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Densities and Viscosities of (*N*,*N*-Dimethylformamide + Water) at Atmospheric Pressure from (283.15 to 353.15) K

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Densities and viscosities of (*N*,*N*-dimethylformamide + water) have been measured from $T = (283.15$ to $353.15)$ K in the entire mole fraction composition. Densities are measured with a vibrating tube densimeter, while two different Cannon-Fenske viscosimeters are used for the viscosity measurements. Excess molar volumes and viscosity deviations from the composition weighted average of the pure component viscosities are calculated from experimental measurements and represented with Redlich–Kister equations. Excess molar volumes present negative deviations from ideality at all investigated temperatures and become more negative with decreasing temperature. Viscosity deviations are positive for all the temperatures and mole fractions considered in this work.

Introduction

In this work, densities of aqueous solutions of *N*,*N*-dimethylformamide (DMF) have been measured using a vibrating tube densimeter from (283.15 to 353.15) K at atmospheric pressure. Also, kinematic viscosities of these mixtures have been measured using two different Cannon-Fenske viscosimeters from (293.15 to 353.15) K. Excess molar volumes and viscosity deviations from the composition weighted average of the pure component viscosities are calculated and represented with Redlich–Kister[1] type equations.

Experimental

Apparatus and Procedures. Densities of water, DMF, and their binary mixtures are measured using a vibrating tube densimeter (Anton Paar, DMA 5000). An explanation of the apparatus has been given before.[2] The reproducibility in the density and temperature measurement provided by the manufacturer is $\pm\ 0.001\ \mathrm{kg \cdot cm^{-3}}$ and $\pm\ 0.001$ K, respectively. The uncertainties of the thermometer and the density measurements are $\pm\ 0.01$ K on the international temperature scale of 1990 (ITS-90) and $\pm\ 5 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$, respectively. The true uncertainty in the density measurements is probably better than $\pm\ 3 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. As stated before,[2] the uncertainty in the excess volume is $0.008\ \mathrm{cm^3 \cdot mol^{-1}}$. Kinematic viscosities are measured using two different Cannon-Fenske viscosimeters, sizes 25 and 50 with flow ranges of $(0.5$ to $2) \cdot 10^{-6}\ \mathrm{m^2 \cdot s^{-1}}$ and $(0.8$ to $4) \cdot 10^{-6}\ \mathrm{m^2 \cdot s^{-1}}$, respectively. Measurements are performed following the ASTM 445 standard. A digital thermometer F250 (Automatic System) measures the temperature with an uncertainty of 0.01 K. The efflux time is measured with a digital stopwatch having an accuracy of 0.01 s. Each datum is an average of at least five experiments with a maximum deviation in the kinematic viscosity of ± 0.1 %, and the estimated accuracy[2] is better than $\pm\ 0.004\ \mathrm{mPa \cdot s}$.

Table 1. Comparison of Experimental Densities and Viscosities of DMF

	$\rho/\mathrm{g \cdot cm^{-3}}$		$\eta/\mathrm{mPa \cdot s}$	
T/K	this work	lit.	this work	lit.
283.15	0.95896	0.96045[4]		
288.15	0.95417	0.95530[4]		
		0.952359[5]		
293.15	0.94939	0.95045[4]	0.864	0.889[4]
		0.948051[5]		
298.15	0.94460	0.94559[4]		
		0.942915[5]		
		0.944[10]		
		0.94381[11]		
		0.94403[12]		
303.15	0.93983	0.94069[4]	0.766	0.7647[4]
		0.938876[5]		0.7485[7]
		0.9386[7]		
308.15	0.93505	0.93561[4]		
		0.933964[5]		
		0.9344[7]		
313.15	0.93027	0.93103[4]	0.684	0.6831[4]
		0.929549[5]		0.6683[7]
		0.9296[7]		
318.15	0.92549	0.92628[4]		
		0.924674[5]		
		0.9251[7]		
323.15	0.92071	0.92154[4]	0.617	0.6128[4]
		0.9204[7]		0.6004[7]
328.15	0.91592	0.91671[4]		
333.15	0.91113	0.91197[4]	0.559	0.5565[4]
338.15	0.90632	0.90702[4]		
343.15	0.90151	0.90225[4]	0.510	0.5084[4]
348.15	0.89669	0.89721[4]		
353.15	0.89186	0.89224[4]	0.470	0.4602[4]

Samples. Fischer Co. supplied water grade HPLC with a mole fraction purity grater than 99.95 %. DMF is obtained from Mallinckrodt AR (ACS) with a stated mole fraction purity of 99.4 %. Pure components are used as received. The mixtures are prepared gravimetrically using an analytical balance (Ohaus model AS120S) with a precision of ± 0.1 mg. The overall uncertainty in the mole fractions is better than ± 0.002.

