Surface Tension Calculation of Mixed Solvents with Respect to Solvent Composition and Temperature by Using Jouyban–Acree Model

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Applicability of a solution model, i.e. Jouyban–Acree model (JAM), for calculating surface tension of binary and ternary solvents at various temperatures has been shown employing experimental surface tension data collected from the literature. The accuracy of the model was evaluated by calculating average percentage deviation (APD) between calculated and observed values. The obtained overall APD ($\pm$ S.D.) for JAM using binary solvent data were 4.06 ($\pm$ 4.27) and 8.07 ($\pm$ 9.78)%, respectively for correlative and predictive analyses. The corresponding values for the best similar model from the literature were 8.86 ($\pm$ 6.40) and 37.10 ($\pm$ 27.65)% and the mean APD differences between JAM and previously published model were significant ($p < 0.003$). The capability of JAM for correlating surface tension of ternary solvents at various temperatures was also shown and the overall APD was 1.39 ($\pm$ 0.37)%.

Key words surface tension; mixed solvent; mathematical model; prediction

Surface and/or interfacial tension is a measurable quantity, which represents the surface and/or interfacial activity and differs from the assumed ideal value when the system becomes non-ideal. Surface tension plays an important role in the functioning of respiratory system. Surface tension of the fluid lining the alveoli is decreased by a mixture of surface active agents mainly, dipalmitoyl lecithin. Respiratory distress syndrome and atelectasis are two major clinical syndromes of increasing the surface tension of the fluid lining the alveoli.¹⁾ Prokop *et al.*²⁾ reported the relationships between recoil pressure and surface area of the lung and the surface tension of the lung fluid. Several important phenomena in the pharmaceutical and analytical areas are related to the surface activity. This includes suspension and emulsion formulations, solubilization techniques and explaining the retention mechanisms in HPLC. The primary droplet size of the nebulized solutions was correlated to the surface tension of the solution.³⁾ Binary and ternary solvents have been used in many pharmaceutical formulations and also validated analytical methods at ambient and higher and/or lower temperatures. The surface tension data of mixed solvents are required in practice and the aim of this work is to present a simple mathematical model for calculating such data.

Computational Methods

The basic solution model, i.e. the combined nearly ideal binary solvent/Redlich–Kister equation (CNIBS/R-K), presented by Acree⁴⁾ was used to correlate different physico-chemical properties in mixed solvent systems; including the solubility of drugs in water-cosolvent mixtures,⁵⁾ electrophoretic mobility of analytes in mixed solvent electrolyte systems,^{6–8)} the instability rate constants in binary solvent systems,⁹⁾ the acid dissociation constants in water-organic solvent mixtures,¹⁰⁾ the dielectric constant¹¹⁾ and surface tension¹²⁾ of solvent mixtures. Theoretical basis of the CNIBS/R-K equation for describing the chemical potential of solutes dissolved in mixed solvents⁴⁾ and acid dissociation constants in aqueous-organic mixtures¹⁰⁾ have been provided in earlier papers.

The Jouyban–Acree model (JAM) representing the surface tension of binary solvent mixtures at a constant temperature has been proposed in our earlier work¹²⁾ as:

$$\ln \gamma_m = \phi_1 \ln \gamma_1 + \phi_2 \ln \gamma_2 + \phi_1 \phi_2 \sum_{i=0}^2 K_i (\phi_1 - \phi_2)^i \quad (1)$$

Where γ_m , γ_1 and γ_2 are the surface tensions of the mixture and solvents 1 and 2, respectively, ϕ_1 and ϕ_2 are the volume (weight or mole) fractions of solvents 1 and 2 in the mixture and K_i represent the model constants calculated using a least square method.¹³⁾ The model could be extended for calculating the surface tension of ternary solvents as:

$$\begin{aligned} \ln \gamma_m = & \phi_1 \ln \gamma_1 + \phi_2 \ln \gamma_2 + \phi_3 \ln \gamma_3 + \phi_1 \phi_2 \sum_{i=0}^2 K_i (\phi_1 - \phi_2)^i \\ & + \phi_1 \phi_3 \sum_{i=0}^2 K_i' (\phi_1 - \phi_3)^i + \phi_2 \phi_3 \sum_{i=0}^2 K_i'' (\phi_2 - \phi_3)^i \\ & + \phi_1 \phi_2 \phi_3 \sum_{i=0}^2 K_i''' (\phi_1 - \phi_2 - \phi_3)^i \end{aligned} \quad (2)$$

