{-1})
1	pentane	469.70	0.6214	15.49	55	*sec*-butylbenzene	664.00	0.8580	28.03
2	hexane	507.50	0.6548	17.89	56	*tert*-butylbenzene	660.00	0.8665	27.64
3	heptane	540.30	0.6795	19.65	57	chlorobenzene	632.40	1.1009	32.99
4	octane	568.80	0.6986	21.14	58	*o*-dichlorobenzene	729.00	1.3003	36.70
5	nonane	594.60	0.7138	22.38	59	aniline	699.00	1.0175	42.12
6	decane	617.70	0.7263	23.37	60	styrene	647.00	0.9001	32.00
7	2-methylbutane	460.40	0.6142	14.44	61	m-cresol	705.80	1.0302	35.69
8	2-methylpentane	497.50	0.6500	16.88	62	anisole	645.60	0.9893	35.10
9	3-methylpentane	504.50	0.6598	17.61	63	1-pentene	464.80	0.6353	15.45
10	2,2-dimethylbutane	488.80	0.6450	15.81	64	*cis*-2-pentene	476.00	0.6508	16.80
11	2,3-dimethylbutane	500.00	0.6570	16.88	65	*trans*-2-pentene	475.00	0.6431	16.41
12	2-methylhexane	530.40	0.6744	18.81	66	1-hexene	504.00	0.6686	17.90
13	3-methylhexane	535.30	0.6829	19.31	67	1-heptene	537.30	0.6970	19.80
14	2,3-dimethylpentane	537.40	0.6909	19.47	68	1-octene	566.70	0.7110	21.28
15	2,4-dimethylpentane	519.80	0.6683	17.66	69	1-nonene	592.00	0.7253	22.56

16	2,2,3-trimethylpentane	563.50	0.7121	20.22	70	1-decene	615.00	0.7370	23.54
17	2,2,4-trimethylpentane	544.00	0.6878	18.33	71	methanol	512.60	0.7866	22.07
18	2,2,5-trimethylhexane	568.00	0.7072	19.59	72	ethanol	513.90	0.7849	21.97
19	dichloromethane	510.00	1.3168	27.20	73	1-propanol	536.80	0.7996	23.32
20	iodomethane	528.00	2.2650	30.34	74	2-propanol	508.30	0.7813	20.93
21	chloroform	536.40	1.4800	26.67	75	1-butanol	563.10	0.8058	24.93
22	tetrachloromethan	556.40	1.5844	26.43	76	2-butanol	536.10	0.8026	22.54
23	carbon disulfide	552.00	1.2555	31.58	77	1-pentanol	588.20	0.8108	25.39
24	ethyl bromide	503.90	1.4505	23.62	78	2-pentanol	560.40	0.8054	23.45
25	ethyliodide	554.00	1.9244	28.46	79	1-hexanol	611.00	0.8153	25.81
26	1,1-dichloroethane	523.00	1.1680	24.07	80	1-octanol	652.50	0.8223	27.10
27	1,2-dichloroethane	566.00	1.2457	31.86	81	2-methyl-1-propanol	547.80	0.7978	22.55
28	1,1,1-trichloroethane	545.00	1.3303	25.18	82	2-methyl-2-propanol	506.20	0.7812	19.96
29	1,1,2,2-tetrachloroethane	661.20	1.5872	35.58	83	3-methyl-1-butanol	579.40	0.8071	23.71
30	pentachloroethane	646.00	1.6749	34.15	84	formic acid	580.00	1.2140	37.13
31	1,2-dibromo-tetrafloroethane	487.80	2.1630	24.40	85	acetic acid	592.70	1.0439	27.10
32	1,2-dibromoethane	646.00	2.1687	39.55	86	propionic acid	612.00	0.9881	26.20
33	1-chloropropane	503.00	0.8830	21.30	87	butyric acid	628.00	0.9529	26.05
34	2-chloropropane	485.00	0.8563	19.16	88	isobutyric acid	609.00	0.9431	24.58
35	1-bromopropane	535.50	1.3452	25.26	89	propylamine	497.00	0.7121	21.75
36	2-bromopropane	522.50	1.3060	23.25	90	isopropylamine	471.80	0.6821	17.48
37	1-iodopropane	589.40	1.7400	28.80	91	butylamine	531.90	0.7369	23.44
38	2-iodopropane	574.60	1.6946	26.58	92	diethylamine	496.50	0.7016	19.85
39	1-chlorobutane	542.00	0.8810	23.18	93	dipropylamine	555.80	0.7329	22.31
40	1-chloro-2-methylpropane	526.50	0.8773	21.65	94	diisopropylamine	523.10	0.7100	19.14
41	2-chloro-2-methylpropane	507.80	0.8420	18.30	95	dibutylamine	607.50	0.7571	24.12
42	1-chloropentane	552.00	0.8770	24.40	96	acetone	508.10	0.7844	24.02
43	nitromethane	588.00	1.1313	36.53	97	2-butanone	536.80	0.7994	23.96
44	nitroethane	595.00	1.0427	32.13	98	3-pentanone	561.00	0.8020	24.74
45	1-nitropropane	606.00	0.9961	30.10	99	ethyl ether	466.70	0.7078	16.65
46	2-nitropropane	597.00	0.9835	29.29	100	propyl ether	530.60	0.7419	19.98
47	benzene	562.20	0.8736	28.22	101	isopropyl ether	500.30	0.7207	17.27
48	toluene	591.80	0.8622	27.93	102	n-butyl ether	580.00	0.7641	22.44
49	*m*-xylene	617.10	0.8601	28.47	103	butylethylether	531.00	0.7500	20.13
50	*o*-xylene	630.30	0.8759	29.76	104	ethylene glycol	645.00	1.1101	47.99
51	*p*-xylene	616.20	0.8566	28.01	105	acetonitrile	545.50	0.7765	28.66
52	Ethylbenzene	617.20	0.8625	28.75	106	propionitrile	564.40	0.7768	26.75
53	Isopropylebenzene	631.10	0.8579	27.69	107	butyronitrile	582.20	0.7865	26.92
54	Butylbenzene	660.50	0.8560	28.72	108	benzonitrile	699.40	1.0000	38.79

