Extended scaled particle theory for surface tension prediction of liquid mixtures

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By extending the scaled particle theory (SPT) with six conditions adapted to Carnahan–Starling equation of state, SPT^6-CS, (D.W. Siderius, D.S. Corti. J. Chem. Phys. **127**, 144502 (2007)) a new expression for surface tension prediction of binary mixtures was obtained. The results of calculations are compared with those obtained from the SPT with three conditions, SPT^3 (J.L. Lebowitz, E. Helfland, E. Praestgaard. *J. Chem. Phys.*, **43**, 774 (1965)). The results revealed that in spite of their simplicity, the studied models are in fairly good agreement with the experimental data. In addition, the results show that the obtained expression fitted very well with surface tension experimental data of binary alkane mixtures at different temperatures.

Keywords: surface tension; scaled particle theory; mixtures

1. Introduction

Scaled particle theory (SPT) presented by Reiss, Frisch, Lebowitz (RFL) [1] was developed to predict the work of cavity formation in the hard sphere fluids. This theory makes use of exact relations for cavities with smaller scales than a hard sphere diameter, whereas it utilises an approximation for cavities larger than a hard sphere diameter. In SPT, by equating the relation obtained for the work of cavity formation with the macroscopic work, one can yield some thermodynamic properties of fluids [2]. In this regard, much work has been done to calculate different characteristics of fluids by using SPT [3–17].

As mentioned above, for cavities larger than a hard sphere diameter an approximation is used which includes an interpolation function with some coefficients. To obtain the coefficients of the applied interpolation it is necessary to use some exact condition. These conditions are based on the geometry and thermodynamics of the system. In the early versions of SPT just three exact conditions were used to obtain the interpolation function [1], but developed versions of this theory use six conditions [18–20].

Although many attempts have been made to develop this theory for the prediction of pure fluids surface tension, less work has been done on applying SPT to the mixtures [21,22]. Lebowitz *et al.* [21] developed SPT^3 (SPT with three exact conditions) to make it applicable to surface tension prediction of mixtures. After developing SPT and using more

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exact conditions to obtain interpolation function [18–20] it is necessary to extend these recent versions of theory such as, SPT[6]-CS [20] (SPT with six exact conditions adapted to Carnahan–Starling EOS) to fluid mixtures.

In this work, the SPT[6]-CS is extended to multicomponent mixtures. The obtained expression is then applied to some binary mixtures and the results are compared with experimental data along with those obtained from SPT[3].

2. Theory

In SPT it begins with considering a hard sphere system with a diameter of a, at a temperature T and a number density $\rho = N/V$, where N is the number of hard spheres and V is the volume. If a hard sphere with a diameter b is introduced to the system of a cavity, a region where no fluid molecule centre exists, will be formed with radius of r [2]:

$$r = \frac{a+b}{2}. \tag{1}$$

In this system, the reversible work for inserting or growing a cavity of radius r is given by [18]

$$W = 4\pi\rho kT \int_0^r G(r, \rho)\lambda^2 \, d\lambda, \tag{2}$$

where k is the Boltzmann constant, T is the temperature and G is known as the central function of SPT and is related to a number of hard sphere thermodynamic properties. ρG represents the local density of hard spheres at the cavity surface.

According to fluctuation theory, the probability of randomly observing a cavity of radius at least r, $P_0(r)$, can be related to the work of the cavity formation as follows [18]:

$$P_0(r) = \exp[-\beta W(r)] \tag{3}$$

where $\beta = \frac{1}{kT}$. Introducing Equation (2) into Equation (3) results in [2]:

$$G(r, \rho) = \frac{1}{4\pi\rho r^2} \frac{\partial \ln P_0(r)}{\partial r}. \tag{4}$$

According to the geometry of the system $P_0(r)$ is known only for a small range of r, so it is common that an approximation as a series in the following form can be used [18]:

$$G(\lambda, \rho) = \sum_{i=0}^{\infty} \frac{A_i}{r^i}, \tag{5}$$

where A_is are fitting coefficients and depend on the fluid density and are obtained through applying some exact condition stemming from the geometry or thermodynamic arguments. In the early works on SPT only three exact conditions were applied, so that the expression included three terms with three coefficients. Recently, some new attempts have been made to increase the number of expressions involved in G by introducing more exact conditions. These exact conditions can stem from the geometry of the hard spheres [19] or both the geometry and the thermodynamics of the hard sphere systems [18].