Where K_i , K_i' , K_i'' and K_i''' are the model constants.¹²⁾

To correlate the surface tensions of binary solvents at various temperatures (T), an extended form of JAM could be used for calculating the surface tension with respect to solvent composition and temperature, and is proposed in this work as:

$$\ln \gamma_{m,T} = \phi_1 \ln \gamma_{1,T} + \phi_2 \ln \gamma_{2,T} + \phi_1 \phi_2 \sum_{j=0}^2 \left[\frac{A_j (\phi_1 - \phi_2)^j}{T} \right] \quad (3)$$

Where $\gamma_{m,T}$, $\gamma_{1,T}$ and $\gamma_{2,T}$ are the surface tensions of the mixture and solvents 1 and 2 at temperature T , respectively, and A_j represent the model constants. The proposed model could also be extended to ternary solvents at different temperatures as:

$$\begin{aligned} \ln \gamma_{m,T} = & \phi_1 \ln \gamma_{1,T} + \phi_2 \ln \gamma_{2,T} + \phi_3 \ln \gamma_{3,T} + \phi_1 \phi_2 \sum_{j=0}^2 \left[\frac{A_j (\phi_1 - \phi_2)^j}{T} \right] \\ & + \phi_1 \phi_3 \sum_{j=0}^2 \left[\frac{B_j (\phi_1 - \phi_3)^j}{T} \right] + \phi_2 \phi_3 \sum_{j=0}^2 \left[\frac{C_j (\phi_2 - \phi_3)^j}{T} \right] \\ & + \phi_1 \phi_2 \phi_3 \sum_{j=0}^2 \left[\frac{D_j (\phi_1 - \phi_2 - \phi_3)^j}{T} \right] \end{aligned} \quad (4)$$

Where $\gamma_{3,T}$ is the surface tension of the solvent 3 at temperature T , ϕ_3 denotes the volume (weight or mole) fraction of the third solvent and A_j , B_j , C_j and D_j are the model constants. These model constants are computed by regressing $(\ln \gamma_{m,T} - \phi_1 \ln \gamma_{1,T} - \phi_2 \ln \gamma_{2,T} - \phi_3 \ln \gamma_{3,T})$ against $\phi_1 \phi_2 / T$, $\phi_1 \phi_2 (\phi_1 - \phi_2) / T$, $\phi_1 \phi_2 (\phi_1 - \phi_2)^2 / T$, $\phi_1 \phi_3 / T$, $\phi_1 \phi_3 (\phi_1 - \phi_3) / T$, $\phi_1 \phi_3 (\phi_1 - \phi_3)^2 / T$, $\phi_2 \phi_3 / T$, $\phi_2 \phi_3 (\phi_2 - \phi_3) / T$, $\phi_2 \phi_3 (\phi_2 - \phi_3)^2 / T$, $\phi_1 \phi_2 \phi_3 / T$, $\phi_1 \phi_2 \phi_3 (\phi_1 - \phi_2 - \phi_3) / T$ and $\phi_1 \phi_2 \phi_3 (\phi_1 - \phi_2 - \phi_3)^2 / T$ using a no intercept least square analysis.

Connors and Wright¹⁴⁾ have proposed Eq. 5 for calculating surface tension

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of mixed solvents at a constant temperature. Eq. 5 is:

$$\gamma_m = \gamma_1 - \left[1 + \frac{b\phi_1}{1-a\phi_1} \right] \phi_2 (\gamma_1 - \gamma_2) \quad (5)$$

where a and b are the model constants. Hoke and Patton¹⁵⁾ have also correlated Connors model constants with temperature using:

$$a = M_0 + M_1 T + M_2 T^2 \quad (6)$$

and

$$b = P_0 + P_1 + P_2 T^2 \quad (7)$$

By combining Connors model with Hoke and Patton's equation, the following equation could be obtained:

$$\gamma_m = \gamma_1 - \left[1 + \frac{H_1\phi_1 + H_2\phi_1 T + H_3\phi_1 T^2}{1 - (H_4\phi_1 + H_5\phi_1 T + H_6\phi_1 T^2)} \right] \phi_2 (\gamma_1 - \gamma_2) \quad (8)$$

in which H_1 – H_6 are the model constants. This combination enables Connors' model to calculate surface tension at different temperatures and solvent compositions.

