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Refractive Index Correlation of Solvent Mixtures at Various Temperatures

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Applicability of a quantitative relationship, *i.e.*, the Jouyban-Acree model, to correlate the refractive index of solvent mixtures with mixture composition and temperature of the mixtures is shown using 29 data sets at various temperatures, with an overall average percentage deviation (OAPD) as accuracy criterion. The OAPD of the Jouyban-Acree model is also compared with those of two previously published equations and the OAPD (± SD) of the proposed and previous equations were 0.02 ± 0.02, 0.04 ± 0.05 and 0.04 ± 0.05, respectively. The differences between OAPD of the Jouyban-Acree model with those of previous models were statistically significant ($p < 0.003$)

Key Words: Refractive index, Mathematical modelling, Solvent mixtures, Jouyban-Acree model.

INTRODUCTION

Refractive index (RI) is one of the physical properties of a solven,t which affects the solution of a number of problems in pharmaceutical and chemical areas. RI values of most of the common solvents are available in literature. Binary and higher order solvent mixtures were used to overcome a number of practical limitations of mono-solvent systems including poor solubility of a solute and/or insufficient analytical performance of mono-solvent systems in chemical analysis. Different models have been reported to calculate RI of mixed solvents at a fixed temperature, including Lorentz-Lorenz, Gladstone-Dale, Arago-Biot, Heller, Wiener, Eykman and Oster equations. Jimenez *et al.*[1] compared these models using RI data of 1,2-ethandiol + 1-propanol and 1,2-ethandiol + 1-butanol and found that the accuracy order of the models was as Wiener, Heller, Newton, Gladstone-Dale, Lorentz-Lorenz, Eykman, Arago-Biot and Oster equations[1]. The main limitation of these models is that they correlate RI values to the solvent composition as independent variable at a constant temperature and the models could not be used to predict RI values at other temperatures. However, RI of the

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solvent depends strongly on temperature and mixed solvent systems at various temperatures have been used in many analytical methods where refractive index detectors were used as detection system. It is obvious that by changes in the RI of the system, fluctuations appear on the detection output and make noises. To provide a single model to correlate RI of mixed solvents at various temperatures, Jimenez and co-workers[1] proposed a two independent variables model as:

$$RI_{m,T} = J_0 + J_1 f_1 + J_2 f_1^2 + J_3(T - 298.15) + J_4(T - 298.15)^2 + J_5 f_1(T - 298.15) + J_6 f_1^2(T - 298.15) + J_7 f_1(T - 298.15)^2 + J_8 f_1^2(T - 298.15)^2 \quad (1)$$

where $RI_{m,T}$ is refractive index of the mixture at temperature T, J_0–J_8 are the model constants, f_1 is the mole fraction of the solvent 1 in the mixture. Lee and co-workers[2] have used eqn. (2) for computing $RI_{m,T}$ and shown its accuracy using RI data of water + 1,3-propandiol at 298–323 K.

$$RI_{m,T} = M_0 + M_1 f_1 + M_2 f_1^2 + M_3 T + M_4 f_1 T + M_5 f_1^2 T + M_6 T^2 + M_7 f_1 T^2 + M_8 f_1^2 T^2 \quad (2)$$

where M_0–M_8 are the model constants. The aim of this communication is to propose an alternative model for calculating RI of solvent mixtures at various temperatures and compare its accuracy with eqns. (1) and (2).

RESULTS AND DISCUSSION

The Jouyban-Acree model has been presented for calculating different physico-chemical properties of solvent mixtures at various temperatures including dielectric constants[3], surface tensions[4], absolute viscosities[5] and density[6]. The adopted model for calculating RI of binary solvent mixtures at various temperatures is:

$$\ln RI_{m,T} = f_1 \ln RI_{1,T} + f_2 \ln RI_{2,T} + f_1 f_2 \sum_{j=0}^{2} \left[\frac{A_j (f_1 - f_2)^j}{T} \right] \quad (3)$$

where f_2 is the volume (mole/weight) fraction of solvent 2 in the mixture, $RI_{1,T}$ and $RI_{2,T}$ are the values of solvents 1 and 2 at T, and A_j is the model constant.

The performance of the equations for calculating the refractive index of the systems at various temperatures has been tested with 29 systems including aqueous and non-aqueous binary liquid mixtures collected from literature[1,2,7-13]. The agreements between experimental (RI_{exp}) and calculated (RI_{calc}) refractive indices for the systems were shown in the form of average percentage deviation (APD):

$$APD = \frac{100}{N} \sum_{1}^{N} \left\{ \frac{|RI_{calc} - RI_{exp}|}{RI_{exp}} \right\}$$

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

$$OAPD = \frac{\sum_{1}^{29} APD}{29}$$

In order to examine the validity of eqns. (1)–(3) for the correlation of the refractive indices of binary solvent mixtures at various temperatures, the data were fitted to the models and the APD values were computed using back-calculated refractive indices listed in Table-1.