Table 2. Calculated molecular diameters (a_W, a_β, a_E, a_V, a_P, a_S and a_σ) of various pure compounds and Absolute average deviation percent (AAD%) in calculating surface tension of pure fluids by using different molecular diameters

No.	Compound	a_β	a_σ	a_W	a_V	a_P	a_E	a_S	AAD% σ_β	AAD% σ_σ	AAD% σ_W	AAD% σ_v	AAD% σ_P	AAD% σ_E	AAD% σ_S
1	Pentane	5.36	5.09	5.69	5.61	4.39	5.69	5.10	32.10	0.34	95.84	76.19	43.33	96.15	1.29
2	Hexane	5.73[5.65]	5.54	6.01	5.97	4.64	6.01	5.56	12.11	0.09	71.86	64.43	52.59	72.98	1.45
3	Heptane	6.05[5.97]	5.92	6.29	6.30	4.88	6.29	5.92	5.44	0.12	55.73	56.87	58.52	55.46	0.12
4	Octane	6.35[6.32]	6.26	6.55	6.59	5.09	6.55	6.27	6.90	0.11	42.78	50.23	63.07	42.11	0.56
5	Nonane	6.63	6.57	6.80	6.86	5.29	6.80	6.58	7.88	0.14	32.34	44.50	66.37	32.98	0.72
6	Decane	6.89	6.85	7.02	7.11	5.48	7.02	6.85	4.45	0.10	24.04	39.86	68.97	23.57	0.34
7	2-methylbutane	5.36	5.04	5.69	5.61	4.39	5.69	5.06	37.48	0.13	102.36	82.40	40.35	102.77	1.98
8	2-methylpentane	5.73	5.50	6.00	5.97	4.65	6.01	5.53	26.88	0.14	77.62	70.02	50.34	78.83	2.88
9	3-methylpentane	5.73	5.51	6.00	5.97	4.62	6.01	5.51	26.86	0.36	79.04	71.19	52.01	80.29	0.36
10	2,2-dimethylbutane	5.73	5.46	6.00	5.97	4.62	6.01	5.45	32.58	0.64	84.78	76.97	48.44	86.10	0.12
11	2,3-dimethylbutane	5.73	5.48	6.00	5.97	4.61	6.01	5.48	30.76	0.54	84.04	76.02	50.56	85.39	0.54
12	2-methylhexane	6.05	5.90	6.18	6.17	4.87	6.29	5.90	17.75	0.07	37.86	36.37	57.50	58.22	0.07
13	3-methylhexane	6.05	5.89	6.29	6.30	4.86	6.29	5.89	19.07	0.18	61.21	62.39	58.04	60.98	0.18
14	2,3-dimethylpentane	6.05	5.87	6.29	6.30	4.84	6.29	5.87	22.33	0.07	66.61	67.87	58.12	66.37	0.17
15	2,4-dimethylpentane	6.05	5.86	6.29	6.30	4.87	6.29	5.86	22.11	0.17	63.52	64.67	55.46	63.36	0.23
16	2,2,3-trimethylpentane	6.35	6.17	6.55	6.59	5.03	6.55	6.17	22.59	0.08	59.88	68.50	61.59	59.26	0.08
17	2,2,4-trimethylpentane	6.35	6.17	6.55	6.59	5.07	6.55	6.17	21.22	0.02	55.67	63.53	59.12	55.11	0.22
18	2,2,5-trimethylhexane	6.63	6.47	6.80	6.86	5.27	6.80	6.50	19.55	0.46	46.02	59.18	62.64	46.86	2.47
19	dichloromethane	4.30	4.33	4.74	4.45	3.66	4.76	4.39	3.45	0.74	82.06	18.26	49.75	89.97	8.79
20	iodomethane	4.26	4.35	4.71	4.41	3.61	4.73	4.34	11.02	0.31	71.04	8.81	54.68	78.47	1.36
21	chloroform	4.72[4.77]	4.77	5.19	5.01	4.12	5.13	4.77	0.45	0.45	83.91	39.54	48.96	67.37	0.45
22	tetrachloromethane	5.09[5.15]	5.16	5.49	5.38	4.42	5.45	5.17	1.87	0.66	58.25	33.21	53.13	47.69	0.58
23	carbon disulfide	4.15[4.26]	4.32	4.49	4.13	3.73	4.63	4.34	7.44	0.22	28.35	20.87	48.38	60.89	2.57
24	ethyl bromide	4.54[4.55]	4.52	4.95	4.73	3.83	4.97	4.56	4.07	0.46	80.71	29.98	48.77	85.68	4.82
25	ethyliodide	4.77[4.81]	4.83	5.15	4.97	3.97	5.17	4.84	2.27	0.26	59.66	21.04	58.16	64.73	1.57

