A global model to predict density of non-aqueous binary solvent mixtures at various temperatures

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The combined form of the Jouyban-Acree model and the calculated Abraham solute parameters has been used to predict the density of binary solvent mixtures at various temperatures. The proposed model has been trained using 290 binary solvent systems at different temperatures (278.15 to 353.15 K) and concentration ranges. The results are discussed in terms of mean relative deviations (MRDs) between computed and experimental densities as an accuracy criterion. The MRD of the proposed model is 1.2 ± 1.9 %, indicating that the proposed model, together with the calculated Abraham parameters, is accureate to reproduce the concentration and temperature dependence of density values of binary solvent mixtures.

Density of mono-solvents and solvent mixtures at various temperatures is widely used in processing and product formulations in many industries. Despite the reported experimental density of mixed solvents at ambient temperature, to avoid extensive density measurements and time consuming literature search, a number of models have been developed to predict density of solvent mixtures. These include the Tovar[1], the Lee[2], the Jimenez[3], and the Jouyban-Acree[4] models. Some of these models require the experimental densities of mono-solvents and density data in mixed solvents to calculate the model constants which may restrict their practical applications. Details of the models and a comprehensive comparison of their correlation and prediction capabilities are presented in a previous publication by our group[4]. It was found that among the investigated models, the Jouyban-Acree model provided the most accurate results for prediction of density values[4].

The aim of this work is to propose globally trained versions of the Jouyban-Acree model to predict the density of binary solvent mixtures at various temperatures using the minimum number of experimental data (densities in mono-solvents). Abraham solute parameters for the individual solutes have been calculated and the accuracy with which these parameters allow prediction of the published density of binary solutions is investigated. Finally, an *ab initio* prediction method has been developed and tested using 290 solvent systems.

Methodology

Density data of non-aqueous binary solvents at various temperatures were collected from the available literature. The Abraham parameters of these liquids were computed using Pharma-Algorithm[5] software[®]. Then, the density data and the calculated parameters were analysed using SPSS 11.0 software.

The Jouyban-Acree model for calculating the density of binary solvents at various temperatures is given by Eq. (1),

$$
\begin{aligned}
\ln \rho_{m,T} = {} & x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} \\
& + J_0 \left[\frac{x_1 x_2}{T} \right] + J_1 \left[\frac{x_1 x_2 (x_1 - x_2)}{T} \right] \\
& + J_2 \left[\frac{x_1 x_2 (x_1 - x_2)^2}{T} \right]
\end{aligned} \qquad \ldots(1)
$$

where $\rho_{m,T}$, $\rho_{1,T}$ and $\rho_{2,T}$ are density of mixed solvents and pure solvents 1 and 2 at temperature T, x_1 and x_2 are the fractions of the solvents 1 and 2, and J_0-J_2 are the model constants. These constants are computed by a least squares analysis[4]. Equation (1) calculates the density of a given binary solvent mixture at various temperatures and it could be re-trained for other sets of binary solvent mixtures.

In order to provide a more comprehensive model, physico-chemical properties of the solvents which

influence the density of a given binary mixture were included. Abraham and co-workers proposed the linear free energy relationship (LFER) to calculate various physico-chemical properties (PP) as follows (Eq. 2),

$$\log PP = c + eE + sS + aA + bB + vV \qquad \dots(2)$$

where c, e, s, a, b and v are the model constants which are indicators of solvent (or system) properties, E is the excess molar refraction, S is dipolarity/polarizability of the analyte, A denotes the analyte's hydrogen-bond acidity, B is the analyte's hydrogen-bond basicity and V is the McGowan volume of the analytes (for the numerical values of these parameters see Table 1 and supplementary data Table S1). The numerical values of c, e, s, a, b and v are not available for most of the investigated solvents and there is no available software to compute these parameters. However, the numerical values of E, S, A, B and V could be calculated using Pharma-Algorithms[5] software®. To incorporate solute-solvent interactions, both parameters are required, but in the case of physico-chemical properties of two solvents in the absence of any solute, the solute parameters of Abraham can also be employed to represent the interactions between two solvents in the mixtures. Therefore, J_i terms of Eq. (1) which stands for the various solvent-solvent interactions in the solution[6], may be represented by Abraham solute parameters and hence Eq. (1) may be re-written as Eq. (3),

