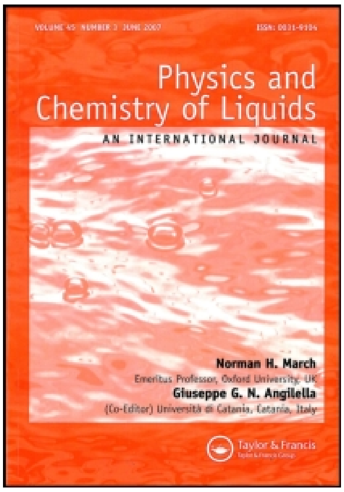

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Estimation of the surface tension of liquid carbon dioxide

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The surface tension of liquid carbon dioxide has practical significance in material science, environmental science and chemical engineering separation processes as well as in the secondary or tertiary recovery of petroleum. The surface tension of liquid carbon dioxide is estimated by semi-empirical and statistical formulae and the results are compared and analysed with experimental data. It is shown that the methods proposed by Brock, Hakim, Miqueua and Zuo are better methods for estimating the surface tension of liquid carbon dioxide and have relatively less percentage deviation from experimental data.

Keywords: carbon dioxide; surface tension; statistical theory; corresponding-states method; ultrasound velocity

1. Introduction

The surface tension of pure fluids which reveals some characteristics of a molecules' structure and state, furnishes a fascinating subject for study [1] and has practical significance for material science, environmental science and chemical engineering separation processes as well as in the secondary or tertiary recovery of petroleum. Several theories and methods, such as the parachor-dependent Macleod–Sugden method [2], density gradient theory [3] and corresponding-states method [4], have been proposed for calculation of surface tension of pure fluid and their mixtures. The parachor-dependent Macleod–Sugden method is an empirical model which has been widely used for predicting the surface tension in vapour–liquid equilibrium. The density gradient theory has been successfully used for calculating the interfacial tension of pure fluids and their mixtures [5]. However, calculations using density gradient theory are complex requiring the solution of differential equations. Therefore, simple, accurate and reliable models for calculating surface tension are an engineering requirement.

One such method is based on the statistical thermodynamic theory of heterogeneous fluids. For example, based on Kirkwood–Buff theory, Li Zhi-Bao *et al.* [5] developed formulae for calculation of the surface tension of pure liquids and their mixtures, using the reduced density of vapour and liquid, together with Lennard–Jones fluid parameters (energy parameter and size parameter). Another approach proposed by many investigators to evaluate surface tension uses semi-empirical formulae and statistical theory based on the corresponding-states method [4,6,7], such as the method developed by Brock and Bird [4],

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which uses the critical temperature, pressure and volume to estimate a pure liquid's surface tension. On the other hand, an empirical relationship between surface tension and velocity of ultrasound u in a liquid was discovered by Altenburg and Auerbach, respectively, through an analysis of experimental data [8,9]. Liquid and supercritical carbon dioxide are widely used in chemical engineering, pharmaceutical, environmental, food and energy industries when the uses are closely related to the surface tension of liquid carbon dioxide. For example, the enhanced 'flooding' technique has proven to be effective in increasing petroleum recoveries. The surface tension of liquid carbon dioxide plays a key role in such high recoveries [5]. Carbon dioxide appears to be an almost ideal solvent having the lowest surface tension of any solvent. Numerous separation and cleaning applications take advantage of the CO_2 solubility and/or low surface tension properties. Our investigation calculates the surface tension of liquid carbon dioxide by semi-empirical and statistical formulae, and the results are compared and analysed with experimental data.

2. Theory

Brock and Bird [4] have proposed a relationship between critical constants and surface tension σ:

$$\sigma = (-0.951 + 0.432/Z_c)(1 - T_r)^{11/9}\left(P_c^2 T_c\right)^{1/3}. \tag{1}$$

In Equation (1), Z_c and T_r are the critical compressibility factor and reduced temperature, respectively. These are expressed as

$$Z_c = \frac{1}{R}\left(\frac{P_c V_c}{T_c}\right), \tag{2}$$

$$T_r = \frac{T}{T_c}, \tag{3}$$

where T and R are the absolute temperature and gas constant, respectively, and P_c, T_c and V_c are the critical constants of the liquid.