26	1,1-dichloroethane	4.80	4.79	5.18	5.00	4.03	5.20	4.86	1.55	0.35	68.66	30.65	52.04	75.31	9.20
27	1,2-dichloroethane	4.80[4.81]	4.87	5.22	5.06	3.98	5.20	4.88	7.79	0.11	74.01	31.44	61.15	66.64	1.27
28	1,1,1-trichloroethane	5.16	5.20	5.48	5.36	4.27	5.51	5.20	5.11	0.08	45.20	23.13	58.62	51.91	0.08
29	1,1,2,2-tetrachloroethane	5.48[5.54]	5.58	5.75	5.68	4.44	5.79	5.59	5.96	0.45	30.24	16.17	69.81	38.44	1.00
30	pentachloroethane	5.77	5.87	6.00	5.97	4.67	6.05	5.87	12.31	0.01	22.13	15.95	70.56	31.54	0.01
31	1,2-dibromo-tetrafloroethane	5.44	5.60	5.75	5.68	4.57	5.76	5.48	16.30	0.23	20.65	10.01	61.30	22.58	12.71
32	1,2-dibromoethane	5.04	5.21	5.39	5.25	4.13	5.41	5.19	21.12	0.58	34.53	7.38	69.43	40.35	2.43
33	1-chloropropane	4.88	4.78	5.26	5.10	4.05	5.27	4.80	11.33	0.67	83.25	45.82	49.53	87.40	1.56
34	2-chloropropane	4.88	4.76	5.25	5.09	4.06	5.27	4.75	14.50	0.46	84.24	48.19	46.25	88.30	0.59
35	1-bromopropane	4.99	4.99	5.36	5.22	4.13	5.37	5.00	0.10	0.49	65.34	34.35	56.67	68.05	0.72
36	2-bromopropane	4.99	4.99	5.36	5.22	4.15	5.37	4.99	0.58	0.01	62.36	33.24	54.45	64.97	0.01
37	1-iodopropane	5.20	5.24	5.53	5.42	4.26	5.55	5.25	5.70	0.92	50.23	27.26	62.67	55.11	0.37
38	2-iodopropane	5.20	5.24	5.53	5.42	4.28	5.55	5.26	5.14	0.51	48.13	26.42	60.53	52.80	2.00
39	1-chlorobutane	5.29	5.24	5.62	5.53	4.32	5.63	5.24	6.83	0.36	65.95	45.01	57.13	68.22	0.11
40	1-chloro-2-methylpropane	5.29	5.19	5.62	5.53	4.32	5.63	5.19	13.03	0.35	74.98	53.05	54.56	77.45	0.35
41	2-chloro-2-methylpropane	5.29	5.13	5.62	5.53	4.35	5.63	5.18	19.64	0.41	80.18	59.00	48.63	82.63	5.78
42	1-chloropentane	5.66	5.63	5.94	5.90	4.60	5.95	5.63	4.04	0.39	52.49	43.42	61.37	53.76	0.39
43	nitromethane	4.10	4.20	4.59	4.26	3.44	4.59	4.21	13.08	0.13	95.33	9.82	58.35	95.55	1.34
44	nitroethane	4.63	4.67	5.05	4.85	3.80	5.05	4.67	5.78	0.33	83.84	29.92	60.50	82.35	0.33
45	1-nitropropane	5.09	5.09	5.45	5.32	4.12	5.45	5.09	0.35	0.81	73.79	41.45	62.61	74.83	0.81
46	2-nitropropane	5.09	5.09	5.45	5.32	4.12	5.45	5.08	0.60	0.16	70.00	39.02	62.31	71.09	1.45
47	Benzene	4.98[5.01]	5.03	5.35	5.21	4.13	5.36	5.06	2.99	0.50	58.46	27.64	59.72	60.17	2.90
48	Toluene	5.40[5.41]	5.43	5.74	5.66	4.40	5.72	5.44	2.44	0.07	55.09	38.29	63.28	51.01	1.88
49	m-xylene	5.76[5.76]	5.79	6.07	6.05	4.64	6.04	5.79	3.59	0.18	50.75	45.27	66.68	42.73	0.07
50	o-xylene	5.76	5.78	6.07	6.05	4.62	6.04	5.78	2.00	0.25	55.00	49.15	67.58	46.45	0.25
51	p-xylene	5.76	5.78	6.07	6.05	4.66	6.04	5.81	2.90	0.75	50.82	45.38	65.98	42.85	3.16
52	ethylbenzene	5.75	5.79	6.05	6.02	4.64	6.03	5.79	4.76	0.09	44.70	38.73	66.80	40.64	0.09
53	isopropylebenzene	6.07	6.08	6.33	6.34	4.86	6.31	6.09	1.39	0.40	41.10	43.36	68.11	36.82	0.24