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T}$$
$$+\frac{x_1 x_2}{T}\begin{bmatrix} W_0 + W_1(E_1 - E_2)^2 \\ +W_2(S_1 - S_2)^2 + W_3(A_1 - A_2)^2 \\ +W_4(B_1 - B_2)^2 + W_5(V_1 - V_2)^2 \end{bmatrix}$$
$$+\frac{x_1 x_2 (x_1 - x_2)}{T}\begin{bmatrix} W_0' + W_1'(E_1 - E_2)^2 \\ +W_2'(S_1 - S_2)^2 + W_3'(A_1 - A_2)^2 \\ +W_4'(B_1 - B_2)^2 + W_5'(V_1 - V_2)^2 \end{bmatrix}$$
$$+\frac{x_1 x_2 (x_1 - x_2)^2}{T}\begin{bmatrix} W_0'' + W_1''(E_1 - E_2)^2 \\ +W_2''(S_1 - S_2)^2 + W_3''(A_1 - A_2)^2 \\ +W_4''(B_1 - B_2)^2 + W_5''(V_1 - V_2)^2 \end{bmatrix}$$
$$\dots(3)$$

where subscripts 1 and 2 are the properties of solvents 1 and 2, and W terms are the model constants representing the two and three body

interaction energies of the solvents. From a mathematical point of view, they are adjustable curve-fit parameters determined from regressing $\left(\ln\rho_{m,T} - x_1\ln\rho_{1,T} - x_2\ln\rho_{2,T} \right)$ against $\dfrac{x_1 x_2}{T}$,

$$\frac{x_1 x_2 (E_1 - E_2)^2}{T}, \quad \frac{x_1 x_2 (S_1 - S_2)^2}{T}, \quad \frac{x_1 x_2 (A_1 - A_2)^2}{T},$$

$$\frac{x_1 x_2 (B_1 - B_2)^2}{T}, \quad \frac{x_1 x_2 (V_1 - V_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)}{T},$$

$$\frac{x_1 x_2 (x_1 - x_2)(E_1 - E_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)(S_1 - S_2)^2}{T},$$

$$\frac{x_1 x_2 (x_1 - x_2)(A_1 - A_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)(B_1 - B_2)^2}{T},$$

$$\frac{x_1 x_2 (x_1 - x_2)(V_1 - V_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)^2}{T},$$

$$\frac{x_1 x_2 (x_1 - x_2)^2 (E_1 - E_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)^2 (S_1 - S_2)^2}{T},$$

$$\frac{x_1 x_2 (x_1 - x_2)^2 (A_1 - A_2)^2}{T}, \quad \frac{x_1 x_2 (x_1 - x_2)^2 (B_1 - B_2)^2}{T}$$

and $\dfrac{x_1 x_2 (x_1 - x_2)^2 (V_1 - V_2)^2}{T}$, using a no intercept least squares analysis. The Abraham solvation parameters account for possible interactions between solvents 1 and 2 in the mixture. The Jouyban-Acree model can be used to predict the density of different binary mixtures at various temperatures by employing the corresponding experimental ρ_1 and ρ_2 values of the mono-solvents at T. The W terms represent the contribution of different types of interactions in the two-body and three-body interaction terms of the original model. In all computations it is assumed that $\rho_1 > \rho_2$.

The fitness of the experimental data to the model was studied by calculating the correlation coefficient and the accuracy criteria. The accuracy of the density was investigated by computing the mean relative deviation (MRD) using Eq. (4),

$$MRD = \frac{100}{N} \sum \left(\frac{\left| \rho^{Calc} - \rho^{Exp} \right|}{\rho^{Exp}} \right) \qquad \dots(4)$$

where N is the number of data points. The individual relative deviations $IRD = 100 \times \left| \rho^{Calc} - \rho^{Exp} \right| \Big/ \rho^{Exp}$
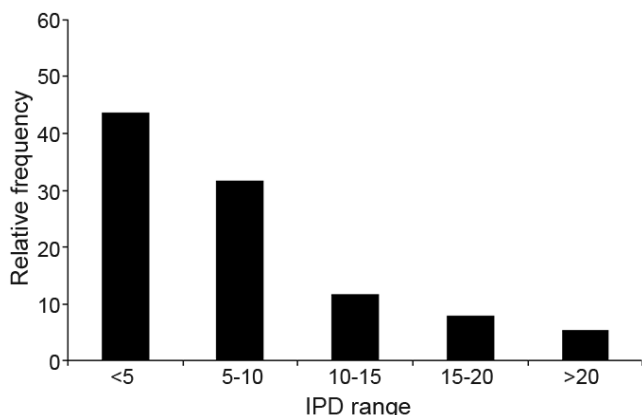
Fig. 1 – The relative frequency of individual relative deviations (IRD) for predicted density of binary mixtures using Eq. (6) employing two experimental density data of mono-solvents.

Fig. 2 – Plot of density values calculated using Eq. (5) versus experimental data.

are also computed to present the error of each data point in 5 subgroups.

Results and discussion

Available density data of binary solvent mixtures at various temperatures were fitted to Eq. (3) and the obtained model is as given in Eq. (5).

