MODELING THE SOLVATOCHROMIC PARAMETER (E_T^N) OF MIXED SOLVENTS WITH RESPECT TO SOLVENT COMPOSITION AND TEMPERATURE USING THE JOUYBAN-ACREE MODEL

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ABSTRACT

Applicability of the Jouyban-Acree model for calculation of solvatochromic parameter (E_T^N) of binary solvents at various temperatures has been shown by employing 12 experimental data sets 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 (±S.D.) were 1.2 (± 0.9) and 2.2 (± 1.8) %, respectively for correlative and predictive analyses.

Keywords: Solvatochromic parameter (E_T^N), Mixed solvents, Mathematical model, Prediction, Jouyban-Acree model, Modeling

INTRODUCTION

Polarity is one of the most important characteristics of a solvent that is determined by its solvation capability for solutes and depends on all possible interactions in the solution including specific and non-specific interactions between solvent and solute. Because of existence of a wide range of solute-solvent and solvent-solvent interactions from dispersion forces to hydrogen bonding, the lack of theoretical expressions for calculation of solvent effects and the inadequacy of definition of solvent polarity in terms of simple physical constants, empirical scales have been introduced to represent the solvent polarities. These scales include Dimorth-Reichardt solvatochromic parameter ($E_T(30)$), Kamlet-Taft's solvatochromic parameters, dielectric constants, solubility parameter, ionizing power, Kovats index etc. A comprehensive review on these parameters has been reported previously (1).

Spectroscopic parameters of solvent polarity were derived from solvent sensitive standard compounds (like dye number 30) which absorb light with different wavelength. $E_T(30)$, the most popular spectroscopic parameter of solvent polarity, is the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium-N-phenoxide betaine dye or dye number 30 which is measured in kcal/mol and its dimensionless normalized value (E_T^N) is presented as $E_T^N = \frac{E_T(solvent) - 30.7}{32.4}$. E_T^N and E_T (30) values of more than 270 pure solvents are reported in the literature (1). In practice $E_T(30)$ or E_T^N is used to explain a number of observations such as retention in mixed solvent mobile phases in reversed phase liquid chromatography (2). In addition to the solvent composition of the mobile phases, temperature is another variable that should be optimized and the E_T^N values of solvent mixtures at various temperatures are required to explain the polarity of solvent mixtures at the desired temperature. The aim of this work was to present a model representing the E_T^N values of mixed solvents at various temperatures using a single mathematical model. The accuracy of the proposed model is evaluated using data sets collected from the literature.

COMPUTATIONAL METHODS

The Jouyban-Acree model was used to correlate different physico-chemical properties including: dielectric constant (3), surface tension (4),

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absolute viscosity (5) and density (6) of solvent mixtures at various temperatures. Theoretical bases of the model for description of the chemical potential of solutes dissolved in mixed solvents (7) and acid dissociation constants in aqueous-organic mixtures (8) have been provided in earlier papers. The Jouyban-Acree model representing the solvatochromic parameter of binary solvent mixtures at a constant temperature is as:

$$\ln\left(E_T^N\right)_m = \phi_1 \ln\left(E_T^N\right)_1 + \phi_2 \ln\left(E_T^N\right)_2 + \phi_1\phi_2 \sum_{i=0}^{2} K_i \left(\phi_1 - \phi_2\right)^i \qquad (1)$$

Where $\left(E_T^N\right)_m$, $\left(E_T^N\right)_1$ and $\left(E_T^N\right)_2$ are the solvatochromic parameters of the mixture and solvents 1 and 2, respectively, ϕ_1 and ϕ_2 are the volume fractions of solvents 1 and 2 in the mixture and K_i represent the model constants calculated by using a no intercept least square method (9). Since, the model contains a number of curve-fitting parameters (K_i terms), it is possible to use weight and/or mole fractions instead of volume fractions. However, it should be noted that the model constants for various fractions will be different. The model could be extended for calculation of the solvatochromic parameter of ternary solvents as:

$$\begin{aligned}\ln\left(E_T^N\right)_m &= \phi_1 \ln\left(E_T^N\right)_1 + \phi_2 \ln\left(E_T^N\right)_2 + \phi_3 \ln\left(E_T^N\right)_3 \\ &+ \phi_1\phi_2 \sum_{i=0}^{2} K_i \left(\phi_1 - \phi_2\right)^i + \phi_1\phi_3 \sum_{i=0}^{2} K_i^{'} \left(\phi_1 - \phi_3\right)^i \\ &+ \phi_2\phi_3 \sum_{i=0}^{2} K_i^{''} \left(\phi_2 - \phi_3\right)^i + \phi_1\phi_2\phi_3 \sum_{i=0}^{2} K_i^{'''} \left(\phi_1 - \phi_2 - \phi_3\right)^i \qquad (2)\end{aligned}$$

Where ϕ_3 denotes the volume fraction of the third solvent, $\left(E_T^N\right)_3$ is the solvatochromic parameter of solvent 3 and K_i , $K_i^{'}$, $K_i^{'}$ and $K_i^{'''}$ are the model constants.

