COMMENTS CONCERNING “STUDY OF MOLECULAR INTERACTION IN BINARY
LIQUID MIXTURES OF ETHYL ACETOACETATE WITH CHLOROFORM AND
DIMETHYLSULPHOXIDE USING EXCESS ACOUSTIC PARAMETERS AND
SPECTROSCOPIC METHODS”

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Abstract

The measured excess molar volume data in the recently published paper for the binary chloroform + ethyl acetoacetate system is shown to differ significantly from previously published data. Excess adiabatic compressibilities reported in the paper are shown to be calculated from an incorrect thermodynamic expression.

Key words and phrases: excess molar volumes, excess adiabatic compressibilities, chloroform, ethyl acetoacetate, dimethylsulphoxide

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In a recent article appearing in This Journal Yadav and coworkers [1] reported experimental densities and ultrasonic velocities for binary chloroform + ethyl acetoacetate and dimethyl sulfoxide + ethyl acetoacetate mixtures at 298 K. Measurements covered the entire range of mole fraction composition. Excess molar volumes, V^E , of the chloroform + ethyl acetoacetate binary system, calculated from the authors' measured densities, exhibited an unusual mole fraction composition dependence as shown in Figure 1 (filled squares). Excess molar volumes generally exhibit either a smooth parabolic or s-shape curve independence which can be described mathematically by the Redlich-Kister equation

$$V^E = x_1 x_2 \sum_{i=0}^n A_i (x_1 - x_2)^i \quad (1)$$

using only a few curve-fit equation coefficients (A_i). The dependence depicted in Figure 1 is highly skewed towards the large chloroform mole fractions (x_1) and the positive numerical V^E values of $2.6 \text{ cm}^3 \text{ mol}^{-1}$ are much larger than would be expected based on the molecular shapes and hydrogen-bonding character of the two molecules. The unusual V^E versus mole fraction shaped curve and the large positive V^E values were likely the result of the authors performing the density measurements at ambient room temperature, $T = 298 \pm 1 \text{ K}$. While the author's claimed uncertainty of $\pm 1 \text{ K}$ may be misprint in the article, there is no mention of constant temperature bath being used in any of the experimental methods. The authors simply state "All the experiments have been done at room temperature ($25 \pm 1^\circ\text{C}$).". To obtain accurate thermodynamic V^E data one needs to maintain better temperature control. An uncertainty of $\pm 1 \text{ K}$ is simply too large of a temperature variation to obtain accurate and precise V^E values. The authors need to clarify this point, and inform journal readers how the temperature was maintained for both the volumetric and acoustical measurements. It is the authors' responsibility to adequately describe the experimental methodology.

A search of the published literature found one additional set of density measurements for binary chloroform + ethyl acetoacetate mixtures. Roy *et al.* [2] previously measured the densities of binary mixtures containing ethyl acetoacetate with dichloromethane, chloroform, carbon tetrachloride, methyl acetate, acetonitrile, nitromethane and acetic acid at 298 ± 0.01 K. The V^E values for the chloroform + ethyl acetoacetate reported by Roy *et al.* [2] are negative over the entire mole fraction range (filled diamonds in Figure 1). The authors explained the negative V^E values in terms of specific interactions, most probably through intermolecular hydrogen bonding the component liquids, dipole-dipole or dipole-induced dipole interactions. We believe that this latter set of V^E values are more realistic because of the much better temperature control (± 0.01 K versus ± 1 K) and the likelihood that chloroform and ethyl acetoacetate would form an intermolecular hydrogen-bonded complex.

Yadav and coworkers [1] also calculated the excess adiabatic compressibility, β_s^E , as

$$\beta_s^E = \beta_{s,\text{mixture}} - x_1 \beta_{s,1} + x_2 \beta_{s,2} \quad (2)$$

where x_i and $\beta_{s,i}$ are the mole fraction and adiabatic compressibility of component i in the binary mixture. Thermodynamic excess quantities are defined as the difference between the observed thermodynamic property and that of an ideal solution. Equation 2 incorrectly assumes that the adiabatic compressibility of an ideal binary solution is a simple mole fraction average of the adiabatic compressibilities of the two components that make up the binary mixture. The excess adiabatic compressibility of a binary mixture is correctly calculated according to Eqn. 3

$$\begin{aligned} \beta_s^E = \beta_{s,\text{mixture}} - \varphi_1 \left[\beta_{s,1} + T \frac{(V_1 \alpha_1)^2}{C_{p,1}} \right] - \varphi_2 \left[\beta_{s,2} + T \frac{(V_2 \alpha_2)^2}{C_{p,2}} \right] \\ + T \left[\frac{(x_1 V_1 + x_2 V_2)(\varphi_1 \alpha_1 + \varphi_2 \alpha_2)^2}{(x_1 C_{p,1} + x_2 C_{p,2})} \right] \end{aligned}$$

(3)

where φ_i is the ideal volume fraction of component i , V_i is the molar volume of component i , α_i is the coefficient of thermal expansion of component i , and $C_{p,i}$ is the molar isobaric heat capacity of pure component i at the temperature of the adiabatic compressibility measurement. The correct equation for calculating β_s^E has been published numerous times in This Journal [3-7] and in other thermodynamic journals [8-13]. The isobaric molar heat capacities, $C_p = 250.2 \text{ J mol}^{-1}$ for ethyl acetoacetate [14] and $C_p = 114.3 \text{ J mol}^{-1}$ for chloroform [15], and coefficient of thermal expansion, $\alpha_i = 1.041 \times 10^{-3} \text{ K}^{-1}$ for ethyl acetoacetate (calculated from the density data of Sheu and Tu [16]) and $\alpha_i = 1.286 \times 10^{-3} \text{ K}^{-1}$ for chloroform [17] are known. There is no reason that we can see for Yadav *et al.* [1] not calculating the excess isentropic compressibilities correctly. While simple mathematical expressions like eqn. 2 are very convenient, it is important to note that the interpretation of molecular interactions based on incorrectly calculated β_s^E values can give rise to erroneous results. [12]

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Figure 1

Figure 1. Excess molar volumes of chloroform (1) + ethyl acetoacetate (2) binary mixtures at 298.15 K. Experimental values were measured by Yadav et al. (filled squares) and by Roy et al. (filled diamonds).