TABLE-1
DETAILS OF DATA SETS, THE REFERENCES, NUMBER OF DATA POINTS (N) AND AVERAGE PERCENTAGE DEVIATIONS (APD), OVERALL APD (OAPD) AND STANDARD DEVIATION (SD) OF THE JOUYBAN-ACREE, JIMENEZ AND LEE MODELS

No.	Solvent 1	Solvent 2	Ref.	N	Jouyban-Acree	Jimenez	Lee
1.	Ethanediol	1-Propanol	1	61	0.1033	0.1091	0.1218
2.	Ethanediol	1-Butanol	1	59	0.0123	0.0061	0.0062
3.	Methanol	1-Chlorobutane	7	39	0.0374	0.0549	0.0549
4.	Ethanol	1-Chlorobutane	7	39	0.0107	0.0203	0.0205
5.	Ethanol	1-Chlorobutane	7	39	0.0107	0.0203	0.0205
6.	1-Butanol	1-Chlorobutane	7	39	0.0075	0.0081	0.0084
7.	4-Methyl-2-pentanone	Ethyl benzoate	8	42	0.0564	0.1149	0.1170
8.	Ethyl chloroacetate	Hexane	9	33	0.0156	0.0131	0.0155
9.	Ethyl chloroacetate	Heptane	9	33	0.0099	0.0108	0.0111
10.	Ethyl chloroacetate	Octane	9	33	0.0152	0.0122	0.0120
11.	Ethyl chloroacetate	Nonane	9	33	0.0072	0.0155	0.0155
12.	Ethyl chloroacetate	Decan	9	33	0.0064	0.0245	0.0245
13.	Ethyl chloroacetate	Dodecane	9	33	0.0066	0.0192	0.0192
14.	1,4-Dioxane	Ethanediol	10	33	0.0416	0.0247	0.0265
15.	1,4-Dioxane	Hexane	10	33	0.0196	0.0249	0.0249
16.	1,4-Dioxane	Tri-*n*-butylamine	10	33	0.0091	0.0083	0.0086
17.	1,4-Dioxane	Tri-*n*-butylamine	10	33	0.0084	0.0135	0.0134
18.	1,3-Propanediol	Water	2	42	0.0053	0.0447	0.0447
19.	Tri-*n*-butylamine	Triethylamine	11	33	0.0289	0.0402	0.0398
20.	Tri-*n*-butylamine	Tetrahydrofuran	11	33	0.0272	0.0510	0.0507
21.	Tri-*n*-butylamine	Tetradecane	11	33	0.0064	0.0062	0.0063
22.	Tri-*n*-butylamine	Tetracholoroethylene	11	33	0.0272	0.0760	0.0767
23.	Tri-*n*-butylamine	Pyridine	11	33	0.0385	0.1349	0.1351
24.	Tri-*n*-butylamine	Trichloroethylene	11	33	0.0190	0.0706	0.0707
25.	Cyclohexane	2,2,4-Trimethylpentane	12	126	0.0222	0.0196	0.0197
26.	1,4-Dioxane	Ethyl acetoacetate	13	33	0.0082	0.0061	0.0066
27.	1,4-Dioxane	Diethyl oxalate	13	33	0.0104	0.0066	0.0073
28.	1,4-Dioxane	Diethyl phthalate	13	33	0.0240	0.0879	0.0879
29.	1,4-Dioxane	Dioctyl phthalate	13	33	0.0564	0.1889	0.1893
				OAPD	0.0225	0.0425	0.0433
				SD	0.0213	0.0458	0.0466

This numerical analysis could be used to screen the experimentally obtained data to detect possible outliers for re-determination. For Jouyban-Acree model the solvent mixture of 1,3-propandiol + water with APD = 0.0053 produced the minimum APD while 1,2-ethandiol + 1-propanol with APD = 0.1033% produced the maximum APD value. Minimum APDs of Jimenez and Lee models were 0.0061 (1,2-ethandiol + 1-butanol) and 0.0063 (tri-*n*-butylamine + tetradecane) and the maximum APDs were 0.1889 (1,4-dioxane + dioctyl phthalate) and 0.1893 (1,4-dioxane + dioctyl phthalate), respectively. The OAPD ± SD of the Jouyban-Acree model and those of previous models were 0.0225 ± 0.0213, 0.0425 ± 0.0458 and 0.0433 ± 0.0466. The OAPD differences between the proposed and the previous models were statistically evaluated using paired *t*-test and the results showed that the proposed model is more accurate than two previous models ($p < 0.003$). There was no significant difference between OAPD of Jimenez and Lee models (paired *t*-test, $p > 0.05$) and this could be justified by mathematical interpretation of their models. The models are originally the same and using a simple algebraic manipulation, eqn. (1) could be converted to eqn. (2).

As a general conclusion, the proposed model was able to represent refractive indices of solvent mixtures at various temperatures more accurately than previously published models.

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