Answers to Reviewers' comments

The analysis of thermophysical properties of the binary systems containing ester ethyl acetate and 1-propanol or 1-butanol

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Reviewer A:

The paper reports experimental data of physical properties of binary mixtures of ester acetate and alcohols at atmospheric pressure and several temperatures. Excess molar volume, viscosity deviations, refractive index deviations and excess isentropic compressibility are also determined.
My recommendation is that this work can be published after minor revisions:

1. The figures could be improved, have a low quality and look with difficulty.

The instructions of the Journal were followed when preparing each figure. For resubmitting the paper, we will try to improve the quality of the figures.

2. Figure feet don't look right, there are symbols that are not correctly indicated.

Due to the large amount of data presented on the graphs and limited number of common symbols that can be used, Origin font was used to match the symbols on the graph. The font will be embedded in the resubmitted paper so the mistakes will be avoided.

3. I am not sure why the authors drew a line in the figures from 1 to 5. If it is not necessary in my opinion they should remove it because it complicates the understanding of the graph.

Lines on Figures 1-5 simply connect the experimental data from this manuscript. As it is written they "are a guide to the eye" and only help that the trend of reported experimental points is easier to notice among the extensive literature data.

Reviewer B:

The authors present experimental data concerning binary mixtures of ethyl acetate and 1-propanol or 1-butanol. The data seem to be accurate and although majority of them have already been reported in the literature, in my opinion they are worth publishing. Additionally I have a few comments or suggestions which are shown below.

Major remarks or reservations

1. The measured properties should be compared with the literature data if the latter are available. From authors' statement "Limited amount of data for investigated systems can already be found in the literature [134-141] although not on [at] all temperatures and for all properties presented in this manuscript" (row 160 and next), it may concluded that the literature data are rare but it is not true. In fact, the available data are quite numerous. For the system 1-propanol + ethyl acetate they contain 10 data sets of densities (the

temperature range (283-313) K and 3 data sets of viscosities (298-313) K. For the system 1-butanol + ethyl acetate – 9 data sets of densities (298-313) K, 3 data sets of viscosities (298-313) K, one data set of sound velocities (303-313) K and one for index of refraction (303 K). See Detherm data base. At this point one can ask if additional measurements really are needed. I do not share these doubts. Any data are useful and discrepancy between already measured justify further determinations. Nevertheless a detailed comparison must be done and arguments supporting superiority of new data with respect to the literature ones, at least formulated.

When preparing the manuscript, the NIST ThermoLit database, as a standard tool, was consulted for the previously reported literature data for all properties of investigated pure substances as well as binary systems. Papers reported and used for graphical comparison in the manuscript are almost all available sources, excluding two papers where measurements were obtained at 303.15 K and were not shown on Figures 4-5 (added in the text of the revised manuscript) and one paper we were not able to acquire (J. Chim. Phys. Phys.-Chim. Biol. 68 (1971) 1442-1448.).
A sentence stating the temperature intervals of available literature data is also added to the manuscript (pages 22-23, lines 165-168):
"For system with 1-propanol available is data for density at (298.15 – 323.15) K and viscosity at (298.15 – 308.15) K, while for system with 1-butanol beside density at (298.15 – 313.15) K and viscosity at 298.15 K and 303.15 K, data for refractive index can also be found only at 298.15 K."
Comparison for all available measured or deviation properties is presented at 298.15 K (ρ, V^E, η and $\Delta\eta$ for system with 1-propanol, and ρ, V^E, η, n_D for system with 1-butanol) and only for reported values (some papers report ρ and η without V^E and $\Delta\eta$ and vise versa). That is the reason why measured and not only deviation properties are shown on the graphs (Reviewer's comment no. 9). Although differences are easier to spot when comparing deviation properties, even smaller amount of papers is available for these properties so the comparison is extended also to directly measured ones.
The maximum deviations are calculated for V^E and $\Delta\eta$ with available literature data at 298.15 K, while average deviations are reported for density, viscosity and refractive index at 298.15 K (page 23, lines 173-177):
"In the case of both binary systems curves that fit experimental data and literature values for excess molar volume and viscosity deviation have rather similar shapes with differences below $9\cdot10^{-8}$ m^3 mol^{-1} for V^E and 0.3 mPa s for $\Delta\eta$. For directly measured properties, dots are also following the same trend and the agreement is satisfactory for both systems with average deviations of 0.6 kg m^{-3} for density, 0.03 mPa s for viscosity and $2\cdot10^{-3}$ for refractive index."

