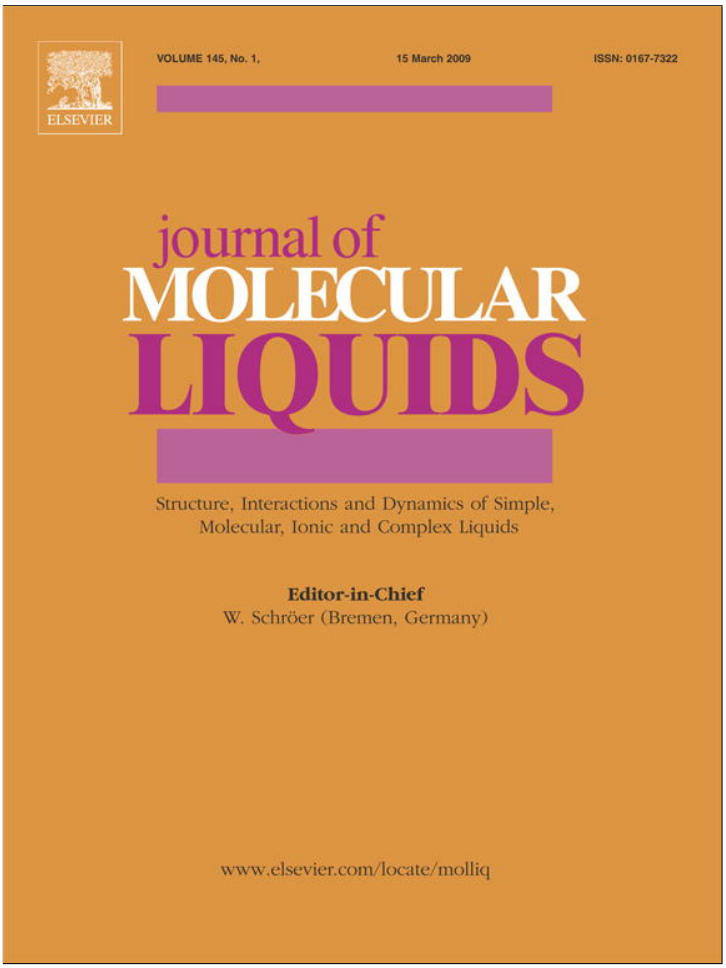

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Comments on "Excess molar volumes and excess viscosities for mixtures of N,N-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures" by M. M. H. Bhuiyan and M. H. Uddin, J. Mol. Liquids, 138(2008)1–3, 139–146☆

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In a recent paper in this journal, Bhuiyan and Uddin [1] reported measured density and viscosity data for liquid N,N-dimethylformamide (DMF, C_3H_7NO), methanol (CH_4O), ethanol (C_2H_6O), and 2-propanol (C_3H_8O) and the binary mixtures of DMF with these alcohols at five temperatures from 303.15 K to 323.15 K at atmospheric pressure.

The authors assess their experimental results for the pure compounds, and thus the purity of these samples, by juxtaposing the measured density and viscosity data in Table 1 with a selection of literature data from references [BU,26,33–35]. [1]They are rated "in good agreement" with each other although the agreement is not quantified by percent deviations. Calculating these percent deviations reveals substantial disagreement between the data of Bhuiyan and Uddin [1] and the literature data, with the former being up to 9.2 % higher than the latter in the case of ethanol.

A more comprehensive comparison is presented here juxtaposing the viscosity data of Bhuiyan and Uddin for the pure components with critically evaluated reference values. For DMF and 2-propanol these were obtained from the DIPPR database [2], while those for methanol and ethanol were calculated with the correlations of Xiang et al. [3] and Kiselev et al. [4], respectively, as implemented in NIST Standard Reference Database 23 (RefProp) [5]. Percent deviations are displayed in Table 1. While Bhuiyan and Uddin do not quote uncertainties of their experimental results, their viscosities agree with the reference values for DMF and 2-propanol within the estimated uncertainty of the latter. The viscosity data for methanol deviate systematically and exceed slightly the uncertainty of 2% that Xiang et al. estimated in their analysis. The ethanol viscosities of Bhuiyan and Uddin are between 4.6% and 10% higher than the reference values. Based on prior viscometry experiences [6], deviations of that magnitude are likely due to serious experimental error.

Table 1
Deviations of the viscosity data of Bhuiyan and Uddin [1] from reference values

	T_{90} / K	η / mPa·s	η / mPa·s	$\Delta\eta/\eta$ / %
	Exp	Reference	[1]	[1] vs. Ref
DMF	303.15	0.7676	0.7753	1.0
	308.15	0.7248	0.7329	1.1
	313.15	0.6858	0.6900	0.62
	318.15	0.6503	0.6530	0.42
	323.15	0.6178	0.6140	−0.62
Methanol	303.15	0.5062	0.5178	2.3
	308.15	0.4723	0.4843	2.5
	313.15	0.4416	0.4515	2.2
	318.15	0.4137	0.4233	2.3
	323.15	0.3883	0.3950	1.7
Ethanol	303.15	0.9867	1.0858	10.0
	308.15	0.8996	0.9732	8.2
	313.15	0.8221	0.8596	4.6
	318.15	0.7530	0.8284	10.0
	323.15	0.6911	0.7493	8.4
2-propanol	303.15	1.771	1.7919	1.2
	308.15	1.538	1.5529	0.98
	313.15	1.341	1.3554	1.1
	318.15	1.174	1.1822	0.67
	323.15	1.032	1.0469	1.4

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[1] Citations referring to those in the paper of Bhuiyan and Uddin [1] are marked by the prefix "BU".