54	butylbenzene	6.37	6.40	6.59	6.63	5.08	6.57	6.40	4.28	0.53	29.45	37.88	70.85	25.73	0.02
No.	Compound	a_{β}	a_{σ}	a_{W}	a_{V}	a_{P}	a_{E}	a_{S}	AAD% σ_{p}	AAD% σ_{σ}	AAD% σ_{W}	AAD% σ_{v}	AAD% σ_{P}	AAD% σ_{E}	AAD% σ_{s}
55	sec-butylbenzene	6.37	6.38	6.59	6.63	5.06	6.57	6.38	1.15	0.11	33.81	42.57	70.39	29.99	0.11
56	tert-butylbenzene	6.37	6.34	6.59	6.63	5.07	6.57	6.39	3.67	0.28	41.08	50.49	69.29	37.02	6.40
57	chlorobenzene	5.33[5.39]	5.45	5.67	5.59	4.36	5.66	5.45	8.10	0.28	39.36	21.82	67.45	36.84	0.28
58	o-dichlorobenzene	5.64	5.76	5.91	5.86	4.46	5.93	5.66	16.06	0.16	25.52	16.21	73.63	30.49	13.36
59	Aniline	5.28[5.33]	5.37	5.63	5.54	4.24	5.62	5.38	5.65	0.40	60.69	35.04	71.71	56.14	1.68
60	Styrene	5.63	5.72	5.95	5.90	4.54	5.92	5.70	11.83	0.00	40.11	31.02	69.08	34.43	4.84
61	m-cresol	5.57	5.57	5.85	5.80	4.61	5.87	5.61	0.02	0.28	58.93	43.83	64.77	64.22	6.37
62	Anisole	5.52	5.65	5.84	5.78	4.49	5.83	5.65	16.23	0.14	33.54	21.52	69.91	31.82	0.71
63	1-pentene	5.21	4.96	5.57	5.47	4.29	5.56	4.95	28.38	0.32	97.26	73.13	42.12	94.03	1.24
64	cis-2-pentene	5.21	4.99	5.57	5.47	4.28	5.56	4.98	25.57	0.38	95.68	70.85	45.12	92.62	0.96
65	trans-2-pentene	5.21	5.00	5.57	5.47	4.28	5.56	4.96	24.68	0.22	92.79	68.76	44.90	89.84	3.38
66	1-hexene	5.59	5.43	5.90	5.85	4.56	5.89	5.43	18.51	0.10	73.18	62.39	51.75	70.63	0.21
67	1-heptene	5.93	5.81	6.20	6.19	4.80	6.19	5.83	14.83	0.03	59.46	57.97	57.72	58.02	2.60
68	1-octene	6.24	6.17	6.47	6.49	5.02	6.46	6.17	8.51	0.26	43.25	48.62	62.67	42.01	0.07
69	1-nonene	6.53	6.49	6.72	6.77	5.22	6.71	6.49	5.08	0.23	32.47	42.93	66.15	31.51	0.35
70	1-decene	6.79	6.77	6.95	7.03	5.42	6.94	6.77	2.51	0.38	24.18	38.57	68.74	23.00	0.20
71	Methanol	3.54[3.47]	3.31	4.03	3.49	3.09	4.10	3.32	21.37	0.56	186.93	23.71	19.90	228.74	1.69
72	Ethanol	4.18[4.13]	3.96	4.61	4.29	3.60	4.66	4.03	22.14	0.03	149.45	50.87	30.64	173.28	8.29
73	1-propanol	4.71[4.63]	4.50	5.07	4.87	3.95	5.12	4.52	16.09	0.70	122.71	61.56	42.39	142.86	1.64
74	2-propanol	4.71[4.64]	4.46	5.07	4.87	3.96	5.12	4.46	21.88	0.18	128.47	67.79	38.01	148.22	0.25
75	1-butanol	5.14[5.13]	5.00	5.46	5.34	4.29	5.50	4.99	18.22	0.40	93.48	59.39	50.61	106.71	0.79
76	2-butanol	5.14	4.92	5.46	5.34	4.28	5.50	4.93	31.63	0.06	110.71	73.83	46.15	125.14	1.22
77	1-pentanol	5.53	5.39	5.80	5.74	4.58	5.84	5.39	19.57	0.39	77.84	60.75	55.16	89.28	0.39
78	2-pentanol	5.53	5.34	5.80	5.74	4.61	5.84	5.40	26.80	0.26	87.71	69.89	50.87	99.62	7.11
79	1-hexanol	5.88	5.75	6.11	6.09	4.83	6.14	5.74	18.05	0.25	65.13	60.27	58.87	74.01	0.97
80	1-octanol	6.48	6.39	6.64	6.69	5.26	6.67	6.32	13.87	0.60	42.13	52.94	65.65	48.86	7.76
81	2-methyl-1-propanol	5.14	4.93	5.46	5.34	4.28	5.50	4.93	29.30	0.36	105.99	70.28	46.91	119.93	0.36
