A New Approach for Prediction of Surface Tension of Binary Liquid Mixture

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Surface tensions of three binary liquid mixtures of hexane-decane, hexadecane-decane at 30°C and benzene-carbon tetrachloride at 50°C have been predicted by a new approach, using surface tension of pure components. Results obtained have been compared with that obtained from Brock and Bird relation and Eberhart relation. Relative merits and limitations of all the relations have been assessed.

INTRODUCTION

Several attempts[1–7] have been made to predict surface tension of pure liquids and liquid mixtures. In the present paper, a new approach has been carried out to predict surface tension of binary liquid mixture. The results obtained have been compared with the results obtained from Brock and Bird relation[8] and Eberhart relation[9, 10] in the light of percentage deviation. Merits and limitations of every method have been discussed.

Theoretical

Brock and Bird relations have been extended[7] for binary liquid mixture, using the relation

$$\frac{\sigma_{mix}}{(P_{c_m}^2 T_{c_m})^{1/3}} = \left(-0.951 + \frac{0.432}{Z_{c_m}}\right)(1 - T_{r_m})^{i \, 11/9} \tag{1}$$

where P_{c_m}, V_{c_m} and T_{c_m} are pseudo critical constants of the mixture and may be obtained from critical constants of pure components as their mole fraction average, *i.e.*

$$P_{c_m} = X_1 P_{c_1} + X_2 P_{c_2}$$

$$V_{c_m} = X_1 V_{c_1} + X_2 V_{c_2} \tag{2}$$

$$T_{c_m} = X_1 T_{c_1} + X_2 T_{c_2}$$

where X_1 and X_2 are mole fractions of first and second component and P_c, V_c, T_c are critical pressure, critical volume and critical temperature. Suffixes 1, 2 represent first and second component respectively.

T_{r_m} and Z_{c_m} are obtained by the relation

$$T_{r_m} = \frac{T}{T_{c_m}} \; ; \quad Z_{c_m} = \frac{P_{c_m} \cdot V_{c_m}}{R \cdot T_{c_m}} \tag{3}$$

where R is gas constant, taken as 0.08205 lit. atm. $\deg^{-1}$ mole^{-1}.

Eberhart[9] gave a relation for surface tension of binary liquid mixture as

$$\sigma_{mix} = \frac{S_{X_1\sigma_1 + X_2\sigma_2}}{S_{X_1 + X_2}} \qquad (4)$$

where X_1, X_2 represents mole fractions of first and second component and σ_1 and σ_2 are surface tension of first and second component. S is termed as surface tension enrichment factor, which is temperature dependent. The other notations have their usual meaning.

A new approach for the evaluation of surface tension of binary liquid mixture can be given as

$$\sigma_{mix} = X_1^2\sigma_1 + X_2^2\sigma_2 + 2X_1X_2\sigma_{12} \qquad (5)$$

where σ_1 and σ_2 are the surface tension of first and second component and σ_{12} is a constant, the value of which is obtained from surface tension of pure component, at equimolecular composition, as

$$\sigma_{12} = 0.5\sigma_1 + 0.5\sigma_2 \qquad (6)$$

The value of σ_{12} is then used to get surface tension of binary liquid mixture at other composition.

The logarithmic form of the equation can be given as

$$\rho_n\sigma_{mix} = X_1^2\rho_n\sigma_1 + X_2^2\rho_n\sigma_2 + 2X_1X_2\rho_n\sigma_{12} \qquad (7)$$

Equations (5) and (7) (Saxena-equation) can be applied to predict surface tension of binary liquid mixture.

The percentage deviations, from surface tension values, can be obtained by the relation

$$\Delta\% = \left(\frac{\sigma_{mix_{exp}} - \sigma_{mix_{calc.}}}{\sigma_{mix_{exp}}}\right) \times 100 \qquad (8)$$

where $\sigma_{mix_{exp}}$ is the experimental value of surface tension of the mixture, $\sigma_{mix_{calc}}$ is the value of surface tension of the binary liquid mixture calculated from various equations (*e.g.* 1, 4, 5, and 7).

RESULTS AND DISCUSSION

Surface tensions of the binary liquid mixtures n-hexane-decane, hexadecane-decane are evaluated at 30°C and for benzene-carbon tetrachloride at 50°C, using Brock and Bird relation [Eq. (1)], Eberhart relation [Eq. (4)] and by a new approach [Eq. (5) and (7)].

The necessary data required for calculation have been taken from our previous work[7] and other literature[12-14].

The results obtained have been given in Table 1. Surface tension obtained from Brock and Bird relation [Eq. (1)] Eberhart relation [Eq. (4)] and from our new approach [Eq. (5) and Eq. (7)] have been shown in columns third, fourth, fifth and sixth respectively of Table 1.