Another relationship between surface tension and critical parameters was developed by Pitzer [7]. The resulting corresponding-states relation for σ is expressed in term of P_c, T_c, T_r and the acentric factor ω.

$$\sigma = \left(\frac{1.86 + 1.18\omega}{19.05}\right)\left(\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega}\right)^{2/3}(1 - T_r)^{11/9}\left(P_c^2 T_c\right)^{1/3}. \tag{4}$$

A similar correlation was proposed by Riedel [10], who extended the approach to include polar liquids, Hakim *et al.* [11] introduced the Stiel polar factor, x, and proposed the following equations:

$$\sigma = \left(P_c^2 T_c\right)^{1/3} Q_p \left(\frac{1 - T_r}{0.4}\right)^m, \tag{5}$$

$$Q_p = 0.1574 + 0.359\omega - 1.769x - 13.69x^2 - 0.510\omega^2 + 1.298\omega x, \tag{6}$$

$$m = 1.210 + 0.5385\omega - 14.61x - 32.07x^2 - 1.656\omega^2 + 22.03\omega x. \tag{7}$$

From a critical analysis of available experimental surface tension data, Miqueua *et al.* [12]. proposed an extended scaled equation to represent the surface tension:

$$\sigma = kT_c\left(\frac{N_A}{V_c}\right)^{2/3}(4.35+4.14\omega)t^{1.26}\left(1+0.19t^{0.5}-0.25t\right), \tag{8}$$

$$t = 1-\frac{T}{T_c}, \tag{9}$$

where N_A is the Avogadro number.

Zuo and Stenby [13] have used a two-reference fluid corresponding-states approach to estimate surface tensions.

$$\sigma = (e^{\sigma_r}-1)\left(P_c^2T_c\right)^{1/3}. \tag{10}$$

To use this method, σ for the fluid of interest is related to σ_r for two reference fluids, methane and *n*-octane by

$$\sigma_r = \sigma_r^{(1)} + \left(\frac{\omega-\omega^{(1)}}{\omega^{(2)}-\omega^{(1)}}\right)\left(\sigma_r^{(2)}-\sigma_r^{(1)}\right). \tag{11}$$

For methane,

$$\sigma_r^{(1)} = 40.520(1-T_r)^{1.287}, \tag{12}$$

and for *n*-octane,

$$\sigma_r^{(2)} = 52.095(1-T_r)^{1.21548}. \tag{13}$$

A close connection between Flory theory and the corresponding-states theory of Prigogine *et al.* [14], employing a simple cell model of the liquid state, was shown by Patterson *et al.* [6]. Based on Flory statistical theory, they obtained the following equation for the characteristic surface tension σ^*:

$$\sigma^* = k^{1/3}P^{*2/3}T^{*1/3}, \tag{14}$$

where k denotes the Boltzmann constant, and P^* and T^* are the characteristic pressure and temperature, respectively. Here,

$$P^* = \gamma T\tilde{V}^2, \tag{15}$$

where $\gamma = (\partial P/\partial T)_V = \alpha/\beta_T$ is the thermal pressure coefficient at $P=0$, α is the thermal expansion coefficient and β_T the isothermal compressibility.

The reduced volume $\tilde{V}$ for a pure substance in terms of the thermal expansion coefficient is given as,

$$\tilde{V} = \left(\frac{1+(4/3)\alpha T}{1+\alpha T}\right)^3. \tag{16}$$

The characteristic temperature T^* is given as,

$$T^* = T\left(\frac{\tilde{V}^{4/3}}{\tilde{V}^{1/3}-1}\right). \tag{17}$$

Starting from the work of Prigogine and Saraga [15], the equation for reduced surface tension is,

$$\tilde{\sigma}(\tilde{V}) = M\tilde{V}^{-5/3} - \left(\frac{\tilde{V}^{1/3}-1}{\tilde{V}^2}\ln\frac{\tilde{V}^{1/3}-0.5}{\tilde{V}^{1/3}-1}\right), \tag{18}$$

where M is the fractional decrease in the nearest neighbours of a cell due to migration from bulk phases to the surface phases, whose value varies from 0.26–0.31 for a closely packed lattice. In the present calculations, we have used $M = 0.29$. α, β_T are obtained from the equation of state. Thus, on the basis of the corresponding-states principle, the surface tension of a liquid is given by the relation,