Lee *et al.*¹⁶⁾ have used the following equation for calculating surface tension of solvent mixtures based on solvent composition and temperature:

$$\gamma_{m,T} = \sum_{i=0}^2 [L_i \phi_1^i + L_i' (\phi_1^i \cdot T) + L_i'' (\phi_1^i \cdot T^2)] \quad (9)$$

where L_i , L_i' and L_i'' are the model constants calculated using a least square analysis.¹⁶⁾ Lee's model is based on mixture response method and could be rewritten as:

$$\gamma_{m,T} = M_0 + M_1 \phi_1 + M_2 \phi_1^2 + M_3 T + M_4 \phi_1 T + M_5 \phi_1^2 T + M_6 T^2 + M_7 \phi_1 T^2 + M_8 \phi_1^2 T^2 \quad (10)$$

where M_0 – M_8 are the model constants.

The calculated surface tensions were compared with experimental (observed) values and the absolute percentage deviation (APD) was used as an accuracy criterion. The APD was calculated using:

$$\text{APD} = \frac{100}{N} \sum \frac{|\text{calculated} - \text{observed}|}{\text{observed}} \quad (11)$$

where N is the number of data points in each set. The overall APD (OAPD) was defined as:

$$\text{OAPD} = \frac{\sum \text{APD}}{\text{number of data sets studied}} \quad (12)$$

and was used as overall accuracy criterion for comparing different models.

Individual percentage deviation (IPD) is another criterion to check the suitability of a model in practice and calculated as:

$$\text{IPD} = 100 \left(\frac{|\text{calculated} - \text{observed}|}{\text{observed}} \right) \quad (13)$$

Results and Discussion

The available experimental surface tension of aqueous binary solvents at various temperatures were fitted to JAM and Eqs. 8 and 10 and the APD values were computed using back-calculated surface tensions. The details of the data, the number of data points, temperature ranges, surface tension ranges in water and cosolvent and the APD values were listed in Table 1. The JAM produced the minimum and maximum APD values respectively for water-1,3-propanediol (0.34) and water-1-propanol (16.00). Equation 8 showed the same data sets as minimum and maximum values with APD values of 1.17 and 82.07%, respectively. On the other hand, Eq. 10 correlated the surface tension data with minimum and maximum APDs for water-1,3-propanediol (0.77) and water-2-propanol (22.00), respectively. The obtained OAPD and the standard deviations for JAM and Eqs. 8 and 10 are 4.06 ± 4.27 , 26.88 ± 23.85 and 8.86 ± 6.40 , respectively. The OAPD differences between JAM and Eqs. 8 and 10 were statistically tested using paired t -test and the results revealed that JAM is able to correlate surface tension of binary solvents at various temperatures more accurate than Eqs. 8 and 10. It is possible to use more curve-fitting parameters with JAM for increasing its accuracy. As a general rule for mathematical models containing constant terms, the more the number of constant terms the more accurate the results and this has been observed in this study with JAM. The OAPD and standard deviations for different numbers of curve-fitting parameters were shown in Fig. 1. The improvement in accuracy with increase in the number of constant terms reaches a limiting value after the inclusion of about 4 or 5 curve-fitting parameters. Since one of the main purposes of modeling is to predict unmeasured quantities using minimum experimentally derived information, it is suggested to use JAM for calculating surface tension of mixed solvents with $j=2$ which needs a minimum number of five data points. The accuracy

Table 1. Details of Surface Tension of Aqueous Binary Solvent Mixtures, the References, Number of Data Points (N), Temperature (T) and Surface Tension Ranges for Solvents 1 and 2, and the Average Percentage Deviations (APDs) for JAM and Eqs. 8 and 10 Using Correlative Analysis