Siderius and Corti [20] divided the G function into two Laurent series one extends from $r = a/2$ to $a/\sqrt{3}$ and another for $r > a/\sqrt{3}$ as bellows:

$$G(r, y) = \begin{cases} \beta_0(y) + \dfrac{\beta_1(y)}{r} + \dfrac{\beta_2(y)}{r^2} + \dfrac{\beta_3(y)}{r^3} + \dfrac{\beta_4(y)}{r^4} & \dfrac{a}{2} < r \leq \dfrac{a}{\sqrt{3}} \\[3mm] \alpha_0(y) + \dfrac{\alpha_1(y)}{r} + \dfrac{\alpha_2(y)}{r^2} + \dfrac{\alpha_4(y)}{r^4} + \dfrac{\alpha_5(y)}{r^5} & r > \dfrac{a}{\sqrt{3}} \end{cases} \quad (6)$$

It should be noted that for $r > a/\sqrt{3}$ the function G includes six terms but to avoid the emergence of the non-physical logarithmic expression, which would arise from the integration of Equation (6) in Equation (2), the coefficient of r^{-3} has been set to zero ($\alpha_3 = 0$). So, to determine the coefficients of the Equation (6), 10 conditions are needed:

$$G\left(\frac{a}{2}, y\right) = \frac{1}{1-y}, \qquad \qquad \frac{\partial G}{\partial r}\Big|_{r=\frac{a}{2}} = \frac{6y}{(1-y)^2}$$

$$\frac{\partial^2 G}{\partial r^2}\Big|_{r=\frac{a^+}{2}} = \frac{24y + 48y^2}{(1-y)^3} - \frac{48y}{1-y}G(a, y), \quad G(\infty, y) = \frac{P}{\rho kT}$$

$$G(a, y) = \frac{1}{4y}\left(\frac{P}{\rho kT} - 1\right), \qquad \qquad \beta\mu^{ex} = -\ln(1-y) + 24y\int_{a/2}^{a} G(r, \rho)r^2 \quad (7)$$

$$G\left(\frac{a^-}{\sqrt{3}}, y\right) = G\left(\frac{a^+}{\sqrt{3}}, y\right), \qquad \qquad \frac{\partial G}{\partial r}\Big|_{r=\frac{a^-}{\sqrt{3}}} = \frac{\partial G}{\partial r}\Big|_{r=\frac{a^+}{\sqrt{3}}}$$

$$\frac{\partial^2 G}{\partial r^2}\Big|_{r=\frac{a^-}{\sqrt{3}}} = \frac{\partial^2 G}{\partial r^2}\Big|_{r=\frac{a^+}{\sqrt{3}}}, \qquad \qquad \frac{\partial^3 G}{\partial r^3}\Big|_{r=\frac{a^-}{\sqrt{3}}} = \frac{\partial^3 G}{\partial r^3}\Big|_{r=\frac{a^+}{\sqrt{3}}}.$$

As mentioned above SPT has the capability to calculate some thermodynamic properties, but here we focus our attention only on surface tension prediction. Through SPT framework surface tension is calculated by equating the work demanded for the formation of a cavity with the macroscopic work as follows [18]:

$$4\pi\rho kT \int_0^r G(r, \rho)\lambda^2 d\lambda = \frac{4}{3}\pi\rho r^3 + 4\pi r^2\sigma\left(1 - \frac{2\delta}{r} + \cdots\right), \quad (8)$$

where σ is the planar surface tension and δ is the Tolman length which represents a first-order correction for surface tension curvature. Inserting Equation (5) into Equation (8) gives the planar surface tension, σ [18]:

