

Surface Tension Of: Propyl Acetate; Butyl Acetate; 1,2,4-Trimethylbenzene; 1,3,5-Trimethylbenzene and Their Mixtures, Using Corresponding States Correlation

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Abstract: Reduced coordinates, σ^* and T^* , are proposed for the calculation and prediction the surface tension of propyl acetate, butyl acetate, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and their mixtures. σ^* is the reduced surface tension and T^* is the reduced temperature, according to the phenomenological scaling and considering the law of corresponding states correlation, these reduced coordinates result in a single curve for the surface tension as a function of temperature. In the correlation, melting temperature, T_m , is applied as the corresponding temperature for these compounds and their mixtures. The relationship between σ^* and T^* has a linear form and is expressed by: $\sigma^* = a + bT^*$, where a and b are temperature-independent constants. With this relationship the predicted values of surface tension of these compounds and their mixtures are in good agreement with experimental ones. %AAD, percent average absolute deviation, for these four pure compounds is less than 0.71% and for their mixtures is 0.60%.

Key words: Corresponding states correlation, Surface tension, Reduced surface tension, Reduced temperature

INTRODUCTION

Thermophysical properties and phase equilibrium behavior of pure compounds and mixtures are important for the design, operation optimization of various industrial equipments and processes and also for the development and testing of models and theories. Surface tension is one of the most significant thermophysical properties, which touches upon many problems in industries. For instance, it is important for most separation processes involving mass transfer operations like extraction, distillation, absorption and adsorption and for the coating and adhesives industries such as paints, detergents and agrochemicals. The petroleum industry requires the surface tension data. In extraction processes, oil flows through capillary channels and this flow is dominated mainly by surface tension effects. Surface tension is a temperature-dependent quantity, characteristic of the liquid. The surface tension of a liquid can be considered as a direct measure of the intermolecular forces acting at the surface. As the temperature is raised smoothly, the surface tension of a liquid that is in equilibrium with its own vapor decreases smoothly and in a nearly linear fashion and finally at the critical temperature, the surface

tension becomes zero. Corresponding states correlation for prediction of surface tension has been widely applied up to date. Some scientists have tried to develop experimental methods of measuring this thermophysical property. Brooks and Mills measured the surface tension of melts by levitated drop method [1], Lin and Duan measured the surface tension of HFC-143a and HFC-227ea and the binary mixture of these two refrigerants using the differential capillary rise method [2], for some asymmetric systems, Queimada *et al.*, measured the surface tension using the Wilhelmy plate method and also made a corresponding state model of surface tension [3], Yang *et al.*, measured the surface tension of trimethylbenzene, propyl acetate, butyl acetate and their mixtures by the pendant drop method [4], automatic measurement of surface tension from noisy images using a component labeling method was done by Zuo *et al.* [5], Alakoç *et al.*, applied an oscillating capillary jet method to measure surface tension of aqueous nonionic surfactant solutions [6], Bechtel *et al.* developed a novel technique which deduced the surface tension in air of a fluid as a function of surface age [7]. On the other hand; some investigators have interested in developing theoretical models to predict this phenomenological behavior, for

instance, Brock and Bird used correlation method for pure substances [8], also Lielmezs and Herrick proposed a new correlation method for pure substances [9]; Li *et al.* estimated the surface tension by a corresponding states group contribution method [10], Sheikh and Boushehri applied corresponding states correlation for the surface tension of some melts [11], Romero-Martinez *et al.* developed a new method to predict surface tension for isomers of pure hydrocarbons [12], Queimada *et al.*, used the corresponding states theory to predict the surface tension of pure heavy n-alkanes [13], Miqueu *et al.* applied the gradient theory of fluid interfaces to compute the surface tension of binary and ternary mixtures [14]. In recent years, many attempts have been made to connect the interfacial free energy changes to the related bulk physical properties in order to permit the determination of surface tension as a function of temperature. Surface tension reflects changes at the surface caused by different concentrations of solute.