No.	Cosolvent (Solvent 2)	Ref.	N	T range	γ_1 range	γ_2 range	JAM	Eq. 8	Eq. 10
1	Acetone	17	59	293–323	68.0–72.7	19.5–23.2	6.79	42.31	15.14
2	2-Amino-2-methyl-1-propanol	18	84	298–323	67.9–72.0	28.4–31.3	6.57	32.15	10.33
3	3-Amino-1-propanol	19	72	298–323	67.9–72.0	38.1–43.9	1.18	8.83	3.84
4	1-Amino-2-propanol	19	72	298–323	67.9–72.0	31.2–37.3	3.19	16.81	6.74
5	γ -Butyrolactone	20	33	303–343	64.3–71.2	37.9–42.7	1.09	10.88	5.60
6	Diethanolamine	21	66	298–323	67.9–72.0	43.1–47.2	1.51	8.85	3.66
7	Dioxane	22	85	293–353	62.6–72.7	24.7–33.3	2.65	25.61	9.52
8	Ethanol	23	98	293–323	67.9–72.7	19.8–22.3	4.88	47.21	16.32
9	Methanol	24	40	293–323	67.9–72.7	19.5–22.6	0.80	13.68	4.36
10	Methanol	23	98	293–323	67.9–72.7	20.2–22.9	1.36	26.44	8.13
11	N -Methyldiethanolamine	25	84	298–323	67.9–72.0	36.8–38.9	4.10	17.44	5.89
12	Monoethanolamine	18	78	298–323	67.9–72.0	44.8–48.9	1.59	7.80	3.04
13	1,3-Propanediol	16	42	298–323	67.9–71.8	51.1–53.1	0.34	1.17	0.77
14	1-Propanol	23	98	293–323	67.9–72.7	21.3–23.7	16.00	82.07	20.60
15	2-Propanol	23	98	293–323	67.9–72.7	18.7–21.7	10.95	75.21	22.00
16	Triethanolamine	23	66	298–323	67.9–72.0	41.8–45.9	1.99	13.65	5.85
							$4.06 \pm 4.27^{***}$	$26.88 \pm 23.85^*$	$8.86 \pm 6.40^{**}$

*,** The mean differences between JAM and the previous models are statistically significant (paired t -test, $p < 0.0005$).

Fig. 1. OAPD ($\pm$ S.D.) of JAM with Different j Values for Correlating Surface Tension of Binary Solvents at Various Temperatures

Fig. 2. IPD Distribution for Correlative Analysis of Surface Tension Data of Binary Solvents at Various Temperatures Using Three Studied Equations

of the models for calculating surface tension was also evaluated by studying the distribution of IPD for correlative studies. The IPD values sorted in three error ranges, *i.e.* ≤ 4 , 4–10 and $>10\%$ and the findings were shown in Fig. 2. For JAM, more than 85% of IPD values are ≤ 10 and only *ca.* 15% of data points produced IPD more than 10 whereas the corresponding frequencies for Eq. 10 were 32 and 68%. Considering these findings, it is observed that JAM is able to provide more accurate correlation in comparison with previously published similar models.

As a general rule, a model with good correlation abilities, shows better prediction capability than that of poor correlative models. To test the prediction capability of the models and test the rule on real experimental data, a minimum number of experimental surface tensions were employed to train the models. The training points involve the surface tension of pure water and cosolvent at all temperatures under investigation and three surface tensions from binary mixtures with nearly constant volume/mole fraction intervals, *i.e.* $\phi_1=0.3$, 0.5 and 0.7 at the highest and lowest temperatures of interest. After training the models, the surface tensions at other solvent compositions and temperatures were predicted using interpolation technique. The obtained APD values were listed in Table 2. Figure 3 shows IPD distribution of the equations under investigation in three error subgroups for predictive

Table 2. Prediction Capability of Equations Studied after Training with a Minimum Number of Experimental Data Points

