

Letter to the Editor

About “Studies of viscosity and excess molar volume of binary mixtures of propane-1,2 diol with water at various temperatures” by U.R. Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande, P.R. Patil [Fluid Phase Equilib. 192 (2001) 63–70][☆]

The above-mentioned paper presents new experimental data on excess molar volume and viscosity of the propane-1,2-diol + water binary system. Since our group systematically investigates (P , V , T , x) properties of mixtures, we have read this paper with special interest.

It is surprising how many drawbacks are visible in the article at first sight. Partly, they might be classified as more or less formal mistakes (which will be given at the end of this comment for the sake of completeness), nevertheless, there are a great many others, which are more substantial.

The first question is the way of the densimeter calibration: since the vibrating-tube densimetry is an indirect method where the relation between density and measured period of vibration contains two independent parameters, the densimeter calibration is carried out by means of two fluids of known density. Surprisingly, the authors say that (only) water was used for calibration. Furthermore, they state good agreement of the observed water density with the literature value even if it is clear that the density of the substance used for calibration must agree, within an experimental error, with the tabulated value applied (unless the density is determined by independent measurement, e.g. by pycnometry, which seems not to be the case). In the end it seems certain that the calibration of the densimeter was not carried out thoroughly at all the temperatures studied. Consequently the reported values of densities of water in Table 1 are systematically lower than the recommended literature ones [2], the difference increasing with temperature and reaching up to $0.00006 \text{ g cm}^{-3}$.

The results of measurements given in Table 1 and Fig. 1 of the original paper show an objectionable characteristic: whereas the mole fraction concentration range up to $x_1 = 0.4863$ is covered with eight mixture samples, the remaining half contains only one mixture data point. Considering that both components of the mixture are completely miscible [2], I cannot find any reason of it. Moreover, the curves in Fig. 1 (and analogously in Fig. 2) are not calculated from the fitting equation as one could expect, but they are arbitrarily drawn through the experimental points.

In general, and especially with regard to the said V^E data distribution along the x -axis, the very bad results when fitting the data by the Redlich–Kister equation are striking. The data do not seem to be so extremely bad to show standard deviation of the order $0.1 \text{ cm}^3 \text{ mol}^{-1}$, especially if 89% of data covers less than 50% of concentration range and only one point the other half. To solve the problem, we have correlated the data on using our program [1], applying both the simple least-square and maximum likelihood principle. The comparison of the original correlation with ours is given in the following Table 1. As to values of constants and standard deviations for the case of simple least-square method, the comparison needs no

[☆] PII of original article S0378-3812(01)00621-5.

Table 1

Coefficients A_i [$A_i = a_i$ ($\text{cm}^3 \text{mol}^{-1}$)] of Eq. (2) of the original paper and standard deviations $\sigma(V^E)$ [$\sigma(V^E) = \sigma$ ($\text{cm}^3 \text{mol}^{-1}$)] and $\sigma(x)$ determined by the authors of the original paper and by our methods (for least-square methods, $\sigma(x) = 0$)

T (K)	Original regression				Our least-square method				Our maximum likelihood method				
	A_0	A_1	A_2	$\sigma(V^E)$	A_0	A_1	A_2	$\sigma(V^E)$	A_0	A_1	A_2	$\sigma(x)$	$\sigma(V^E)$
303.15	−3.1624	1.0009	1.4505	0.095	−2.47015	1.45017	−0.12722	0.021	−2.47003	1.45005	−0.12826	0.00002	0.021
308.15	−3.0720	0.9894	1.3674	0.092	−2.39742	1.38811	−0.16090	0.019	−2.39732	1.38801	−0.16177	0.00002	0.019
313.15	−2.9971	1.0078	1.2650	0.089	−2.33229	1.33664	−0.21208	0.016	−2.33220	1.33655	−0.21280	0.00001	0.016
318.15	−2.9109	0.9870	1.2129	0.086	−2.26498	1.28039	−0.22326	0.015	−2.26491	1.28031	−0.22388	0.00002	0.015

comment. The original computation is obviously erroneous, and a thorough check of the used least-square regression program should be recommended. In spite of it, the deviations, even for our computations, are still too high for this type of mixture/experimental apparatus. Assuming the data to be of not very good quality, we have try to decide whether the inaccuracies or changes in composition x , due to, e.g. the sample manipulation, do not propagate into the deviations in density ρ , which is common with the simple least-square procedures. Therefore, the principle of maximum likelihood has been applied with inaccuracies in x and ρ estimated on the basis of our analogous measurements [3]. However, no significant effect of the inaccuracies in x has been found, as it can be observed from the respective values of standard deviations in V^E . They are nearly identical for both procedures and still several times higher than expected for the best- or good-quality data.

As to the viscosity data, the comments are quite analogous. Moreover, since aqueous solutions are measured, the calibration of viscometer should be done with water.

In the end we give a list of further more or less serious drawbacks: the right name of the diol employed is propane-1,2-diol (not propane-1,2 diol used throughout the article). The quantities M_1 , M_2 on page 64 are molecular masses (not weights). The values of superscript i in Eq. (2) should be specified. The correct unit of quantity V^E in Table 1 is certainly not (cm mol^{-1}). The parameters a_i in Table 2 are not dimensionless. The experimental values of $\Delta\eta$ are not reported in Table 2 as is presented in the middle of page 66. The quantity Q in Eq. (5) is unnecessary and should be replaced by $\Delta\eta$. The parameters in Table 3 should be designated H (not a). They are not dimensionless, too. The units in Table 3 should be (mPa s) and not ($\text{cm}^3 \text{mol}^{-1}$). The unit of quantity ΔS^* both in Table 4 and in Fig. 4 is also incorrect. No temperature dependence can be traced in Fig. 3 contrary to the figure heading and the text.

In conclusion it can be stated that most of the errors indicated could and should be corrected in the reviewing and editing process. The experimental data themselves seem to be, in the end, of a not very good quality and, moreover, the way of data processing and paper presentation is too poor.

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