82	2-methyl-2-propanol	5.14	4.87	5.46	5.34	4.33	5.50	4.95	37.52	0.01	115.51	79.39	39.55	129.63	9.18
83	3-methyl-1-butanol	5.53	5.35	5.80	5.74	4.56	5.84	5.35	26.23	0.39	87.05	69.21	52.93	99.07	0.39
84	formic acid	3.64	3.59	4.13	3.63	3.13	4.19	3.62	7.66	0.45	172.05	5.17	43.78	219.34	4.05
85	acetic acid	4.26	4.10	4.68	4.39	3.57	4.73	4.10	23.79	0.05	149.96	48.57	43.46	174.79	0.05
86	propionic acid	4.77	4.60	5.13	4.95	3.94	5.17	4.61	24.32	0.19	123.37	62.44	49.04	139.79	0.82
87	butyric acid	5.20	5.05	5.51	5.40	4.27	5.55	5.05	22.57	0.71	98.80	65.11	53.81	111.89	0.71
88	isobutyric acid	5.20	5.02	5.51	5.40	4.28	5.55	5.02	25.91	0.08	102.45	68.74	51.83	115.50	0.08
89	propylamine	4.82	4.65	5.21	5.05	3.95	5.22	4.67	21.90	0.53	113.20	64.31	48.50	115.18	1.73
90	isopropylamine	4.82	4.54	5.21	5.05	3.95	5.22	4.56	35.60	0.10	128.80	79.52	40.29	130.77	1.93
91	butylamine	5.25	5.12	5.59	5.49	4.24	5.59	5.12	17.32	0.52	90.42	63.20	55.99	91.89	0.52
92	diethylamine	5.26	5.08	5.62	5.52	4.28	5.60	5.08	22.37	0.07	98.22	72.81	50.75	92.99	0.07
93	dipropylamine	5.97	5.86	6.23	6.23	4.78	6.22	5.86	12.76	0.79	60.41	59.97	61.49	57.10	0.79
94	diisopropylamine	5.97	5.81	6.23	6.23	4.80	6.22	5.80	19.41	0.18	66.76	66.32	57.16	63.51	1.38
95	dibutylamine	6.55	6.49	6.75	6.81	5.21	6.73	6.49	7.73	0.25	39.24	51.75	67.56	35.83	0.22
96	Acetone	4.55[4.49]	4.50	4.98	4.77	3.94	4.98	4.46	1.22	0.05	96.42	40.52	43.23	94.89	4.59
97	2-butanone	5.02	4.92	5.39	5.25	4.26	5.39	4.92	12.63	0.01	91.01	54.92	47.89	92.02	0.01
98	3-pentanone	5.42	5.34	5.74	5.66	4.54	5.74	5.31	9.77	0.37	71.80	53.35	54.05	72.78	3.86
99	ethyl ether	5.11[5.03]	4.91	5.47	5.35	4.42	5.47	4.92	11.93	0.76	87.45	60.48	35.15	88.25	0.18
100	propyl ether	5.84	5.76	6.11	6.09	4.96	6.11	5.76	9.46	0.11	52.29	48.62	51.06	51.93	0.43
101	isopropyl ether	5.84	5.70	6.11	6.09	4.98	6.11	5.70	16.69	0.55	59.97	56.30	45.61	59.61	0.55
102	n-butyl ether	6.45	6.43	6.63	6.67	5.42	6.64	6.43	2.86	0.46	27.97	36.03	59.65	30.03	0.11
103	butylethylether	5.84	5.74	6.11	6.09	4.96	6.11	5.77	12.10	0.05	56.87	53.02	50.48	56.50	2.88
104	ethylene glycol	4.43[4.45]	4.44	4.78	4.51	3.72	4.88	4.47	1.34	0.35	95.85	12.48	60.97	151.65	4.85
105	acetonitrile	3.97	3.99	4.48	4.12	3.49	4.48	3.95	1.35	0.57	116.53	19.96	42.21	115.91	4.41
106	propionitrile	4.54	4.50	4.97	4.74	3.89	4.97	4.50	4.61	0.08	98.88	38.63	47.17	100.33	0.08
107	butyronitrile	4.99	4.96	5.37	5.23	4.23	5.37	4.96	4.74	0.21	82.21	46.05	52.49	81.99	0.21
108	benzonitrile	5.43	5.58	5.77	5.70	4.59	5.75	5.58	19.64	0.50	35.62	20.58	67.15	31.02	0.95
	Overall AAD1 %								**13.31**	**0.31**	**71.45**	**46.98**	**55.65**	**75.38**	**1.88**
	Overall AAD2 %								**11.26**	**1.30**	**11.52**	**32.42**	**14.62**	**12.16**	**1.95**