No. ^{a)}	N	JAM	Eq. 8	Eq. 10
1	45	9.15	94.00	57.36
2	66	14.80	139.86	42.09
3	54	1.99	131.86	11.09
4	54	3.18	96.59	20.25
5	17	2.35	125.57	39.24
6	48	3.29	923.16	12.29
7	63	4.39	162.52	33.09
8	78	10.22	87.33	53.22
9	26	1.33	116.56	36.48
10	78	2.19	110.25	40.63
11	66	7.42	282.09	23.16
12	60	2.47	300.18	9.50
13	24	0.48	125.59	3.91
14	78	35.35	79.62	103.15
15	78	26.13	155.31	86.94
16	48	4.37	115.49	21.12
		$8.07 \pm 9.78^{***}$	$190.37 \pm 205.31^*$	$37.10 \pm 27.65^{**}$

a) The key for the numbers is the same as in Table 1. **, ** The mean differences between JAM and the previous models are statistically significant (paired *t*-test, $p < 0.003$).

Fig. 3. IPD Distribution for Predictive Analysis of Surface Tension Data of Binary Solvents at Various Temperatures Using Three Studied Equations

analysis. The relative frequency of IPDs $<10\%$ for JAM and Eqs. 8 and 10 are 71, 0 and 16%, respectively. This means that using JAM and minimum number of data points, it is possible to predict unmeasured surface tensions and the probability of prediction error less than 10% is 0.70 whereas for Eq. 8 all predicted points produced prediction errors more than 10 and the corresponding probability for Eq. 10 is 0.16.

Applicability of JAM for correlating the surface tension of ternary solvent mixtures at various temperatures has been evaluated using 10 experimental data sets. The details of data sets and APD values were listed in Table 3. As seen from low OAPD value, JAM is capable of providing accurate correlation for surface tension of ternary solvents at various temperatures and it is expected to be an accurate model for predicting surface tension of ternary solvents using a minimum number of experimental data. To the best of our knowledge, there is no such a similar model in the literature to compare

Table 3. Details of Surface Tension of Aqueous Ternary Solvent Mixtures, the References, Number of Data Points (*N*), Temperature (*T*) Ranges and Average Percentage Deviation (APD), Overall APD (OAPD) and Its Standard Deviation Values for JAM

No.	Solvent (2)+Solvent (3)	Ref.	<i>N</i>	<i>T</i> range	APD
1	3-Amino-1-propanol+2-amino-2-methyl-1-propanol	19	36	298—323	1.38
2	1-Amino-2-propanol+2-amino-2-methyl-1-propanol	19	36	298—323	1.96
3	3-Amino-1-propanol+diethanolamine	19	36	298—323	0.99
4	1-Amino-2-propanol+diethanolamine	19	36	298—323	1.59
5	3-Amino-1-propanol+triethanolamine	19	36	298—323	1.28
6	1-Amino-2-propanol+triethanolamine	19	36	298—323	1.85
7	<i>N</i> -Methyldiethanolamine+2-amino-2-methyl-1-propanol	25	36	298—323	1.27
8	<i>N</i> -Methyldiethanolamine+diethanolamine	25	36	298—323	1.27
9	<i>N</i> -Methyldiethanolamine+monoethanolamine	25	36	298—323	0.73
10	Monoethanolamine+2-amino-2-methyl-1-propanol	18	36	298—323	1.54
				OAPD±S.D.	1.39±0.37

its accuracy with JAM.

Conclusion

JAM produced accurate calculations for surface tension data of mixed solvent systems at various temperatures. Its accuracy was better than those of similar mathematical models from the literature for calculating surface tension of binary solvents. The binary and ternary systems considered in the present communication were limited to those mixtures containing water as one of the solvent components as we wanted to test the descriptive/predictive ability of JAM on systems covering as wide of a range of surface tensions as possible, and water is a common solvent in many pharmaceutical formulations. There is no reason that the model cannot be applied to totally non-aqueous systems as well. Therefore, it is suggested to be employed in practical applications either for screening experimentally obtained surface tensions for detecting possible outliers or for predicting unmeasured surface tensions of mixed solvents at various temperatures after training using a minimum number of experimental data. The expected mean percentage deviation for the predicted data is *ca.* 8%. The applicability of JAM for correlating surface tension of ternary solvents at various temperatures is also shown and the results revealed its good potential for modeling such data.

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