Finding a relationship between the surface tension of an organic compound, (propyl acetate, butyl acetate, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) and also its mixture and any of its other properties, which allowed predicting the surface tension, was investigated in this work. Propyl acetate, butyl acetate, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene, have many applications in researches and industries, for instant, 1,2,4-trimethylbenzene is used as a sterilizing agent and in the manufacture of dyes, perfumes and resins. Because the boiling temperatures of most of compounds have been reliably determined than the critical temperatures, the main aim of this work was to introduce a beneficial and simple correlation between the surface tension at different temperatures and the boiling point of an organic compound or its mixture. Therefore, σ^* and T^* , the reduced surface tension and reduced temperature respectively, are used to predict the surface tension of these compounds and also their mixtures.

Correlation with Selected Physical Properties:

The normal boiling point is a known constant which characterizes the vaporization process and the different intermolecular forces of various compounds such as organic compounds and also their mixtures. Surface tension can be correlated with the normal boiling point, T_b , meaningfully. Melting temperature, T_m , is chosen as a corresponding temperature for different substances.

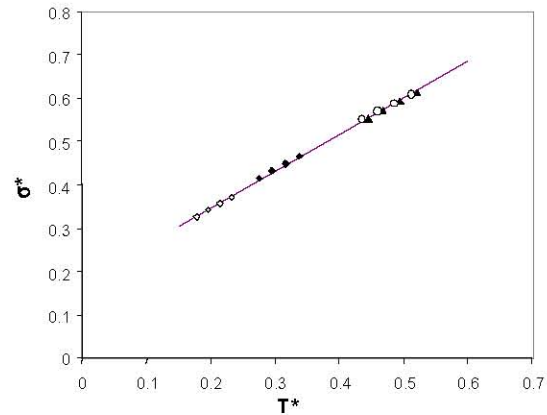


Fig. 1: Correlation results of the reduced surface tension, σ^* , versus the reduced temperature, T^* , for: \diamond , propyl acetate; \blacklozenge , butyl acetate; \blacktriangle , 1,2,4-trimethylbenzene; \circ , 1,3,5-trimethylbenzene. The solid line represents the best linear fit

Therefore the phenomenological reduced coordinates which have star superscripts, are expressed as:

$$T^* = \frac{(T_b/T) - 1}{(T_b/T_m) - 1} \tag{1}$$

and

$$\sigma^* = \frac{\sigma/T}{\sigma_m/T_m} \tag{2}$$

Where T is absolute temperature (K), σ and σ_m are the surface tension at temperatures T and the melting point respectively and σ^* introduces the attractive potential energy. The experimental data on surface tension were taken from work by Yang *et al.* [4] to make the correlation for these organic compounds. Figure 1 illustrates the correlation that was obtained.

For binary mixtures the reduced coordinates are Eqs. [1] and [2], but σ_m , T_b and T_m in them are:

$$\sigma_m = x(1)\sigma_{m1} + x(2)\sigma_{m2} \tag{3}$$

$$T_b = x(1)T_{b1} + x(2)T_{b2} \tag{4}$$

$$T_m = x(1)T_{m1} + x(2)T_{m2} \tag{5}$$

$x(2)=1-x(1)$, $x(i)$ is mole fraction of compound i and σ_{mi} is surface tension at the melting point of compounds i ; T_{bi} and T_{mi} are the boiling temperature and the melting temperature of compounds i respectively.

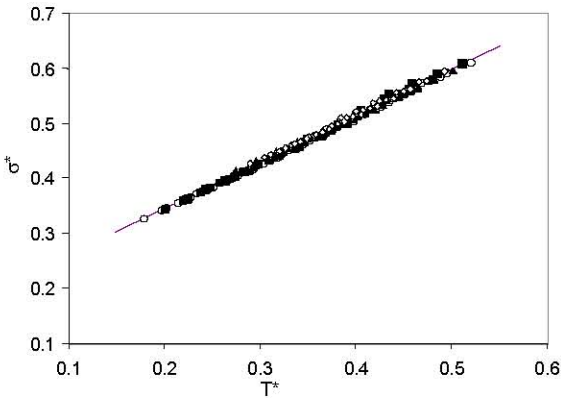


Fig. 2: Correlation results of the reduced surface tension, σ^* , versus the reduced temperature, T^* , for: \circ , (propyl acetate+1,2,4-trimethyl benzene); \blacksquare , (propyl acetate +1,3,5-trimethylbenzene); \blacktriangle (butyl acetate+1,2,4-trimethylbenzene); \diamond (butyl acetate +1,3,5-trimethylbenzene). The best linear fit is shown by the solid line

For making the correlation for the binary mixtures, the experimental data also were taken from Yang *et al.*, work [4]. Figure 2 illustrates the correlation for binary mixtures with different mole fractions.