To correlate the solvatochromic parameters of binary solvents at various temperatures (T), an extended form of Jouyban-Acree model could be used as:

$$\begin{aligned}\ln\left(E_T^N\right)_{m,T} &= \phi_1 \ln\left(E_T^N\right)_{1,T} + \phi_2 \ln\left(E_T^N\right)_{2,T} \\ &+ \phi_1\phi_2 \sum_{j=0}^{2} \left[\frac{A_j \left(\phi_1 - \phi_2\right)^j}{T}\right] \qquad (3)\end{aligned}$$

Where $\left(E_T^N\right)_{m,T}$, $\left(E_T^N\right)_{1,T}$ and $\left(E_T^N\right)_{2,T}$ are the solvatochromic parameters 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:

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

Where $\left(E_T^N\right)_{3,T}$ is the solvatochromic parameter of the solvent 3 at temperature T and A_j, B_j, C_j and D_j are the model constants. These model constants are computed by regressing $(\ln\left(E_T^N\right)_{m,T} - \phi_1 \ln\left(E_T^N\right)_{1,T} - \phi_2 \ln\left(E_T^N\right)_{2,T} - \phi_3 \ln\left(E_T^N\right)_{3,T})$ 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.

The calculated E_T^N's were compared with experimental (observed) values and the absolute percentage deviation (APD) was used as an accuracy criterion. The APD was calculated using:

$$APD = \frac{100}{N} \sum \frac{|\,Calculated - Observed\,|}{Observed} \qquad (5)$$

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

$$OAPD = \frac{\sum APD}{Number\ of\ data\ sets\ studied} \qquad (6)$$

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

$$IPD = 100\left(\frac{|\,Calculated - Observed\,|}{Observed}\right) \qquad (7)$$

RESULTS AND DISCUSSION

The available experimental E_T^N of binary solvents at various temperatures were fitted to Jouyban-Acree model and the APD values were computed using back-calculated E_T^N s. This analysis is called correlative analysis. The details of the data, the number of data points, and the APD values are listed in Table 1. The Jouyban-Acree model produced the minimum and maximum APD values respectively for solvent systems like methanol+

Table 1. Details of binary solvent mixtures at various temperatures, the references, number of data points (N), and the average percentage deviations (APDs) for Jouyban-Acree model using correlative and predictive analyses

No.	Solvent 1	Solvent 2	T range	Ref.	Correlative		Predictive	
					N	APD	N	APD
1	Methanol	1-Propanol	298.15-323.15	10	20	0.4	10	0.8
2	Methanol	Acetonitrile	298.15-323.15	10	20	1.8	10	4.7
3	1-Propanol	Acetonitrile	298.15-323.15	10	20	2.1	10	3.4
4	t-Butanol	Dimethyl sulphoxide	298.15-348.15	11	24	0.5	9	0.8
5	i-Propanol	Dimethyl sulphoxide	298.15-348.15	11	30	0.7	18	0.9
6	Methanol	Dimethyl sulphoxide	298.15-348.15	11	27	0.4	15	0.6
7	t-Butanol	Acetonitrile	298.15-348.15	11	21	0.5	9	1.0
8	i-Propanol	Acetonitrile	298.15-348.15	11	27	1.3	15	2.4
9	Methanol	Acetonitrile	298.15-348.15	11	24	3.1	12	6.1
10	t-Butanol	Nitromethane	298.15-348.15	11	24	0.4	12	0.8
11	i-Propanol	Nitromethane	298.15-348.15	11	27	1.4	15	2.1
12	Methanol	Nitromethane	298.15-348.15	11	24	1.8	12	2.9
				OAPD(±SD))		1.2(± 0.9)		2.2 (± 1.8)