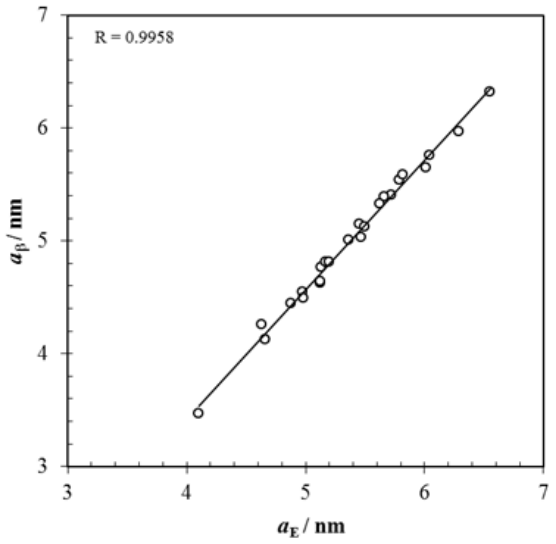

Figure 1. Relation between a_β and a_E. Regression line: $a_\beta = 1.146\, a_E - 1.1591$.

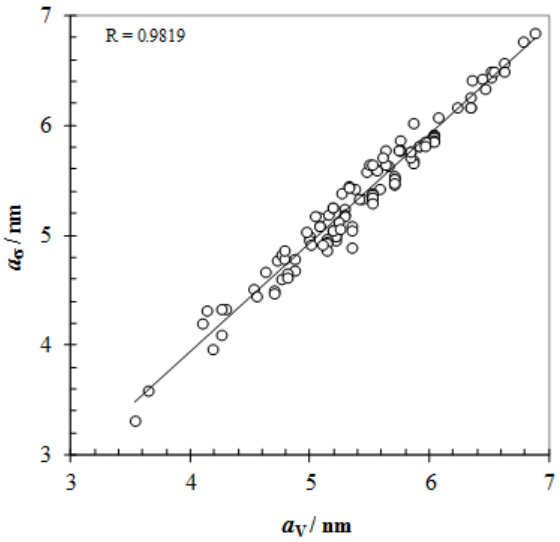

Figure 2. Relation between a_σ and a_W. Regression line: $a_\sigma = 0.9923\, a_V - 0.0329$.