$$\sigma = \frac{kT}{\pi a^2}3y\alpha_1, \quad (9)$$

where y is packing fraction and expressed as:

$$y = \frac{\pi}{6}\rho a^3. \quad (10)$$

Siderius and Corti [20] used Carnahan–Starling (CS) EOS to express $P/\rho kT$ and $\beta\mu^{ex}$ in an analytical form, so they were able to present the coefficients of Equation (6)

analytically. The SPT[6]-CS expression for calculating surface tension was obtained as follows:

$$\sigma = \left(\frac{kTy}{\pi a^2}\right)f(y), \tag{11}$$

where, $f(y)$ is expressed as [20]:

$$f(y) = \left[\frac{\left\{\begin{array}{c} -3667.1y + 11225.2y^2 - 16300.9y^3 + 11111.1y^4 \\ -2570.7y^5 - 3667.1(1-y)^4\ln(1-y) \end{array}\right\}}{357.7y(1-y)^4}\right]. \tag{12}$$

Lebowitz *et al.* [21] extended the SPT[3] equation for pure fluid [1]:

$$\sigma = \frac{kT}{\pi a^2}\left[\frac{3y}{1-y} + \frac{1}{2}\left(\frac{3y}{1-y}\right)^2\right], \tag{13}$$

and obtained the following equation for mixtures:

$$\sigma = \left(\frac{3kT}{2\pi}\right)\left[2\left(\frac{y_1}{1-y_3}\right) + 3\left(\frac{y_2}{1-y_3}\right)^2\right], \tag{14}$$

where, $y_L = \frac{\pi}{6}\sum_{i=1}^{m}\rho_i a_i^L$. They used this equation to predict the surface tension of some binary mixtures.

The packing fraction, y, is defined as the fraction of the volume occupied by the collective volume of the spheres [23] and can be presented as:

$$y = \frac{V_{hs}\ \text{(Volume occupied by hard spheres)}}{V} = \frac{(\pi/6)Na^3}{V}. \tag{15}$$

For a mixture, the volume occupied by hard spheres is:

$$V_h = \frac{\pi}{6}\sum_{i=1}^{m}n_i a_i^3, \tag{16}$$

where n_i refers to the number of hard spheres i. Combining Equation (15) with Equation (16) leads to:

$$y_{\text{mix}} = \frac{(\pi/6)\sum_{i=1}^{m}n_i a_i^3}{V} = (\pi/6)\sum_{i=1}^{m}\rho_i a_i^3. \tag{17}$$

By inserting y_{mix} in Equations (11) and (12) one can obtain the following expression for the surface tension of mixtures:

$$\sigma = \left(\frac{kTy_1}{\pi}\right)f(y_{\text{mix}}), \tag{18}$$

where $y_1 = \pi/6\sum_{i=1}^{m}\rho_i a_i$.

Working on an SPT[3] framework by introducing mean averages of hard sphere diameters and packing fractions into Equation (13), a mixing rule can be derived as:

$$\sigma = \frac{kT}{\pi a_M^2} \left[\frac{3y_M}{1 - y_M} + \frac{1}{2} \left(\frac{3y_M}{1 - y_M} \right)^2 \right],$$ (19)

where $a_M = \sum_{i=1}^{m} x_i a_i$, $\rho_M = \sum_{i=1}^{m} x_i \rho_i$, $y_M = (\pi/6)\rho_M a_M^3$ and x is mole fraction of each component.

In the following section, the results of surface tension calculations for binary mixtures by extended SPT[6]-CS, are presented and are compared with experimental data and the surface tensions calculated by using extended SPT[3].

