Comments Regarding “Study of Molecular Interactions In Binary Mixtures of Formamide with 2-Methoxyethanol and 2-Ethoxyethanol at Varying Temperatures”

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Abstract

Communication shows that there are several errors in the experimental density and excess molar volume data reported in the manuscript, as well as errors associated with the computation of the infinite dilution partial molar volumes of formamide, 2-methoxyethanol and 2-ethoxyethanol.

Key Words: Excess Molar Volume, Formamide, 2-Methoxyethanol, 2-Ethoxyethanol, Density

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In a recent paper appearing in Physics and Chemistry of Liquids journal Singh et al. [1] reported densities, refractive indices, ultrasonic velocities and viscosities of binary formamide + 2-methoxyethanol and formamide + 2-ethoxyethanol mixtures over the entire binary composition range. Measurements were performed at atmospheric pressure and at 10 K intervals over the temperature range from 293 K to 313 K. The excess molar volumes, \( V^{\text{ex}} \), given numerically in Tables 1 and 2, and depicted graphically in Figure 1 of the manuscript, show a fairly large volume contraction upon mixing. For example, in the case of the binary formamide + 2-ethoxyethanol system the excess molar volume attains a value of \( V^{\text{ex}} = -2.33 \text{ cm}^3 \text{ mol}^{-1} \) at a formamide mole fraction composition of \( x_{\text{form}} = 0.1539 \) at both 293 and 303 K. If one carefully examines the experimental data in Table 2 of the manuscript one discovers that the numerical entries at 293 K are repeated again at 303 K for the entire set of nine mixture compositions plus both pure solvent components. This is hard to believe as organic liquids normally expand with increasing temperature. There are clearly errors in the numerical entries in Table 2.

Singh et al. described the calculated molar excess quantities with the Redlich-Kister polynomial equation:

\[
Y^{\text{ex}} = x_{\text{form}} (1 - x_{\text{form}}) \sum_{i=1}^{5} a_i (2x_{\text{form}} - 1)^{i-1}
\]  

(1)

and then used the equation coefficients obtained from the regression analyses of the \( V^{\text{ex}} \) data to calculate the partial molar volumes of formamide at infinite dilution in the 2-alkoxyethanol,

\[
V_{\text{form}}^{\text{o}} = V_{\text{form}}^{\ast} + \sum_{i=1}^{5} a_i (-1)^{i-1}
\]  

(2)

and the partial molar volumes of the 2-alkoxyethanol at infinite dilution in formamide, \( V_{\text{alkoxy}}^{\ast} \).
\[ V'_{alkoxy} = V'_{alkoxy} + \sum_{i=1}^{5} a_i \]  

where \( V'_{form} \) and \( V'_{alkoxy} \) denote the molar volumes of the pure liquid formamide and 2-alkoxyethanol, respectively. Substitution of the numerical \( a_i \) values in Table 5 for the formamide + 2-methoxyethanol system at 303 K into eqns. 2 and 3 yields

\[
V'_{form} = 40.0092 - 1.6192 (-1)^0 + 19.1550 (-1)^1 + 10.4608 (-1)^2 - 39.8062 (-1)^3 - 30.4968 (-1)^4 \\
= 39.0052 \text{ cm}^3 \text{ mol}^{-1} \tag{4}
\]

and

\[
= 37.3544 \text{ cm}^3 \text{ mol}^{-1} \tag{5}
\]

which are not even close to the values of \( V'_{form} = 40.2505 \text{ cm}^3 \text{ mol}^{-1} \) and \( V'_{methoxy} = 81.2550 \text{ cm}^3 \text{ mol}^{-1} \) given by the authors in Table 8. Similarly, the partial molar volumes at infinite dilution for the binary formamide + 2-ethoxyethanol system are miscalculated. The values of \( V'_{form} \) and \( V'_{alkoxy} \) given in Table 8 are not consistent with the Redlich-Kister equation coefficients reported in the paper.

Singh et al. [1] also described the viscosity deviation, \( \Delta \eta \), in terms of the Redlich-Kister polynomial equation, with the calculated \( a_i \) values given in Table 6 of the manuscript. Careful examination of equation 1 reveals that \( \Delta \eta = x_{form} (1 - x_{form}) a_1 \) at \( x_{form} = 0.50 \) because the other terms in the polynomial equation are zero at this binary mixture composition. The numerical value of the first equation coefficient that is given in Table 6 for the binary formamide + 2-ethoxyethanol system at 293 K is \( a_1 = -0.8950 \), which would result in a calculated value of \( \Delta \eta \approx -0.224 \text{ mPa s} \) at \( x_{form} = 0.50 \). The numerical entries of \( \Delta \eta \) given in Table 4 are all positive
values. There are errors in this set of equation coefficients. One also notes that the first equation coefficient for $\Delta k_s$ in the formamide + 2-methoxyethanol system at 303 K is positive yet all of the values in Table 3 are negative, and that the first four equation coefficients for $H^{ex}$ in the formamide + 2-ethoxyethanol system at 293 K are positive yet all of the estimated numerical $H^{ex}$ values in Table 4 are negative.

A search of the published chemical literature found independent excess molar volume data for binary formamide + 2-methoxyethanol and formamide + 2-ethoxyethanol mixtures. Awasthi and Awasthi [2] determined the ultrasonic velocities and densities of both binary systems at 303 K, 313 K and 323 K. It should be noted that there are significant differences in the $V^{ex}$ values reported by the two research groups. The excess molar volumes reported by Awashti and Awasthi are not nearly as negative as the values reported by Singh et al., $V^{ex} \approx -1.30$ cm$^3$ mol$^{-1}$ [1] versus $V^{ex} \approx -0.33$ cm$^3$ mol$^{-1}$ [2] for the formamide + 2-methoxyethanol system at $x_{form} = 0.63$ and 313 K, and $V^{ex} \approx -2.58$ cm$^3$ mol$^{-1}$ [1] versus $V^{ex} \approx -0.56$ cm$^3$ mol$^{-1}$ [2] for the formamide + 2-ethoxyethanol system at $x_{form} = 0.50$ and 313 K. At least one of the two sets of experimental data is in error.

In cases where significant differences in published values exist it is sometimes difficult to know which set(s) of values is/are in error. There is one additional set of excess molar volume data for the binary formamide + 2-methoxymethanol system. Roy and coworkers [3] measured the viscosities, densities, and speeds of sound for the binary mixtures of formamide with 2-methoxyethanol, acetophenone, acetonitrile, 1,2-dimethoxyethane, and dimethyl sulfoxide at 298 K, 308 K and 318 K. The excess molar volume data of Roy and coworkers: $V^{ex} \approx -0.36$ cm$^3$ mol$^{-1}$ at 308 K and $x_{form} = 0.63$; and $V^{ex} \approx -0.38$ cm$^3$ mol$^{-1}$ at 318 K and $x_{form} = 0.63$, is in reasonably good agreement with the published values of Aswathi and Aswathi. One further
notes that the published values of Roy and coworkers fell on smooth curves when plotted versus mole fraction of formamide, and did not exhibit the unusual compositional dependence depicted in Figure 1a in the Singh et al. paper near $x_{\text{form}} = 0.30$. Given the above observations readers may wish exercise caution in using the mathematical Redlich-Kister equations given in the paper, and in using the experimental density and excess molar volume data of the binary formamide + 2-methoxyethanol and formamide + 2-ethoxyethanol given by Singh et al.

References