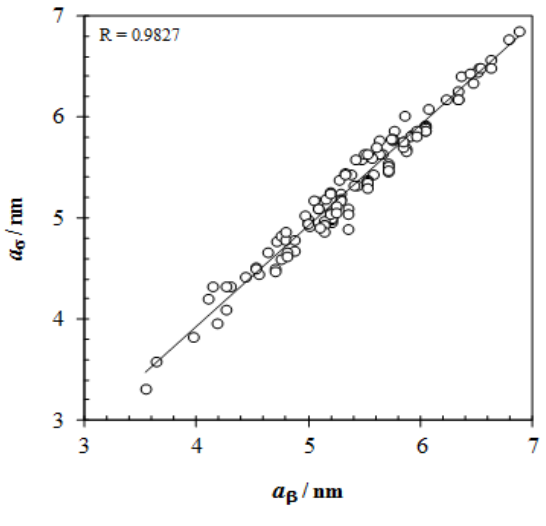

Figure 3. Relation between a_σ and a_β. Regression line: $a_\sigma = 0.9929\, a_\beta - 0.0337$.

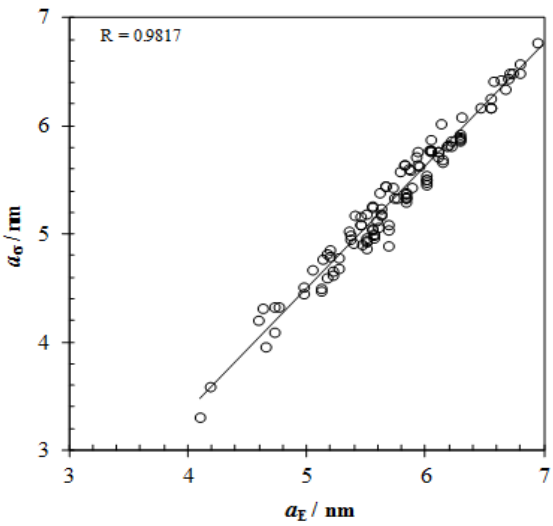

Figure 4. Relation between a_σ and a_E. Regression line: $a_\sigma = 1.1329\, a_E - 1.1670$.

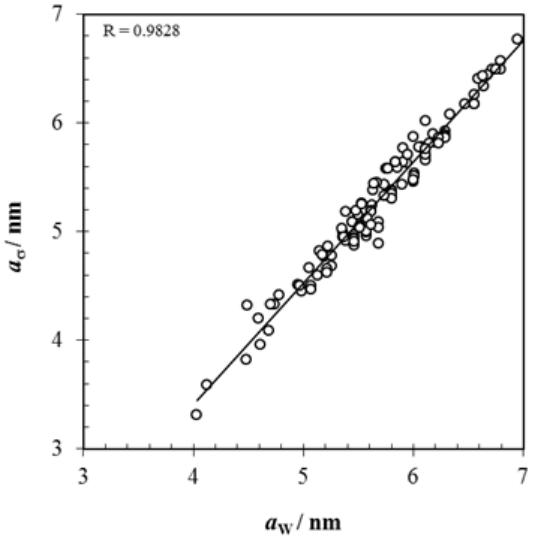

Figure 5. Relation between a_σ and a_W.
Regression line: $a_\sigma = 1.1148\, a_W - 1.0481$.

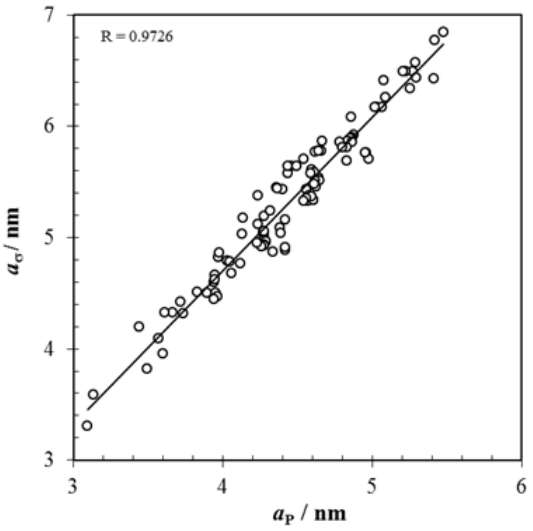

Figure 6. Relation between a_σ and a_P.
Regression line: $a_\sigma = 1.3789\, a_P - 0.8133$.