3. Results and discussion

For surface tension calculations Equations (14) and (18) were used respectively for extended SPT[3] and extended SPT[6]-CS. Also, the surface tensions of binary mixtures were calculated by original SPT[3], and the mixing rules, as presented by Equation (19). The results of surface tension calculations are presented as absolute average deviation percent, AAD%, in Tables 1 and 2. The absolute average deviation is defined as:

$$\text{AAD\%} = (1/N_P) \sum_{1}^{N_P} \frac{|\sigma_{\text{exp}} - \sigma_{\text{cal}}|}{\sigma_{\text{exp}}} \times 100,$$ (20)

where σ_{exp} and σ_{cal} are respectively the experimental and calculated surface tensions and N_P is the number of experimental data points. Also, Tables 1 and 2 report the hard sphere diameters a_i and a_i^* respectively, obtained from Equations (14) and (18) for pure components. The hard sphere diameters of pure components were used in surface tension calculation of binary mixtures.

The results presented in Tables 1 and 2 indicate that all three models of SPT (extended SPT[6]-CS, extended SPT[3] and original SPT[3] with mixing rules), in spite of their simple forms, have high capability in prediction of surface tensions. It can be observed in Table 1 that for hard sphere molecules (e.g. Nitrogen–Argon) there is a fairly good agreement with experimental data. However, none of the three applied models have better prediction ability for surface tension of binary mixtures of studied alkane–alcohol binary systems. That is, as Table 1 shows, for some binary mixtures extended SPT[3] has better prediction whereas in the others the application of the mixing rule has better prediction.

Also the results for benzene–carbon tetrachloride (in Table 1) indicate good agreement with experimental data for extended SPT[3] and SPT[6]-CS, but this is not the case for benzene–alkanes. This can be attributed to the fact that the intermolecular potential fields of the molecular models used in obtaining SPT's equations are spherically symmetrical; consequently, the molecules with sphere shape are expected to conform to SPT's predictions [41]. Also as expected, the results for binary mixtures containing alkanols do not have agreement with experimental data and this can be due to the polar nature of alkanols and the fact that SPT models are proposed for non-polar molecules [41].

It is interesting to note, from the reported results in Table 2, that for the binary alkanes where the molecular interactions are not significant the extended SPT[6]-CS has remarkably better conformity with experimental data. However, when the number of carbons in the alkane components is largely different and the deviation from spherically symmetrical – as

Table 1. The hand sphere diameters a and $a*$ for binary mixtures calculated by Equation (14) and (18) respectively, and AAD% of predicted surface tensions for SPT3, SPT6-CS and mixing rule models by using Equation (20).

Binary mixture	T (K)	a_1 (Å)	a_2 (Å)	a_1^* (Å)	a_2^* (Å)	SPT³	SPT⁶-CS	Mixing rule	N_P	Ref.
CO–Methane	91	3.25	3.75	3.38	3.62	5.36	6.52	3.04	11	[24]
Argon–Methane	91	3.20	3.75	3.22	3.62	2.42	3.15	10.25	11	[24]
Nitrogen–CO	84	3.26	3.41	3.36	3.44	1.35	1.42	1.27	10	[24]
Nitrogen–Ar	84	3.26	3.29	3.36	3.25	1.77	1.95	4.68	19	[24]
Ethanol–Glycole	293	3.98	4.71	4.03	4.49	7.38	8.86	5.78	8	[25]
Heptane–1-Butanol	298	5.92	4.87	5.76	4.79	3.11	3.52	3.32	12	[26]
Heptane + 1-Hexanol	298	5.92	5.73	5.76	5.52	3.22	3.05	3.53	13	[26]
Heptane + 1-Octanol	298	5.92	6.36	5.76	6.07	2.91	2.99	2.02	13	[26]
Octane–Ethanol	298	6.26	3.96	6.03	4.03	2.07	5.37	6.48	19	[27]
Octane + 1-Propanol	298	6.26	4.51	6.03	4.48	3.36	5.05	1.31	19	[27]
Octane + 1-Butanol	298	6.26	4.88	6.03	4.79	3.03	3.50	1.94	19	[27]
Octane + 1-Pentanol	298	6.26	5.38	6.03	5.21	3.12	3.44	2.99	18	[27]
Octane + 1-Hexanol	298	6.26	5.75	6.03	5.52	2.82	2.91	3.30	19	[27]
Octane + 1-Heptanol	298	6.26	6.08	6.03	5.82	2.96	3.04	3.49	19	[27]
Octane + 1-Octanol	298	6.26	6.39	6.03	6.09	2.57	2.73	2.67	19	[27]
1-Propanol-Benzyl Alcohol	298	4.51	5.60	4.48	5.32	4.21	4.37	3.76	9	[28]
Cyclohexane–Hexane	303	5.36	5.52	5.22	5.45	1.02	1.05	1.19	7	[29]
Cyclohexane–Heptane	307	5.33	5.87	5.21	5.73	2.33	2.41	2.19	11	[30]
Tetrahydrofuran–Hexane	298	4.80	5.55	4.70	5.46	5.79	5.94	7.20	14	[31]
2,2,4-Trimethylpentane–Cyclohexane	298	6.18	5.41	6.00	5.24	3.48	3.63	2.05	21	[32]
Benzene–Cyclohexane	293	5.05	5.40	4.88	5.23	2.05	2.08	2.42	9	[33]
Benzene–Hexane	293	5.05	5.60	4.88	5.48	5.22	5.31	6.67	8	[33]
Benzene–Carbon tetrachloride	298	5.03	5.18	4.88	5.02	0.16	0.17	1.93	8	[34]
Benzene–Dodecane	303	5.01	7.34	4.87	6.96	4.40	5.76	1.85	7	[35]
Benzene–Acetone	298	5.03	4.48	4.88	4.45	1.46	1.09	2.74	10	[34]
Toluene–Heptane	307	5.39	5.87	5.21	5.73	1.71	1.78	2.70	7	[36]