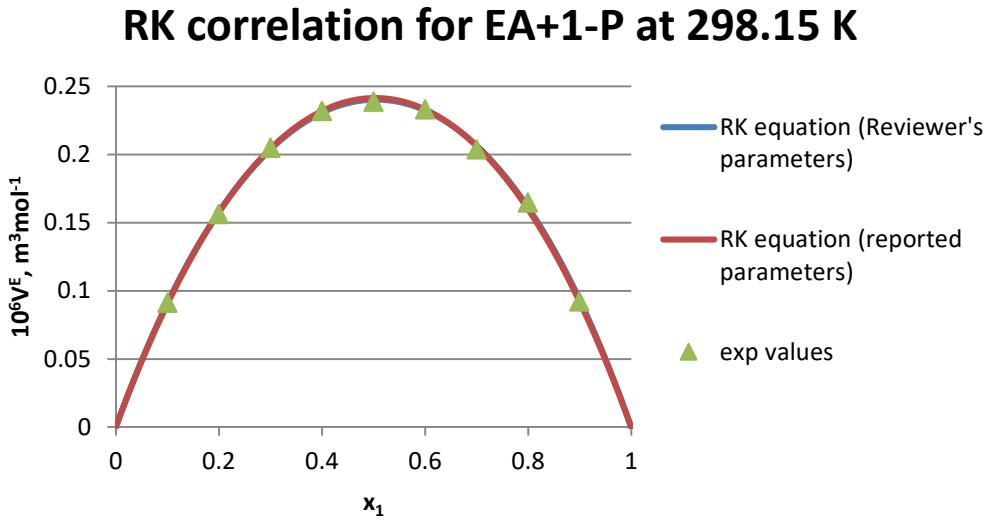
2. What was a form of the objective function which was minimized to adjust the Redlich-Kister parameters? I correlated excess volumes of the 1-propanol + ethyl acetate system at 298.15 K with the objective function being the sum of squares of residuals between calculated and experimental excess volumes. I got the following values of the parameters: 0.9610, 0.01749, 0.1001 with the standard deviation defined by eqn. (7) equal to 0.022. The authors' parameters do not minimize the objective function giving the standard deviation of 0.025. Please check all data sets.

The objective function used to optimize RK parameters in Fortran PowerStation is:

$$OF = \frac{1}{m}\sum_{i=1}^{m}\left(\frac{Y_{i,exp} - Y_{i,calc}}{Y_{i,exp}}\right)^2 \rightarrow \min$$

where Y represent values of excess molar volume, viscosity deviation, refractive index deviation or excess isentropic compressibility, experimental (exp) and calculated (calc), and m is the number of experimental data points.

For excess molar volume for system ethyl acetate + 1-propanol at 298.15 K minor differences exist between Reviewer's and reported values of parameters which do not influence the final result of RK correlation:



Differences may occur due to the raw experimental data used by authors for this basic correlation and not entirely the reported ones (decimal places and repeated measurements).

But the mistakes are made in reported values of root-mean-square deviations. The value of σ that is obtained by Reviewer's parameters is 0.0022×10^{-6} m^3mol^{-1}, and by reported parameters 0.0025×10^{-6} m^3mol^{-1}, and not 0.0020×10^{-6} m^3mol^{-1} as stated in the Table 3 of the manuscript. Values of σ for all properties are checked and corrected in the revised text.

3. As the data were measured at 8 temperatures, what I do appreciate, the simultaneous correlation with respect to mole fraction and temperature should be done. It can be performed with the temperature-dependent Redlich-Kister parameters.

Since the Redlich-Kister equation is the basic tool for correlation of experimental data and is used as so-called "mathematic experiment" to check the trend and to smooth the experimental dots, it is not common to apply it on temperature interval yet to each temperature individually, especially since the trend and the shape can significantly differ from temperature to temperature going from, for example, symmetric negative values to S-shaped trend with both positive and negative values of deviation property. When this is the case even different number of parameters in RK equation is used at different temperatures.

Minor remarks

4. I suggest to remove "alcohol" from the title. I think that nobody has doubts that 1-propanol and 1-butanol are alcohols.