RESULTS AND DISCUSSION

Figure 1, illustrates the correlation of these coordinates (σ^* and T^*). The solid line is the linear fit to the experimental data which was obtained by linear regression as:

$$\sigma^* = 0.8468T^* + 0.1785, \quad [6]$$

with the linear correlation coefficient of 0.9992. The percentage deviations were calculated for these organic compounds (propyl acetate, butyl acetate, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) and the results are given in Table 1.

Table 1: The calculated surface tension, σ_{cal} , at different temperatures for pure organic compounds calculated with Eq. [6]. σ_{exp} , are the experimental values

Compound	T(K)	σ_{cal} (mN/m)		Deviation (%)
		Eq. [6]	σ_{exp} (mN/m)	
Propyl acetat	298.15	24.17	23.99	0.75
	303.15	23.54	23.36	0.77
	308.15	22.90	22.73	0.75
	313.15	22.27	22.10	0.77
Butyl acetate	298.15	24.83	24.89	-0.24
	303.15	24.23	24.35	-0.49
	308.15	23.63	23.82	-0.80
	313.15	23.03	23.28	-1.07
1,2,4-Trimethylbenzene	298.15	29.47	29.17	1.03
	303.15	28.88	28.67	0.73
	308.15	28.30	28.17	0.46
	313.15	27.72	27.67	0.18
1,3,5-Trimethylbenzene	298.15	28.14	28.09	0.18
	303.15	27.56	27.67	-0.40
	308.15	26.99	27.24	-0.92
	313.15	26.41	26.82	-1.53

Table 2: The calculated surface tension, σ_{cal} (mN/m), at different temperatures for organic mixtures calculated with Eq. [7]. σ_{exp} (mN/m) are the experimental values. $x(i)$ is mole fraction and $x(2)=1-x(1)$. Dev is deviation

$x(1)$	σ_{cal}	σ_{exp}	Dev(%)	$x(1)$	σ_{cal}	σ_{exp}	Dev(%)
Eq. [7]				Eq. [7]			
$\{x(1)CH_3COOCH_2CH_2CH_3(1) + x(2)1,2,4-C_6H_3(CH_3)_3(2)\}$							
T=298.15 K				T=303.15 K			
0	29.31	29.17	0.48	0	28.72	28.67	0.17
0.1002	28.82	28.61	0.73	0.0982	28.23	28.09	0.50
0.2008	28.31	28.06	0.89	0.1994	27.72	27.53	0.69
0.3020	27.79	27.51	1.02	0.3006	27.19	26.96	0.85
0.4003	27.27	26.97	1.11	0.3996	26.67	26.40	1.02