Table 2. The hand sphere diameters a and a^* for binary alkanes calculated by Equation (14) and (18) respectively, and AAD% of predicted surface tensions for SPT3, SPT6-CS and mixing rule models by using Equation (20).

Binary mixture	T (K)	a_1 (Å)	a_2 (Å)	a_1^* (Å)	a_2^* (Å)	SPT^3	SPT^6-CS	Mixing rule	N_p	Ref.
Hexane–Octane	303	5.49	6.23	5.43	6.02	1.78	1.51	2.50	8	[37]
Hexane–Octane	313	5.43	6.19	5.41	6.00	1.69	1.41	2.38	8	[37]
Hexane–Octane	323	5.36	6.14	5.39	5.99	1.57	1.28	2.23	8	[37]
Hexane–Octane	333	5.30	6.10	5.38	5.97	1.41	1.10	2.05	8	[37]
Hexane–Octane	343	5.24	6.04	5.36	5.96	1.02	0.78	1.59	8	[37]
Hexane–Octane	353	5.19	5.98	5.36	5.94	0.91	0.62	1.51	8	[37]
Hexane–Tetradecane	303	5.49	7.78	5.43	7.35	3.60	1.49	10.69	5	[37]
Hexane–Tetradecane	313	5.42	7.76	5.41	7.34	4.02	1.82	10.76	5	[37]
Hexane–Tetradecane	323	5.36	7.72	5.39	7.33	4.33	2.08	10.78	5	[37]
Hexane–Tetradecane	333	5.30	7.69	5.38	7.31	4.47	2.15	10.67	5	[37]
Hexane–Tetradecane	343	5.24	7.66	5.36	7.30	4.37	1.99	10.37	5	[37]
Hexane–Tetradecane	353	5.19	7.63	5.36	7.29	3.97	1.55	9.83	5	[37]
Tetradecane–Octane	303	7.78	6.24	7.35	6.02	1.16	0.28	5.17	7	[37]
Tetradecane–Octane	313	7.76	6.20	7.34	6.01	1.17	0.27	5.04	7	[37]
Tetradecane–Octane	323	7.73	6.15	7.33	5.99	1.18	0.25	4.91	7	[37]
Tetradecane–Octane	333	7.70	6.10	7.32	5.98	1.30	0.34	4.89	7	[37]
Tetradecane–Octane	343	7.66	6.05	7.30	5.96	1.53	0.53	4.96	7	[37]
Tetradecane–Octane	353	7.63	5.99	7.29	5.94	1.83	0.79	5.11	7	[37]
Dodecane–Hexane	298	7.35	5.55	6.97	5.46	2.67	1.28	7.85	5	[38]
Dodecane–Hexane	303	7.34	5.52	6.96	5.45	3.16	1.51	8.95	6	[38]
Dodecane–Hexane	308	7.32	5.49	6.96	5.44	2.56	1.24	7.14	5	[38]
Dodecane–Hexane	313	7.31	5.46	6.95	5.43	2.79	1.36	7.48	5	[38]
Decane–Heptane	293	6.88	5.96	6.55	5.77	0.79	0.41	2.33	5	[39]
Decane–Heptane	303	6.84	5.91	6.53	5.76	0.93	0.53	2.41	5	[39]
Decane–Heptane	313	6.81	5.87	6.52	5.74	1.00	0.58	2.42	5	[39]
Decane–Heptane	323	6.78	5.81	6.50	5.72	1.41	0.96	2.75	5	[39]
Decane–Heptane	333	6.74	5.76	6.49	5.70	1.71	1.25	2.99	5	[39]
Hexadecane + Heptane	293	8.23	5.96	7.74	5.77	2.38	0.69	9.91	5	[39]
Hexadecane + Heptane	303	8.21	5.91	7.73	5.76	2.74	1.02	9.96	5	[39]
Hexadecane + Heptane	313	8.18	5.87	7.72	5.74	3.30	1.53	10.20	5	[39]
Hexadecane + Heptane	323	8.15	5.87	7.70	5.72	4.02	2.20	10.57	5	[39]

