NOTE

Application of Refractive Index Mixing Rules in Binary Liquid Mixtures

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A comparative study of five mixing rules of refractive index has been carried out to test their validity for four binary liquid mixtures at wide range of composition and temperature. Comparison of various rules has been expressed in terms of average percentage deviation. All mixing rules perform well within the limit of experimental error but the performance of Heller's relation (H) and Wiener's relation (W) are comparatively better than those of others.

The most widely used theoretical rules for predicting refractivity of binary liquid mixtures are due to Lorentz-Lorenz[1, 2] (L-L) and Wiener[3] (W). The Gladstone Dale[4] (G-D), Argo-Biot[5] (A-B) and Heller's[6] (H) relations are found to follow either Lorentz-Lorenz equation or Weiner's equation for dilute solutions especially when the refractive indices of both the liquids are nearly the same. Most of the mixing rules do not account for the changes in volume and refractivity on mixing. This problem was attacked recently by Aminabhavi *et al.*,[7, 8] who pointed out the usefulness of mixing rules in treating the binary refractive index and density-data.[9]

The various mixing rules used to evaluate the refractive indices of the binary mixtures are:

Lorentz-Lorenz (L-L) relation[1, 2]:

$$\left[\frac{\eta_{12}^2-1}{\eta_{12}^2+2}\right]\frac{1}{P_{12}}=\left[\frac{\eta_1^2-1}{\eta_1^2+1}\right]\frac{W_1}{P_1}+\left[\frac{\eta_2^2-1}{\eta_2^2+2}\right]\frac{W_2}{P_2} \qquad (1)$$

Wiener's (W) relation[3]:

$$\left[\frac{\eta_{12}^2-\eta_1^2}{\eta_{12}^2+2\eta_1}\right]=\phi_2\left[\frac{\eta_2^2-\eta_1^2}{\eta_2^2+2\eta_1^2}\right] \qquad (2)$$

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Gladstone-Dale (G-D) relation[4]:

$$\left[\frac{\eta_{12}-1}{P_{12}}\right]=\left[\frac{\eta_1-1}{P_1}\right]W_1+\left[\frac{\eta_2-1}{P_2}\right]W_2 \tag{3}$$

Argo-Biot (A-B) relation[5]:

$$\eta_{12}=\eta_1\,\phi_1+\eta_2\phi \tag{4}$$

Heller's (H) relation[6]:

$$\left[\frac{\eta_{12}-\eta_1}{\eta_1}\right]=\frac{3}{2}\,\phi_2\left[\frac{m_1^2-1}{m_1^2+2}\right] \tag{5}$$

In all above the relations the notations used have their usual meanings as given earlier.[7]

TABLE-1
AVERAGE PERCENTAGE DEVIATION OF REFRACTIVE INDEX FOR BINARY LIQUID MIXTURES USING VARIOUS MIXING RULES

Systems	(L-L) (Eqn. 1)	(W) (Eqn. 2)	(G-D) (Eqn. 3)	(A-B) (Eqn. 4)	(H) (Eqn. 5)
			T = 298.15 K		
Bromoform + butanol-1	−0.1088	−0.0012	−0.3940	−0.2286	−0.0249
Bromoform + pentanol-1	−0.8578	−0.0989	−0.7502	−0.5427	−0.0065
Bromoform + hexanol-1	−2.3588	−0.1359	−2.2620	−0.7587	−0.0524
Bromoform + heptanol-1	−3.3689	−0.2261	−2.1177	−0.9766	−0.0727
			T = 303.15 K		
Bromoform + butanol-1	−0.0079	−0.6426	−0.2118	−0.2460	−0.0857
Bromoform + pentanol-1	−1.3168	−0.1282	−1.3464	−0.5402	−0.0567
Bromoform + hexanol-1	−2.1827	−0.0661	−0.6196	−0.9260	−0.0661
Bromoform + heptanol-1	−4.6209	−0.1491	−3.0938	−0.9936	−0.0456
			T = 308.15 K		
Bromoform + butanol-1	−0.2690	−0.1375	−0.2207	−0.2337	−0.0244
Bromoform + pentanol-1	−0.8293	−0.5443	−0.2450	−0.5268	−0.0406
Bromoform + hexanol-1	−2.1294	−0.1291	−1.8546	−0.8058	−0.0551
Bromoform + heptanol-1	−3.1258	−0.3068	−2.6005	−0.5328	−0.3687

In the present work, an attempt has been made to study the validity of various mixing rules for predicting refractivity of four binary mixtures comprising bromoform as first component and butanol-1, pentanol-1, hexanol-1 and heptanol-1 as the second component at wide range of composition at temperature. The refractive index for above four systems has been evaluated at 298.15 K, 303.15 K and 308.15 K using various mixing rules. The average percentage deviations have been determined for their validity and comparison. The results have been shown in Table-1. The first column of the table comprises systems under investigation. The second, third, fourth, fifth and sixth columns contain the average percentage deviation in refractive index, obtained from Lorentz relation

(L-L), Wiener's relation (W), Glad-stone Dale relation (G-D), Argo Biot-relation (A-B) and Heller's relation (H) respectively.

The experimental values and other data required for calculation has been collected from the literature.[10]

A close look at the table reveals that all the mixing rules give good agreement with the experimental values. Deviations in all the cases are all negative showing theoretical results are higher than the experimental values. This may be attributed to polar nature of alcohols, used as second component, and to the fact that hydrogen bond plays role in reducing the experimental values of refractive index. It is more pronounced in theoretical results obtained by Argo-Biot relation. The deviation is highest here, as seen in column fifth of the table. Argo-Biot relation is actually mole fraction average relation, only useful in the mixture where interaction is the least. It has been well observed in my previous work.[11]

In all the systems, Heller's relation gave the best result with minimum average percentage deviation followed by Wiener relation, as observed in columns sixth and fourth, respectively of the table.

From the above investigation it may be concluded that all the five theoretical mixing rules discussed are interrelated in simple quantitative manner and perform well within the limits of experimental error. The deviation between the theoretical and observed values of refractive index for all the systems under the present investigation may be reduced if the concept of excess volume (V^E), which is an indirect measurement of interaction, is taken into consideration in various mixing rules, as suggested by Aminabhavi *et al.*[7, 8]

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(*Received*: 29 December 1997; *Accepted:* 17 February 1998) AJC-1461