The percentage deviation values, obtained from Brock and Bird relation,

TABLE-1
CALUCLATED AND EXPERIMENTAL SURFACE TENSION FOR BINARY LIQUID MIXTURES

X_1	σ_{exp} (dynes/cm)	σ (dynes/cm) (Brock and Bird) (Eq. 1) (Ref. 7)	σ (dynes/cm) (Eberhart) (Eq. 4) (Ref. 7)	σ (dynes/cm) (Saxena) (Eq. 5)	$Ln\sigma_{exp}$ (Ref. 7)	$Ln\sigma$ (Saxena) (Eq. 7)	(Δ%) (Brock and Bird) (Eq. 8)	(Δ%) (Eberhart) (Eq. 8)	(Δ%) (Saxena) (Eq. 8)	(Δ%) (Saxena) (Eq. 8)
n-Hexane-decane-30°C					$\sigma_1 = 17.64$ $\sigma_{12} = 20.13$ $\sigma_2 = 22.61$					
0.1420	22.28	22.05	21.94	21.91	3.1036	3.0851	1.03	1.51	1.67	0.59
0.2671	21.68	21.51	21.77	21.28	3.0764	3.0552	0.78	-0.41	1.82	0.68
0.5031	20.44	20.37	21.45	20.11	3.0175	2.9975	0.34	-4.94	1.60	0.66
0.6002	19.98	19.87	21.31	19.63	2.9947	2.9732	0.55	-6.65	1.75	0.71
Hexadecane-decane-30°C					$\sigma_1 = 29.02$ $\sigma_{12} = 25.81$ $\sigma_2 = 22.61$					
0.0509	23.16	23.00	23.70	22.94	3.1424	3.1319	0.71	-2.33	0.95	0.33
0.1744	23.82	23.91	25.17	23.73	3.1705	3.1642	-0.38	-5.67	0.38	0.19
0.2854	24.18	24.57	25.98	24.31	3.1855	3.1877	-1.60	-7.44	-0.54	0.69
0.4014	24.78	25.53	26.89	25.18	3.2100	3.2223	-3.04	-8.51	-1.62	0.38
Benzene-carbon tetracholride 50°C					$\sigma_1 = 24.65$ $\sigma_{12} = 23.70$ $\sigma_2 = 22.89$					
0.3040	24.39	23.42	24.11	23.39	3.1947	3.1523	3.97	1.15	4.07	1.31
0.5764	24.09	23.91	24.56	23.87	3.1818	3.1723	0.75	-1.98	0.90	0.29
0.6238	23.78	23.93	24.63	23.97	3.1688	3.1716	-0.84	-3.57	-0.82	-0.22
0.7829	23.47	24.26	24.81	24.24	3.1557	3.1879	-3.38	-5.70	-3.29	-1.02
0.8862	23.41	24.45	24.90	24.43	3.1531	3.1959	-4.43	-6.38	-4.37	-1.35

Eberhart relation and from our two new approach have been shown in column eight, ninth, tenth and eleventh of the Table 1.

A close look on percentage deviation ($\Delta\%$) obtained from above four relations reveals that the surface tension values evaluated from our new approach [Eq. (5)] are very satisfactory and are not much beyond the experimental values. Moreover the percentage deviation obtained from the other approach [Eq. (7)] shows the minimum deviation, as compared to Brock and Bird relation and Eberhart relation, thus it shows superiority over all relations taken for study.

Thus it may be concluded from the present investigation that Equation (5) and (7) provides a better way to predict surface tension of binary liquid mixture as compared to Brock and Bird relation and Eberhart relation.

Brock and Bird relation is limited to non polar liquids and liquid mixture. Moreover the values of pseudo-critical constants P_{c_m}, V_{c_m} and T_{c_m} for mixture, used in Brock and Bird relation are obtained from the mole fraction averages. Results are only on approximation. Eberhart relation requires evaluation of number of thermodynamic parameter for evaluation of surface tension of binary mixture.

Our new approach [Eq. (5) and (7)] thus can be used successfully to predict surface tension of binary liquid mixture, at wide range of temperature and composition, provided surface tension of pure components are known. The relation [Eq. (5) and (7)] also avoids botheration of evaluating other thermodynamic parameters, in comparision to Brock and Bird relation and Eberhart relation.

REFERENCES

1. J.G. Kirkwood, *J. Chem. Phys.*, **3**, 300 (1935).
2. A. Abe and P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
3. D. Patterson and A.K. Rastogi, *J. Phys. Chem.*, **74**, 1067, (1970).
4. V.T. Lam and G.C. Benson, *Can. J. Chem.*, **48**, 3773 (1970).
5. I. Prigogine, Molecular Theory of Solutions, North-Holland Pub. Company, Amsterdam (1957).
6. R.L. Mishra and J.D. Pandey, *Chemica Scripta*, **11**, 117 (1977).
7. M.C. Saxena and M.P. Gupta, *Proc. Nat. Acad. Sci. (India)*, **54A**, 163 (1984).
8. J.R. Brock and R.B. Bird, *Am. Inst. Chem. Engg. J.*, **1**, 174 (1965).
9. J.G. Eberhort, *J. Phys. Chem.*, **70**, 1183 (1966).
10. V. Ramkrishna and S.K. Suri, *Indian J. Chem.*, **5**, 310 (1965).
11. R.C. Reid and T.K. Sherwood, The properties of Gases and Liquids, 2nd Ed., Chapter 8, McGraw-Hill, New York (1966).
12. C.R.C. Handbook of Chemistry and Physics, Cole Presd, Boca Raton (Florida), 60th Ed., F44 (1979–80).
13. A.K. Kudchadper, H. Ghalib and B.J. Zwoliriski, *Chem. Rev.*, **68**, 659 (1968).
14. Timmerman's Physico-chemical Constants of Pure Organic Compounds, Elsevier Pub. Co. Inc., New York (1950).