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{V}). \tag{19}$$

On the other hand, to estimate surface tension, Hugill and van Welsenes [16] employed a corresponding-states type expression for the parachor Pa.

$$Pa = 40.1684(0.151 - 0.0464\omega)T_c^{13/12}/P_c^{5/6}. \tag{20}$$

Thus, the surface tension can be expressed as in the following using Pa

$$\sigma = [(Pa)(\rho_l - \rho_v)]^4. \tag{21}$$

In Equation (21) ρ_l and ρ_v are the molar densities of liquid and vapour, respectively.

We also attempted to estimate the surface tension of liquid carbon dioxide using experimental ultrasonic velocities and thus check the validity of empirical relations between ultrasonic velocity and surface tension. Auerbach [8] has proposed a relationship between the ultrasonic velocity u in the liquid and the surface tension:

$$\sigma = 6.3 \times 10^{-4} \rho u^{3/2}, \tag{22}$$

where ρ is the density of the medium, u is its ultrasonic velocity.

Altenburg [9] has also proposed an alternative relationship between ultrasonic velocity and surface tension and molecular weight Mw of carbon dioxide

$$\sigma = 3.69 \times 10^{-10} \rho^{2/3} (Mw)^{1/3} u^2. \tag{23}$$

3. Results and discussion

Table 1 presents a comparison of results for the surface tension of liquid carbon dioxide at different temperatures calculated by the methods outlined in Section 2 with experimental surface tension values from the results of Quinn [17] and Jasper [18]. Table 2 gives the absolute percentage deviations between surface tensions estimated by these methods at different temperatures and experimental data. The average absolute percentage deviation (AAPD) is also given. For the Auerbach and Altenburg methods, the density and ultrasound velocity of carbon dioxide under different temperatures come from the National Institute of Standards and Technology [19].

Tables 1 and 2 show that there are differences between the surface tension of carbon dioxide estimated by various methods and experimental results obtained at

Table 1. Surface tension of liquid carbon dioxide at different temperatures.

	Surface tension ($mN\,m^{-1}$)									
T (°C)	Exp.	Hugill	Brock	Pitzer	Halkim	Miqueua	Zuo	Patterson	Auerbach	Altenburg
−52.2	16.54*	15.94	15.08	16.12	15.66	15.42	15.45	15.83	21.25	12.84
−42.7	13.88*	13.68	13	13.9	13.47	13.26	13.29	13.94	18.4	10.82
−32.3	11.25*	11.27	10.79	11.54	11.14	10.96	11.01	12.11	15.47	8.81
−30	10.08	10.74	10.32	11.03	10.64	10.47	10.52	11.74	14.85	8.39
−20	8.06	8.51	8.29	8.86	8.51	8.36	8.42	10.23	12.23	6.66
−10	6.14	6.38	6.35	6.79	6.48	6.35	6.43	8.88	9.7	5.05
0	4.34	4.38	4.51	4.82	4.57	4.46	4.54	7.66	7.26	3.56
10	2.67	2.56	2.8	2.99	2.81	2.72	2.8	6.64	5.02	2.29
15	1.90	1.76	2.01	2.15	2	1.93	2	6.23	4	1.75
20	1.19	1.04	1.27	1.36	1.25	1.2	1.26	5.94	3.02	1.25
25	0.57	0.44	0.6	0.64	0.59	0.55	0.59	5.95	2.03	0.78
30	0.07	0.035	0.065	0.07	0.061	0.055	0.062	9.21	0.879	0.288

Note: *Data from [17], and other data from [18].

Table 2. The absolute percentage deviation between the surface tension of liquid carbon dioxide estimated by different methods and experimental data.