(*Continued*)

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Table 2. Continued.

| Binary mixture	T (K)	a_1 (Å)	a_2 (Å)	a_1^* (Å)	a_2^* (Å)	SPT^3	SPT^6-CS	Mixing rule	N_p	Ref.
Hexadecane + Heptane	333	8.13	5.76	7.69	5.70	4.70	2.85	10.94	5	[39]
Hexadecane + Decane	293	8.23	6.88	7.74	6.55	0.47	0.33	3.81	5	[39]
Hexadecane + Decane	303	8.21	6.84	7.73	6.53	0.77	0.22	3.96	5	[39]
Hexadecane + Decane	313	8.18	6.81	7.72	6.52	1.04	0.45	4.11	5	[39]
Hexadecane + Decane	323	8.15	6.78	7.70	6.50	1.06	0.46	4.04	5	[39]
Hexadecane + Decane	333	8.13	6.74	7.69	6.49	1.19	0.57	4.06	5	[39]
Eicosane + Hexadecane	313	8.91	8.18	8.36	7.72	0.20	0.13	1.15	7	[39]
Eicosane + Hexadecane	323	8.89	8.15	8.36	7.70	0.40	0.28	1.37	7	[39]
Eicosane + Hexadecane	333	8.87	8.13	8.35	7.69	0.32	0.19	1.26	7	[39]
Eicosane + Hexadecane	343	8.85	8.10	8.34	7.67	0.57	0.41	1.47	7	[39]
Eicosane–Decane	313	8.90	6.81	8.36	6.51	2.51	1.04	10.32	7	[38]
Eicosane–Decane	323	8.88	6.77	8.35	6.50	2.65	1.15	10.19	7	[38]
Eicosane–Decane	333	8.87	6.74	8.35	6.49	2.61	1.06	9.92	7	[38]
Eicosane–Decane	343	8.85	6.70	8.34	6.47	2.79	1.21	9.85	7	[38]
Docosane–Decane	323	9.22	6.77	8.66	6.50	2.66	0.77	12.36	7	[38]
Docosane–Decane	333	9.22	6.74	8.66	6.49	3.20	1.20	12.52	7	[38]
Docosane–Decane	343	9.20	6.70	8.65	6.47	3.69	1.65	12.66	7	[38]
Tetracosane–Decane	333	9.51	6.74	8.66	6.49	3.54	1.13	14.88	7	[38]
Tetracosane–Decane	343	9.51	6.70	8.94	6.47	3.50	1.00	14.48	7	[38]
Eicosane–Heptane	313	8.9	5.86	8.36	5.74	4.39	1.40	15.90	5	[40]
Eicosane–Heptane	323	8.88	5.81	8.35	5.72	5.06	2.00	16.04	5	[40]
Eicosane–Heptane	333	8.87	5.75	8.34	5.70	5.75	2.60	16.21	5	[40]
Eicosane–Heptane	343	8.85	5.72	8.34	5.70	5.38	2.24	15.68	5	[40]
Docosane–Heptane	323	9.22	5.81	8.66	5.72	5.67	2.09	18.41	5	[40]
Docosane–Heptane	333	9.22	5.75	8.66	5.70	6.50	2.82	18.61	5	[40]
Docosane–Heptane	343	9.20	5.72	8.65	5.70	6.30	2.61	18.20	5	[40]
Tetracosane–Heptane	333	9.51	5.75	8.93	5.70	7.18	3.06	20.80	5	[40]
Tetracosane–Heptane	343	9.51	5.72	8.94	5.70	7.44	3.32	20.69	5	[40]