Table 2: Continued

0.4993	26.74	26.44	1.13	0.5030	26.11	25.86	0.97
0.6006	26.19	25.93	1.00	0.6003	25.57	25.34	0.91
0.7006	25.64	25.44	0.79	0.6979	25.03	24.83	0.81
0.7991	25.08	24.96	0.48	0.7993	24.45	24.34	0.45
0.8991	24.51	24.48	0.12	0.8992	23.88	23.86	0.08
1	23.93	23.99	-0.25	1	23.29	23.36	-0.30
T=308.15 K				T=313.15 K			
0	28.14	28.17	-0.11	0	27.55	27.67	-0.43
0.0986	27.64	27.57	0.25	0.1005	27.03	27.05	-0.07
0.1998	27.17	26.99	0.67	0.2001	26.51	26.46	0.19
0.3028	26.57	26.41	0.61	0.2999	25.98	25.86	0.46
0.4004	26.05	25.83	0.85	0.4001	25.44	25.26	0.71
0.5036	25.49	25.27	0.87	0.4998	24.89	24.69	0.81
0.6003	24.95	24.74	0.85	0.6001	24.33	24.15	0.75
0.6977	24.40	24.22	0.74	0.7002	23.76	23.61	0.64
0.8000	23.81	23.72	0.38	0.7998	23.18	23.10	0.35
0.9005	23.23	23.23	0	0.9002	22.59	22.61	-0.09
1	22.65	22.73	-0.35	1	22.00	22.10	-0.45
$\{x(1)CH_3COOCH_2CH_2CH_3(1) + x(2)1,3,5-C_6H_3(CH_3)_3(2)\}$							
T=298.15 K				T=303.15 K			
0	27.99	28.09	-0.36	0	27.41	27.67	-0.94
0.0996	27.63	27.63	0	0.1000	27.04	27.18	-0.52
0.2006	27.26	27.16	0.37	0.2012	26.66	26.69	-0.11
0.3006	26.88	26.70	0.67	0.2995	26.28	26.20	0.31
0.4003	26.49	26.27	0.84	0.3998	25.89	25.74	0.58
0.4985	26.09	25.85	0.93	0.4996	25.48	25.30	0.71
0.6001	25.67	25.46	0.82	0.6004	25.05	24.90	0.60
0.6987	25.26	25.09	0.68	0.7007	24.62	24.50	0.49
0.7983	24.83	24.73	0.40	0.7987	24.19	24.12	0.29
0.8995	24.38	24.35	0.12	0.9009	23.74	23.73	0.04
1	23.93	23.99	-0.25	1	23.29	23.35	-0.26
T=308.15 K				T=313.15 K			
0	26.83	27.24	-1.51	0	26.25	26.82	-2.13
0.0985	26.46	26.73	-1.01	0.1004	25.87	26.28	-1.56
0.1992	26.08	26.20	-0.46	0.1999	25.48	25.73	-0.97
0.3018	25.68	25.69	-0.04	0.3004	25.08	25.19	-0.44
0.3991	25.28	25.21	0.28	0.3998	24.67	24.69	-0.08
0.5009	24.86	24.75	0.44	0.5001	24.25	24.21	0.17
0.6012	24.43	24.33	0.41	0.6000	23.82	23.76	0.25
0.6997	24.00	23.91	0.38	0.7005	23.37	23.33	0.17
0.7983	23.56	23.52	0.17	0.8003	22.92	22.92	0
0.8997	23.11	23.11	0	0.9003	22.47	22.50	-0.13
1	22.65	22.73	-0.35	1	22.00	22.10	-0.45
$\{x(1)CH_3COOCH_2CH_2CH_3(1) + x(2)1,2,4-C_6H_3(CH_3)_3(2)\}$							
T=298.15 K				T=303.15 K			
0	29.31	29.17	0.48	0	28.72	28.67	0.17
0.0998	28.85	28.68	0.59	0.1001	28.26	28.18	0.28
0.2001	28.39	28.20	0.67	0.2009	27.80	27.69	0.4
0.2994	27.93	27.73	0.72	0.3006	27.33	27.22	0.4
0.4003	27.46	27.25	0.77	0.4001	26.87	26.73	0.52
0.4958	27.02	26.78	0.9	0.5004	26.40	26.27	0.49
0.6001	26.53	26.33	0.76	0.6006	25.93	25.80	0.5
0.6999	26.06	25.93	0.5	0.7001	25.46	25.40	0.24
0.7998	25.59	25.57	0.08	0.7997	24.99	25.03	-0.16
0.8997	25.11	25.23	-0.48	0.9000	24.51	24.70	-0.77
1	24.64	24.89	-1.00	1	24.03	24.35	-1.31