	Absolute percentage deviation (%)								
T (°C)	Hugill	Brock	Pitzer	Halkim	Miqueua	Zuo	Patterson	Auerbach	Altenburg
−52.2	3.63	8.83	2.54	5.32	6.77	6.59	4.3	28.5	22.37
−42.7	1.44	6.34	0.14	2.95	4.47	4.25	0.4	32.6	22.05
−32.3	0.18	4.09	2.58	0.98	2.58	2.13	7.6	37.5	21.69
−30	6.55	2.38	9.42	5.56	3.87	4.37	16.5	47.3	16.77
−20	5.58	2.85	9.93	5.58	3.72	4.47	26.9	51.7	17.37
−10	3.91	3.42	10.59	5.54	3.42	4.72	44.6	58.0	17.75
0	0.92	3.92	11.06	5.30	2.76	4.61	76.5	67.3	17.97
10	4.12	4.87	11.99	5.24	1.87	4.87	148.7	88.0	14.23
15	7.37	5.79	13.16	5.26	1.58	5.26	227.9	110.5	7.89
20	12.61	6.72	14.29	5.04	0.84	5.88	399.2	153.8	5.04
25	22.81	5.26	12.28	3.51	3.51	3.51	943.9	256.1	36.84
30	50.00	7.14	0	12.86	21.43	11.43	13057.1	1155.7	311.43
AAPD	9.93	5.13	8.16	5.26	4.74	5.17	1246.14	173.92	42.62
AAPD*	6.28	4.95	8.91	4.57	3.22	4.61	172.41	84.67	18.18

Note: *Not including surface tension at 30°C.

different temperatures. Calculated values based on corresponding-states methods excluding the Patterson method, predict surface tensions to within 10%. Excluding the experimental result near the critical temperature, (30°C), prediction of the surface tension by the Brock, Halkim, Miqueua and Zuo approaches is within 5%. These methods can be very useful when they are used to estimate the surface tension of carbon dioxide. This is to be expected since these results are based on experimental data and critical constants. The lowest average absolute percentage deviation is obtained when the method proposed by Miqueua *et al*. is used. However, a larger difference between the surface tension estimated by Miqueua *et al.* method and experimental data is found when the temperature is near the critical temperature. The results from these corresponding-states methods are nearly identical. Their disadvantage lies in the fact that the influence of pressure on surface tension is not considered. Of the predictive methods, the Brock method is the only one that does not give large percentage deviations for all temperatures.

For the Patterson method based on the Flory statistical theory, the percentage deviations are smaller when the temperature is below −30°C. Estimated percentage deviations increase for temperatures between −30°C and critical point, and it reaches a value of 13057% when the temperature is 30°C. The deviation results from the drawback of Flory statistical theory [20]. Flory theory is strictly applicable to spherical molecules and ignores the effect of molecular shape, where larger percentage deviations are expected for carbon dioxide. Since M in Equation (18) is the fractional decrease in the number of neighbours of a cell in the surface phases compared to the bulk phase, the value of M should vary with temperature and pressure [20]. Patterson and Rastogi [6] have suggested a range of values M from 0.26 to 0.31. Further calculations show that the percentage deviation can be improved by adopting different M value at different temperatures.

When the estimation of surface tension is based on the Auerbach and Altenburg methods using the density and ultrasound velocity of carbon dioxide, they combine the effect of temperatures and pressures on surface tension. There are substantial differences between surface tension estimated by the Auerbach and Altenburg methods and experimental data, especially when the temperature is near the critical point. Surface tensions estimated by the Auerbach method are larger than experimental data and gives unacceptable results for all temperatures. The difference between the measured surface tension values and values estimated by the Altenburg method, initially decrease, and then increase as temperature increases. Surface tensions estimated by the Altenburg method are acceptable only when temperature range is between 15 to 20°C. Estimation of the surface tension of liquid carbon dioxide based on Auerbach and Altenburg methods is generally unacceptable.

4. Conclusion

The surface tension of saturated liquid carbon dioxide is estimated using existing semi-empirical and statistical theory based on the corresponding-states method, and the estimated results are compared and analysed with experimental data. It shows that the methods proposed by Brock, Hakim, Miqueua and Zuo are better methods for estimating the surface tension of carbon dioxide. These methods have relatively less percentage deviations from experimental values, while percentage deviations from the Patterson, Auerbach and Altenbug methods are larger. Adjusting the value of M in the Patterson method can decrease the difference between the estimated and measured value of surface tension of carbon dioxide.

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