As Reviewer suggested, title is slightly changed according to the comment.

5. Figures 1-3 are not illustrative. It is better to draw deviations, preferably relative, instead. As the number of the literature densities and viscosities of pure components is very high, I suggest to relate authors' data rather to empirical correlations based on verified data as for example the DIPRR105 equation for densities and the Vogel equation for viscosities.

The comparison of experimental with literature values can be shown either through the directly measured properties or through the deviations. If deviations are considered, the comparisons in that case can only be made with the measurements performed at the same temperature thus reducing the number of literature sources used. Therefore it is chosen to keep the graphs and state the deviation between the measured and literature values for each property in the text of the manuscript (pages 4-5, lines 81-84):
"The average absolute percentage deviations of experimental from literature data for density, viscosity, refractive index and speed of sound for all three investigated pure substances are 0.06%, 2.72%, 0.04% and 0.13%, respectively."
Concerning the second part of the comment; it is not a practice in this kind of manuscripts to make comparisons with correlations i.e. correlated values, but only with directly measured values, since this kind of comparison brings additional deviations.

6. Table 2. Replace „Etil acetat" by „Ethyl acetate".

The Reviewer's comment is implemented in the manuscript.

7. Table 3. Give units of the standard deviation. The values of parameters should have the same number of significant digits.

The units for the standard deviation for each property are chosen to be stated in the caption of Table 3 for more simple presentation in the table. The number of significant digits (or decimal places) of parameters depends on the significant digits of the correlated property and its uncertainty and is not the same for all properties.

8. Some comments concerning the Redlich-Kister correlation of excess volumes are needed. Standard deviations given in Tab. 3 are about 20 times lower than estimated experimental uncertainty (0.06 cm3/mol). As the number of adjustable parameters was determined correctly, it means that an actual experimental uncertainty is lower or, what is more probable, some significant systematic errors appear. At any rate, this issue requires some comments.

Uncertainties for measured properties included the repeatability of performed measurements and the uncertainty corresponding to the purity of used chemicals calculated by equation proposed in J. Chem. Eng. Data 2013, 58, 2699−2716. The uncertainty of derived deviation properties is calculated using the Law of Propagation of Uncertainty explained in Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. It defines the interval having a level of confidence close to 95% (coverage factor k has value 2) in which certain value lays in.
On the other hand, standard deviations stated in Table 3 are measure of quality of used correlation for adopted experimental values from repeated measurements and have sense to

have smaller values than reported uncertainties, but any other correlation between these two quantities cannot be made.

9. Fig. 4 and 5. Only excess and deviations functions are worth drawing as residuals are relatively high and visible. Solid lines should represent the adjusted Redlich-Kister dependence and not "a guide to the eye".

To this comment partially is already answered in the reply to the Comment 1 of the Reviewer. Since the comparison is only made with previously reported literature values (in any case values were not calculated by the authors of this manuscript), not so many literature sources report deviation properties yet rather directly measured ones. For more complete comparison it is chosen to be presented graphically every property available at 298.15 K in the literature which is also presented in this manuscript. However, as the Reviewer suggested, the differences between experimental and literature values are much easier to notice at deviation properties.
For excess molar volume and viscosity deviation presented as part of Figures 4 and 5, lines were set to represent the values calculated by RK equation.

10. The discussion on the molecular interactions. I am very skeptical as to the value of this section. There are a lot of thermodynamic data, such as phase equilibria and excess enthalpies which should be considered in such a discussion. Only excess volumes, isentropic compressibilities and viscosity deviations are not sufficient as they are not easy to explain and interpret. In addition, excess volumes are typical - relatively low, close to zero and symmetrical and thus no definitive conclusions can be drawn from them.

From reported deviation properties excess molar volume is the most adequate one for interaction interpretation in the manuscripts regarding the thermodynamic and transport characterization of liquid mixtures. Although viscosity and refractive index deviations, as well as excess isentropic compressibility, on their own don't give complete insight into the interaction present in the mixtures, they are valuable addition and can contribute to better understanding what is happening between components of the mixture.
There are properties that could be included in the discussing such as the excess molar Gibbs free energy of activation of viscous flow or partial and excess partial molar volumes. But since rather simple and previously investigated types of compounds are used in this research, presented deviation properties with reference to the molecules structure and literature conclusions are enough for this kind of discussion.