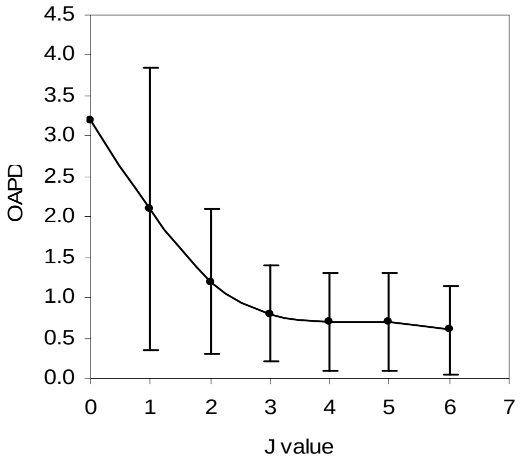

Figure 1. OAPD (±S.D.) of the Jouyban-Acree model with different j values for correlating solvatochromic parameter of binary solvents at various temperatures

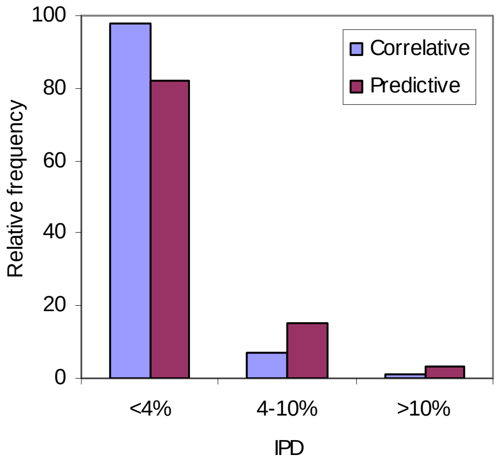

Figure 2. IPD distribution for correlative and predictive analyses of solvatochromic parameter of binary solvents at various temperatures using the Jouyban-Acree model

1-propanol and t-butanol+nitromethane (0.4%) and methanol+acetonitrile (3.1%). The obtained OAPD and its standard deviations is 1.2 ± 0.9% and the results revealed that the proposed model is able to correlate E_T^Ns of binary solvents at various temperatures. It is possible to use more curve-fitting parameters with Jouyban-Acree model to increase the accuracy of the model. As a general rule for mathematical models containing curve-fitting parameters, the more the number of curve-fitting parameters the more accurate the results.

The OAPDs and standard deviations for different numbers of curve-fitting parameters (j values) are shown in Figure 1. The improvement in accuracy with increase in the number of curve-fitting parameters reaches a limiting value after the inclusion of three curve-fitting parameters (j=2). Since one of the main purposes of modeling is to predict unmeasured quantities by minimum experimentally derived information, it is suggested to use the Jouyban-Acree model for calculation of E_T^N of mixed solvents with j=2. The accuracy of the models for calculation of E_T^Ns was also evaluated by studying the distribution of IPD for correlative studies. The relative frequency of IPD values sorted in three error ranges, i.e. ≤4, 4-10 and >10 % and the findings were shown in Figure 2. In more than 97% of the cases IPD values are ≤4 and only in ~0.4% of data points IPD were produced more than 10. To the best of our knowledge, no data of ternary mixtures at various temperatures have been published to check the applicability of equation 4 on real experimental data, however, based on the results which were obtained for binary mixtures, the equation is able to provide accurate results for ternary data.

To test the prediction capability of the model and the rule on real experimental data, a minimum number of experimental E_T^Ns were employed to train the model. The training data points involved the E_T^Ns of pure solvents 1 and 2 at all temperatures under investigation and three E_T^Ns from binary mixtures with nearly constant volume/mole fraction intervals, i.e. ϕ_1=0.3, 0.5 and 0.7 at the highest and lowest temperatures of interest. After training the model, the E_T^Ns at other solvent compositions and temperatures were predicted using interpolation technique. This analysis is called predictive analysis. The obtained APD values are also listed in Table 1. Figure 2 shows IPD distribution in three error subgroups for predictive analysis. The relative frequency of IPDs ≤4 % is 82% which means by using the Jouyban-Acree model and minimum number of data points, it is possible to predict unmeasured E_T^Ns and the probability of prediction error less than 4 % is 0.82.

CONCLUSION

The Jouyban-Acree model produced accurate calculations for E_T^N data of mixed solvent systems at various temperatures. Therefore, it is suggested to be employed in practical applications either for screening experimentally obtained E_T^Ns for detection of possible outliers or for prediction of unmeasured E_T^Ns of mixed solvents at various temperatures after training by using a minimum number of experimental data. The expected mean percentage of deviation for the predicted data is ~ 2.2 %.

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