Total average						2.84	1.93	6.88		
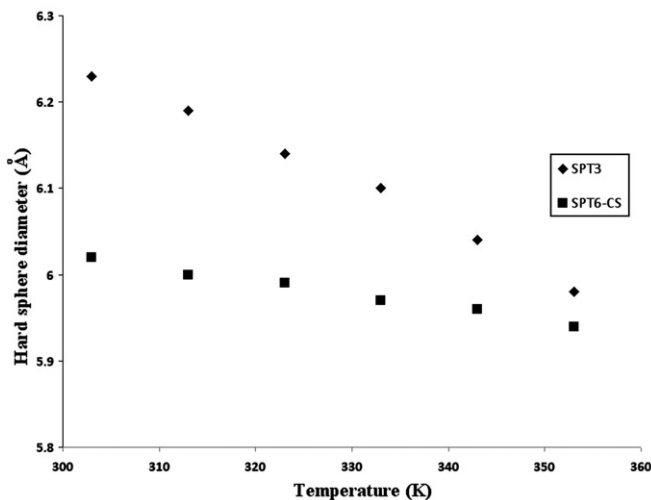
Figure1. Variation of hard sphere diameter of normal octane by changing temperature.

the basic assumption in SPT models – becomes more significant, the disagreement between calculated and experimental results becomes more profound.

It is also observed from Tables 1 and 2 that by increasing temperature the hard sphere diameter of components in the mixtures decreases. This can be explained by the fact that at higher temperatures particles can penetrate to a smaller distance of separation [42]. The temperature dependency of hard sphere diameter, *a*, is expressed by the following equation [43]:

$$a = \int_0^{\sigma_s} (1 - \exp(-u(z)/kT))\mathrm{d}z, \tag{21}$$

where $u(z)$ is the interaction potential and σ_s is the distance where $u(\sigma_s)$ becomes zero. Equation (21) clearly indicates the decreasing trend of hard sphere with increasing temperature.

Figure 1 illustrates the variation of hard sphere diameters *versus* temperature for normal octane calculated by SPT[3] and SPT[6]-CS models.

4. Conclusion

An expression for surface tension prediction of binary mixtures was obtained by extending SPT[6]-CS model for mixtures. Applying the obtained expression for a SPT[6]-CS model along with the extended SPT[3] model and a mixing rule model to 87 binary mixtures revealed that the results obtained for surface tension of binary mixtures by the three models, considering their simplicity, are in fairly good agreement with experimental data. Despite the chain form of alkane molecules which have deviation from hard sphere assumption in SPT, the obtained results calculated from the derived expression for SPT[6]-CS show acceptable capability in the surface tension prediction of alkane binary mixtures in different temperatures, and this can be justified by weak interaction between alkane molecules.

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