Asian Journal of Chemistry Vol. 15, No. 2 (2003), 1158–1160

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 five binary liquid mixtures at a wide range of compositions at 298.15 K. Comparison of various rules has been expressed in terms of average percentage deviation. All the mixing rules perform well within the limit of experimental error but performance of Lorentz-Lorenz (L-L) and Gladstone-Dale (G-D) relation is comparatively better than those of others.

Key Words: Refractive index, Binary liquid mixtures.

The most widely used theoretical rules for predicting refractivity of binary liquid mixtures are due to Lorentz-Lorenz (L-L)[1,2] and Gladstone-Dale (G-D)[3], Wiener (W)[4], Argo-Biot(A-B)[5] and Eykman (EK)[6]. The Gladstone-Dale (G-D), Argo-Biot (A-B) relations are found to follow either Lorentz-Lorenz equation or Wiener equation for dilute solutions especially when the refractive index of both the liquids is nearly the same. Most of the mixing rules do not account for the changes in volume and refractivity on mixing. This problem was attached recently by Aminabhavi *et al.*[8], who pointed out the usefulness of mixing rules in treating the binary refractive index and density data[9–12].

A similar attempt is made here for 5 binary liquid mixtures whose refractive index data are available in the literature[13, 14]. The following mixture rules where used to calculate the refractive index of the binary mixtures.

Lorentz-Lorenz (L-L) relation

$$\left[\frac{n_{12}^2-1}{n_{12}^2+2}\right]\frac{i}{\rho_{12}}=\left[\frac{n_1^2-1}{n_1^2+2}\right]\frac{w_1}{\rho_1}+\left[\frac{n_2^2-1}{n_2^2+2}\right]\frac{w_2}{\rho_2} \quad (1)$$

Gladstone-Dale (G-D) relation

$$\left[\frac{n_{12}-1}{\rho_{12}}\right]=\left[\frac{n_1-1}{\rho_1}\right]w_1+\left[\frac{n_2-1}{\rho_2}\right]w_2 \quad (2)$$

Wiener's (W) relation:

$$\left[\frac{n_{12}^2-n_1^2}{n_{12}^2+2n_1^2}\right]=\phi_2\left[\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right] \quad (3)$$

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Argo-Biot (A-B) relation

$$n_{12} = n_1\phi_1 + n_2\phi_2 \tag{4}$$

Eykman's relation

$$\left[\frac{n_{12}^2 - 1}{n_{12} + 0.4}\right]\overline{V}_{12} = \left[\frac{n_{12}^2 - 1}{n_{12} + 0.4}\right]\overline{V}_{1} + \left[\frac{n_2^2 - 1}{n_2 + 0.4}\right]\overline{V}_{2} \tag{5}$$

In equation (5) $\overline{V}_1$, $\overline{V}_2$ and $\overline{V}_{12}$ are the molar volumes of the pure components and mixture respectively as shown below:

$$\overline{V}_1 = \frac{M_1X_1}{\rho_1}, \quad \overline{V}_2 = \frac{M_2X_2}{\rho_2}, \quad \overline{V}_{12} = \frac{M_1X_1 + M_2X_2}{\rho_{12}}$$

In the above relation M_1, M_2 and X_1, X_2 are the molecular weights and mole fractions of the respective components. Other notations used in the above equations have their usual meanings as given earlier.

In the present paper using density and refractive index data[13], we have made an attempt to study the validity of mixing rules for predicting refractivity of binary mixtures containing water-methanol, water-ethanol, 1-octanol-methanol, 1-octanol-ethanol and 1-octanol-water.

We have computed the refractivity of mixture using mixing rules (eqns. 1–5) and compared those with the experimental values to obtain the average percentage deviation which is recorded in Table-1.

TABLE-1
AVERAGE PERCENTAGE DEVIATION (APD) FOR VARIOUS REFRACTIVE RULES AT 25°C

System	10^3 (APD)				
	L-L (eqn. 1)	G-D (eqn. 2)	Wiener (eqn. 3)	A-B (eqn. 4)	Eykman (eqn. 5)
1. Water + methanol	3.73	4.12	4.62	6.70	456.80
2. Water + ethanol	6.90	8.50	12.22	12.30	976.50
3. Octanol + methanol	22.00	21.70	27.80	22.49	70.30
4. Octanol + ethanol	11.99	10.83	9.43	10.33	5.90
5. Octanol + water	5.70	5.40	13.50	7.90	248.00

Table-1 shows that all the relations give good agreement with the experimental values, especially the Loretz-Lorenz (L-L) and Gladstone-Dale (G-D) relations as also observed by other workers[10–12]. The exception is in the case of system 3, since the Lorentz-Lorenz (L-L) relation is based on a sounder theoretical basis, its performance is found to be better. For the systems 1 and 5, Gladstone Dale (G-D) relation appears to give quite satisfactory result. Wiener's (W) relation has been found to predict satisfactory agreement generally. The systems 1 and 5 exhibit best performance for A-B relations. Ekyman (Ek) relation shows better results in the systems 3 and 4 and debits for other systems. Ultimately it was found that Lorentz-Lorenz (L-L), Gladstone-Dale (G-D) and Wiener (W) relations provide very good results followed by Argo-Biot and Ekyman's relations.

Standard average percentage deviations from minimum to maximum range from 3.7×10^{-3} to 1.009, which are much much better than those reported by other workers[10]. The deviation between the theoretical and observed values of refractive indices for all the systems under the present investigation may be reduced if the concept of excess volume (V^E) is taken into consideration in various mixing rules as suggested by Amminabhavi *et al.*[7–8]

ACKNOWLEDGEMENTS

The authors are grateful to Dr. H.B. Singh, Principal, K.S. Saket P.G. College, Faizabad and Dr. V.N. Srivastava, Head of the chemistry department for encouraging and for providing library facilities during the work.

REFERENCES

1. H.A. Lorentz, Theory of Electrons (Leipzig) (1906).
2. *Wied. Ann*, **9**, 641 (1980); **11**, 70 (1980).
3. D. Dale and F. Gladstone, *Phill. Trans.*, **148**, 887 (1958); **153**, 317 (1964).
4. O. Wiener, *Leipzig Ber*, **62**, 256 (1910).
5. D. F. J. Argo and J.B. Biot, *Mem. Acad. France*, 7 (1906).
6. J.F. Ekyman, *Rec. Pays Bas Belg.*, **14**, 185 (1895).
7. T.M. Aminabhavi and P. Munk, *Macromolecules*, **12**, 1186 (1979).
8. T.M. Aminabhavi, *J. Chem. Engg. Data*, **29**, 54 (1984).
9. E.L. Heri and J.G. Brewer, *J. Chem. Engg. Data*, **16**, 313 (1971).
10. J.D. Pandey, A.K. Shukla, R.K. Shukla and R.D. Rai, *Indian J. Chem.*, **27A**, 336 (1988).
11. M.C. Saxena, *Asian J. Chem.*, **10**, 636 (1998).
12. S.C. Bhatia, Neelima Tripathi and G.P. Dubey, *Indian J. Chem.*, **41A**, 226 (2002).
13. A. Arce, A. Blanco, Anasoto and I. Vidal, *J. Chem. Engg. Data*, **38**, 336 (1993).
14. C.R.C. Handbook of Chemistry and Physics, Cole Press, Boca Raton, Florida, 60th Edn. (1979–80).

(*Received*: 21 September 2002; *Accepted:* 22 January 2003) AJC-3000