Comment on "Viscosity, Density, and Refractive Index of Some (Ester + Hydrocarbon) Binary Mixtures at 303.15 K and 313.15 K" (Rathnam, M. V.; Mohite, S.; Kumar, M. S. S. J. Chem. Eng. Data 2005, 50, 325–329)

Shantilal Oswal*

Department of Chemistry, Veer Narmad South Gujarat University, Surat 395 007, India

In a recent paper, Rathnam et al.¹ reported on the viscosity, density, and refractive index of some (ester + hydrocarbon) binary mixtures at 303.15 K and 313.15 K. The authors stated that they calculated the values of η given in their Table 2 from the Frenkel equation, their eq 3, and the values of ΔR also given in their Table 2 from their eq 4 where the values of R_m were calculated from the Lorentz–Lorentz equation. It was concluded by them that the Frenkel equation predicts the ester + hydrocarbon mixture viscosities reasonably well at both temperatures and that the agreement between experimental and calculated values was good and within the experimental uncertainity. The deviations in molar refraction, ΔR , were very large and positive, having maximum values in the range (12.981 to 19.989) cm³·mol⁻¹. These reported values are unexpectedly high and unreasonable for the systems studied.

I have recalculated these deviations, and it is clear that the authors have made errors in their calculations of both the deviations in molar refraction ΔR and the mixture viscosities from the Frenkel equation and the viscosity deviations $\Delta \eta$. These recalculated values are reported in Table 1 of the Supporting Information. It was assumed that Rathnam et al. used the Lorentz–Lorenz equation in the form below for both the pure fluids and the mixtures:

$$R_{\rm M} = \left(\frac{n_{\rm D}^2 - 1}{n_{\rm D}^2 + 2}\right) (M/\rho) \tag{1}$$

where n_D , M, and ρ represent refractive index, molar mass ($x_1M_1 + x_2M_2$), and density of the fluid. The values of the standard deviations σ between experimental and calculated viscosities

* E-mail: sloswal@sify.com.

from eq 3 based on

$$\sigma = \left[\frac{1}{n-1}\sum\left\{\frac{(\eta_{\exp} - \eta_{cal})}{\eta_{\exp}}\right\}^2\right] 1/2$$
(2)

where *n* is the number of data points are reported in Table 2 of the Supporting Information. A comparison of the values in Table 1 of the Supporting Information and the values in their Table 2 make clear that the authors' results on the deviations in molar refraction ΔR and the viscosities from the Frenkel equation are incorrect.

Editors Note: The authors of the Rathnam et al. paper were asked to respond to this comment by Oswal. They stated that the molar refraction was calculated from $\Delta R = R_M - \sum R_i \phi_i$ where $\phi_i = (x_i M_i / \rho_i) / (\sum_{1}^{i} x_i M_i / \rho_i)$ with R_M calculated from eq 1 above and not from their eq 4 as given in their paper. Calculation of ΔR with this equation does not give the values reported in their Table 1. They stated that their calculated viscosity values were those obtained from their eq 3 while the $\Delta \eta$ values were calculated from their eq 1. Many of the values of both η (eq 3) and $\Delta \eta$ in Table 2 of the Supporting Information of this (Oswal) paper are not consistent with the statement of Rathnam et al.

Supporting Information Available:

Two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

 Rathnam, M. V.; Mohite, S.: Kumar, M. S. S. Viscosity, density, and refractive index of some (ester + hydrocarbon) binary mixtures at 303.15 K and 313.15 K. J. Chem. Eng. Data 2005, 50, 325–329.

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