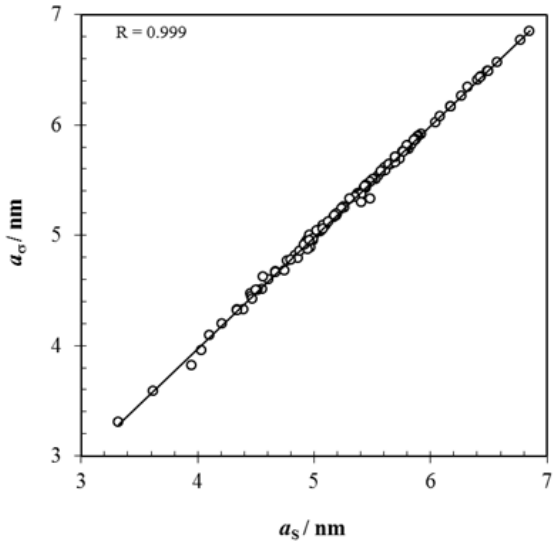

Figure 7. Relation between a_σ and a_S. Regression line: $a_\sigma = 1.0108\, a_S - 0.0709$.

The calculated diameters via Equation (1), (2), (3), (4), (5), (7), (8) and (9) was used to predict surface tension of pure substances at 25 °C. The overall absolute average deviation percent (AAD%) is demonstrated in Table 2 as AAD1%. As seen in Table 2, the difference between diameters which were calculated from all methods is not significant but the difference between overall AAD percent is very large. On the other hand, small variations in the value of the hard sphere diameter cause the most significant changes to the surface tension. The reason for this matter is that the hard sphere is raised to a 3rd power in the packing fraction. This magnifies differences very significantly. Therefore, for prediction surface tension of pure

substances accurately, it is very important to have a good approximation of hard sphere diameter. The overall AAD% from Table 2 shows that the hard sphere diameter which is calculated from Eqs. (8) and (9) can be used in Equation (1) for estimation of pure substances with good accuracy. Calculated surface tension for pure compounds compared with experimental data in Figure 8.

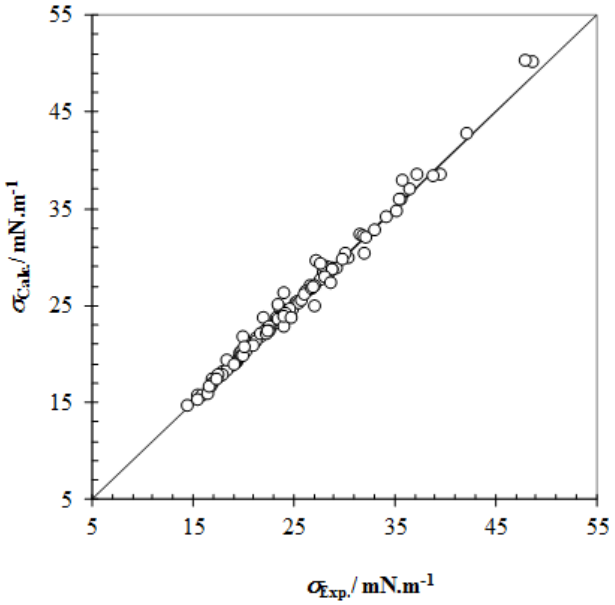

Figure 8. Calculated surface tension based on a_S versus experimental surface tension for pure compounds at 25 °C. The line corresponds to $\sigma_{Calc.} = \sigma_{Exp.}$.

Equations (11) - (16) were used to calculate the hard sphere diameter. Surface tension of pure substances was calculated with new hard sphere diameters. The overall AAD% for new case is reported in Table 2 as AAD2%. Average of AAD1% for the seven methods in Table 2 is 37.8% while average of AAD2% for the seven methods is 12.17%. This confirms that calculation of surface tension with diameters obtained from Equations (11) - (16) decreases the overall AAD%.

Conclusion

In this work, seven methods were presented for calculating the hard sphere diameter of pure substances. These models were applied for 108 pure substances and hard sphere diameter of studied substances calculated. Based on the calculated hard sphere diameters, the correlation among them reported. Surface tension of all studied pure substances was predicted with Scaled Particle Theory (SPT) by using calculated hard sphere diameters (a_W, a_β, a_E, a_V, a_P, a_S, and a_σ) and hard sphere diameters obtained from correlations (Eqs. 10-16). AAD1% shows the overall absolute average deviation percent for surface tension calculation by using calculated hard sphere diameters (a_W, a_β, a_E, a_V, a_P, a_S and a_σ) and AAD2% showed the overall average absolute deviation for surface tension calculation by using predicted hard sphere diameters (Eqs. 10-16). Overall AAD1% shows that using a_S and a_σ produce more accurate results in compare with other

methods for surface tension. For calculating a_σ, surface tension value is required therefore the hard sphere diameter which is calculated from parachors can be used in Eq. (1) for estimation of surface tension of pure substances with good accuracy. Although calculation of surface tension with hard sphere diameters estimated from correlations (obtained in this work), decreases the AAD% significantly. Average of AAD1% for the seven methods is 37.8% while average of AAD2% for the seven methods is 12.17%.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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