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T}$$
$$+ \frac{x_1 x_2}{T} \begin{bmatrix} 101.263(E_1 - E_2)^2 \\ +32.876(A_1 - A_2)^2 \\ -12.805(V_1 - V_2)^2 \end{bmatrix}$$
$$+ \frac{x_1 x_2 (x_1 - x_2)}{T} \begin{bmatrix} 2.023 - 51.335(E_1 - E_2)^2 \\ -26.747(S_1 - S_2)^2 \\ -47.043(A_1 - A_2)^2 \\ +10.738(B_1 - B_2)^2 \\ -19.665(V_1 - V_2)^2 \end{bmatrix}$$
$$+ \frac{x_1 x_2 (x_1 - x_2)^2}{T} \begin{bmatrix} 35.183(E_1 - E_2)^2 \end{bmatrix}$$

…(5)

This model is statistically significant with the F value of 310 ($p < 0.0005$) and covered the $\rho_{m,T}$ range of 0.62 – 2.96 g cm^{-3}. A correlation is considered significant, when the calculated F value is greater than the critical F value obtained from Fisher distribution with the degrees of freedom of (number of variables) and (number of observations – number of variables). In Eq. (5), the degrees of freedom were 10 and 8232, respectively, and the critical F value was 6. When the density data were back-calculated, the resulting MRDs were around 0.0 (i.e. <0.05 % for chlorobutane + butan-1-ol at 288-308 K and ethyl chloroacetate + cyclohexanone at 298-308 K and 9.1 % for
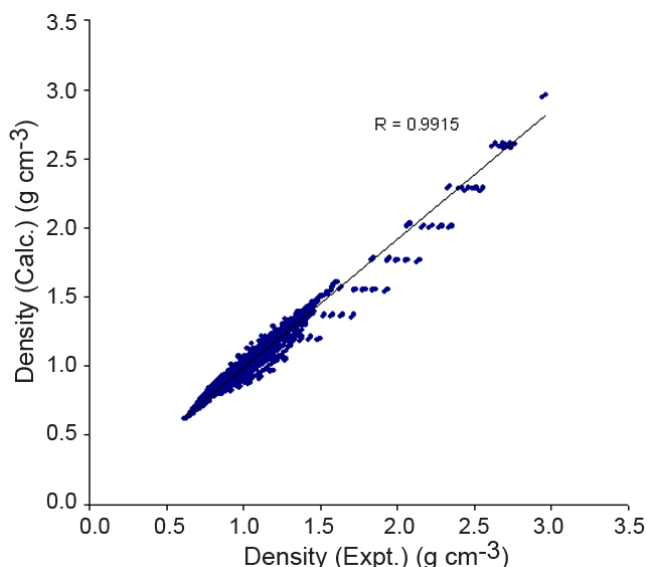
trichloromethane + methanol at 298-308 K) with the overall MRD (± SD) of 1.2 (± 1.3) %. Details of the MRD values for the investigated systems are listed in Table 2 and Supplementary data Table S2. Figure 1 shows the relative frequency of IRDs in different subgroups. It is observed that in more than 65 % of the solvent systems, the IRD is less than 1 %. Details of experimental and calculated density values of the investigated solvent mixtures are listed in Supplementary data Table S3. Figure 2 shows the correlation between the calculated density values from Eq. (5) and the experimental values.

In the present study a trained version of the Jouyban-Acree model is proposed to calculate density of 129 binary mixtures. The model employs two experimental densities of mono-solvents at various temperatures with overall MRDs of 1.1 %. The proposed model provides an accurate method to predict the density of binary solvents from the density of mono-solvents as a function of temperature and concentration. The results show that inclusion of calculated Abraham solute paremters greatly improved the predictions. This model can be recommended for simulation studies in industrial processes.

Supplementary data

Supplementary data associated with this article, viz; Tables S1, S2 and S3, are available in electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA 51A(05) YYYY-YYYY_Suppl Data.pdf.

References

1   Tovar C A, Carballo E, Cerdeiriña C A, Legido J L & Romani L, *Int J Thermophys*, 18 (1997) 761.
2   Lee J - W, Park S B & Lee H, *J Chem Eng Data*, 45 (2000) 166.
3   Jimenez E, Cabanas M, Segade L, Garcia-Garabal S & Casas H, *Fluid Phase Equil*, 180 (2001) 151.
4   Jouyban A, Fathi-Azrbayjani A, Khoubnasabjafari M & Acree Jr W E, *Indian J Chem*, 44A (2005) 1553.
5   Pharma-Algorithms, ADME Boxes, ver. 3.0, (Pharma-Algorithms Inc, Canada) 2006.
6   Flanagan K, Hoover K R, Garza O, Hizon A, Soto T, Villegas N, Acree Jr, W E & Abraham M H, *Phys Chem Liq*, 44 (2006) 377.