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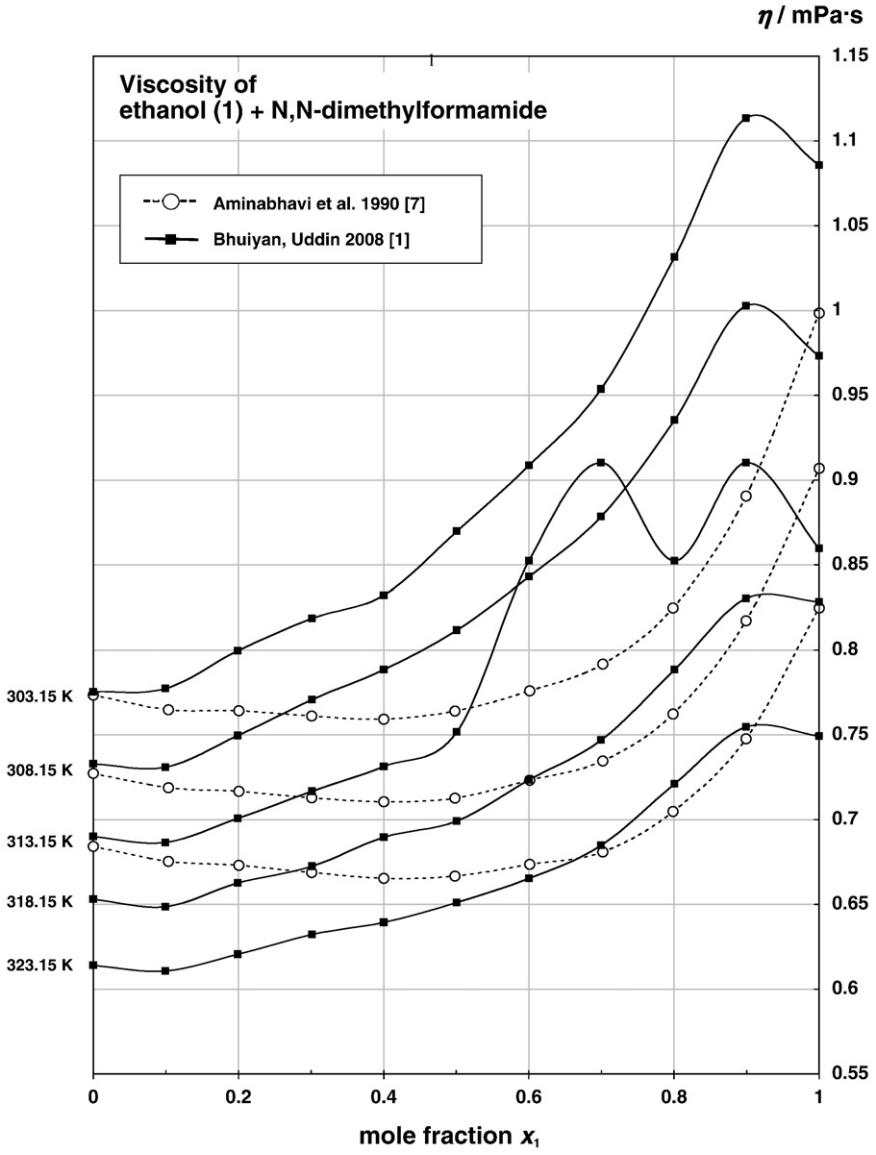

Fig. 1. Comparison of viscosity data for the binary system ethanol(1) + N,N-dimethylformamide at atmospheric pressure. Data are connected by lines to increase the legibility of the graph.

The erroneous viscosities for pure ethanol prompt an examination of the viscosities that Bhuiyan and Uddin report for the binary system of DMF and ethanol. While the authors quote as reference [BU,16] a previous publication by Aminabhavi et al. [7], who reported density and viscosity data for the system ethanol + DMF, they did not compare their experimental results with those of Aminabhavi et al. Fig. 1 shows both data sets in a viscosity-diagram versus mole fraction of ethanol. They overlap at the three temperatures 303.15 K, 308.15 K, and 313.15 K. The diagram shows that a reasonable agreement between the two data sets exists only for pure DMF. At all other compositions, the experimental viscosities of Bhuiyan and Uddin deviate strikingly from those of Aminabhavi et al. They are substantially higher and they exhibit greater scatter. The maximum relative deviation of 33.6 % occurs at 313.15 K and an ethanol mole fraction of $x_1 \approx 0.7$; the viscosity value there may be a transcription or word processing error.

The two data sets differ strikingly in their composition dependence. The viscosity data of Bhuiyan and Uddin exhibit viscosity maxima at $x_1 \approx 0.9$, whereas those of Aminabhavi et al. show viscosity minima at $x_1 \approx 0.4$. The latter is plausible considering that DMF is a larger but less polar molecule than ethanol, whose properties are influenced by associations due to strong hydrogen bonds. Because of the strong associations, the viscosity of ethanol is higher than that of DMF even though ethanol is the smaller molecule. Viscosity minima occur typically in binary systems that consist of a strongly polar compound and a nonpolar or less polar compound when the latter is the larger molecule but has a lower viscosity than the former.

The viscosity data of Aminabhavi et al. have also been confirmed by recent measurements of Yang et al. [8], whose results agree with those of Aminabhavi et al. within 1.5 % and also exhibit viscosity minima versus composition.

It may be concluded that the substantial deviations between literature data and reference values on one hand and the viscosity data by Bhuiyan and Uddin for ethanol and the binary system ethanol + DMF on the other appear to be due to a contaminated sample of ethanol.

It is strongly suggested that authors provide more complete and detailed comparisons with literature data where feasible (including percent deviation plots and graphs of the data). This could strengthen the authors' analysis and be a useful tool for reviewers.

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