Table 2: Continued

T=308.15 K				T=313.15 K			
0	28.14	28.17	-0.11	0	27.55	27.67	-0.43
0.1005	27.67	27.67	0	0.1002	27.08	27.12	-0.15
0.1998	27.21	27.18	0.11	0.1995	26.62	26.55	0.26
0.3004	26.74	26.70	0.15	0.3000	26.15	26.02	0.5
0.4003	26.27	26.21	0.23	0.3996	25.68	25.48	0.78
0.5007	25.80	25.75	0.19	0.5002	25.21	24.99	0.88
0.5991	25.34	25.28	0.24	0.5998	24.73	24.55	0.73
0.6995	24.86	24.87	-0.04	0.6999	24.26	24.20	0.25
0.7999	24.38	24.50	-0.49	0.8004	23.78	23.90	-0.5
0.9004	23.91	24.16	-1.03	0.9005	23.30	23.62	-1.35
1	23.43	23.82	-1.64	1	22.83	23.28	-1.93
$\{x(1)CH_3COOCH_2CH_2CH_2CH_3(1) + x(2)1,3,5-C_6H_3(CH_3)_3(2)\}$							
T=298.15 K				T=303.15 K			
0	27.99	28.09	-0.36	0	27.41	27.67	-0.94
0.1009	27.66	27.72	-0.22	0.1005	27.08	27.29	-0.77
0.2018	27.33	27.34	-0.04	0.1997	26.75	26.90	-0.56
0.3003	27.01	26.98	0.11	0.3000	26.42	26.53	-0.41
0.4005	26.67	26.61	0.23	0.3996	26.09	26.14	-0.19
0.4996	26.34	26.27	0.27	0.5007	25.75	25.79	-0.16
0.5979	26.01	25.93	0.31	0.6007	25.41	25.45	-0.16
0.7016	25.66	25.62	0.16	0.7001	25.07	25.12	-0.2
0.8005	25.32	25.36	-0.16	0.7971	24.74	24.85	-0.44
0.8981	24.99	25.12	-0.52	0.9009	24.38	24.60	-0.89
1	24.64	24.89	-1.00	1	24.03	24.35	-1.31
T=308.15 K				T=313.15 K			
0	26.83	27.24	-1.51	0	26.25	26.82	-2.13
0.1002	26.50	26.84	-1.27	0.0997	25.92	26.39	-1.78
0.1986	26.17	26.44	-1.02	0.2012	25.58	25.97	-1.50
0.2997	25.83	26.05	-0.84	0.2996	25.25	25.57	-1.25
0.4003	25.50	25.66	-0.62	0.3987	24.91	25.16	-0.99
0.5007	25.16	25.29	-0.51	0.5008	24.56	24.79	-0.93
0.5997	24.82	24.94	-0.48	0.5964	24.24	24.42	-0.74
0.7005	24.47	24.60	-0.53	0.6995	23.88	24.07	-0.79
0.8000	24.13	24.32	-0.78	0.7994	23.53	23.79	-1.09
0.9006	23.78	24.07	-1.20	0.9000	23.18	23.54	-1.53
1	23.43	23.82	-1.64	1	22.83	23.28	-1.93

In Figure 2, the correlation of binary mixtures of these organic compounds with different mole fractions $x(i)$ is shown. The solid line in this figure is the linear fit to the experimental data which is obtained by linear regression as:

$$\sigma^* = 0.8486T^* + 0.1743 \quad [7]$$

and the linear correlation coefficient is 0.9984. In Table 2 the percentage deviations calculated, is shown.

By using no critical values especially, the σ^*-T^* relationship, that is applied in this work, is more practical. Surface tension of pure and mixtures of these organic compounds (propyl acetate, butyl acetate, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) can be predicted quite well by Eqs. [6] and [7] and the

correspondence between predicted one and experimental values is both satisfactory and acceptable.

CONCLUSION

Surface tension has an important role in many processes in a number of industrial applications; it also presents substantial information of the molecular influence on the intensity of the interactions in the mixtures. We have applied a method for the prediction the surface tension of pure organic compounds (propyl acetate, butyl acetate, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) and their mixtures. The σ^*-T^* relationship is a simple reliable relationship with a few parameters. The involved parameters, are σ_m , T_b and T_m . Instead of other temperatures such as critical temperature,

boiling temperature is chosen and it can be certified the validity and the range of accuracy of the correlation. On the other hand it has been shown that the law of corresponding states can also apply well for prediction of the surface tension of these four organic compounds and their mixtures with these reduced coordinates (σ^* and T^*). These four pure compounds have different sizes and polarities and therefore dipolar-dipolar interactions, which exist in their binary mixtures, have effective effects on the surface tension of these mixtures. It is worth noting that no specific parameter for size or polarity, is applied in this work and only σ_m , T_b and T_m are used. These mixtures are considered over the full mole fraction range and the comparison between experimental data and calculated ones supports the proposed method. %AAD, percent average absolute deviation, for these four pure compounds is less than 0.71% and for their mixtures is 0.60%.

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