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Table 2. Experimental Densities and Excess Molar Volumes for DMF (1) + Water (2)

x_1	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{V^E}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$	$\frac{V^E}{cm^3 \cdot mol^{-1}}$
	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K	
0	0.99970	0	0.99910	0	0.99820	0	0.99704	0
0.020	1.00031	−0.0750	0.99923	−0.0728	0.99792	−0.0714	0.99639	−0.0705
0.040	1.00142	−0.1594	0.99991	−0.1546	0.99820	−0.1510	0.99631	−0.1483
0.060	1.00280	−0.2530	1.00087	−0.2451	0.99877	−0.2388	0.99653	−0.2339
0.080	1.00413	−0.3472	1.00182	−0.3362	0.99937	−0.3271	0.99680	−0.3197
0.100	1.00532	−0.4426	1.00267	−0.4286	0.99990	−0.4168	0.99703	−0.4069
0.200	1.00764	−0.8484	1.00386	−0.8248	1.00001	−0.8037	0.99613	−0.7851
0.300	1.00440	−1.0925	1.00010	−1.0670	0.99576	−1.0437	0.99140	−1.0225
0.398	0.99783	−1.1604	0.99331	−1.1372	0.98876	−1.1153	0.98418	−1.0952
0.498	0.99056	−1.1268	0.98594	−1.1081	0.98130	−1.0903	0.97664	−1.0741
0.599	0.98302	−0.9951	0.97836	−0.9811	0.97367	−0.9676	0.96896	−0.9553
0.697	0.97607	−0.7986	0.97137	−0.7887	0.96665	−0.7791	0.96192	−0.7704
0.798	0.96984	−0.5711	0.96511	−0.5654	0.96037	−0.5597	0.95563	−0.5546
1	0.95896	0	0.95417	0	0.94939	0	0.94460	0
	$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K	
0	0.99565	0	0.99403	0	0.99221	0	0.99021	0
0.020	0.99467	−0.0701	0.99274	−0.0696	0.99067	−0.0701	0.98843	−0.0706
0.040	0.99425	−0.1464	0.99203	−0.1450	0.98966	−0.1441	0.98714	−0.1436
0.060	0.99414	−0.2300	0.99161	−0.2269	0.98895	−0.2244	0.98617	−0.2224
0.080	0.99411	−0.3135	0.99129	−0.3084	0.98837	−0.3040	0.98533	−0.3004
0.100	0.99405	−0.3985	0.99098	−0.3914	0.98780	−0.3852	0.98453	−0.3797
0.200	0.99219	−0.7683	0.98820	−0.7531	0.98415	−0.7392	0.98005	−0.7261
0.300	0.98699	−1.0028	0.98255	−0.9843	0.97807	−0.9671	0.97355	−0.9505
0.398	0.97957	−1.0761	0.97494	−1.0580	0.97026	−1.0406	0.96556	−1.0236
0.498	0.97195	−1.0582	0.96724	−1.043	0.96250	−1.0282	0.95773	−1.0134
0.599	0.96424	−0.9432	0.95949	−0.9313	0.95473	−0.9198	0.94993	−0.9079
0.697	0.95718	−0.7617	0.95242	−0.7530	0.94764	−0.7446	0.94285	−0.7358
0.798	0.95087	−0.5492	0.94610	−0.5438	0.94133	−0.5388	0.93653	−0.5331
1	0.93983	0	0.93505	0	0.93027	0	0.92549	0
	$T = 323.15$ K		$T = 328.15$ K		$T = 333.15$ K		$T = 338.15$ K	
0	0.98803	0	0.98569	0	0.98319	0	0.98055	0
0.020	0.98600	−0.0705	0.98351	−0.0721	0.98084	−0.0733	0.97804	−0.0745
0.040	0.98449	−0.1434	0.98171	−0.1434	0.97881	−0.1437	0.97581	−0.1446
0.060	0.98326	−0.2209	0.98024	−0.2197	0.97710	−0.2187	0.97386	−0.2181
0.080	0.98219	−0.2972	0.97894	−0.2945	0.97559	−0.2921	0.97214	−0.2900
0.100	0.98117	−0.3749	0.97771	−0.3706	0.97416	−0.3666	0.97051	−0.3630
0.200	0.97589	−0.7140	0.97168	−0.7025	0.96740	−0.6916	0.96307	−0.6810
0.300	0.96899	−0.9345	0.96438	−0.9190	0.95973	−0.9038	0.95503	−0.8889
0.398	0.96081	−1.0068	0.95604	−0.9903	0.95122	−0.9736	0.94636	−0.9571
0.498	0.95292	−0.9987	0.94809	−0.9840	0.94322	−0.9689	0.93832	−0.9535
0.599	0.94511	−0.8960	0.94027	−0.8839	0.93540	−0.8713	0.93049	−0.8584
0.697	0.93803	−0.7267	0.93320	−0.7174	0.92834	−0.7077	0.92346	−0.6978
0.798	0.93173	−0.5274	0.92691	−0.5215	0.92208	−0.5155	0.91722	−0.5087
1	0.92071	0	0.91592	0	0.91113	0	0.90632	0
	$T = 343.15$ K		$T = 348.15$ K		$T = 353.15$ K			
0	0.977759	0	0.974838	0	0.971785	0		
0.020	0.975121	−0.0760	0.972137	−0.0787	0.968964	−0.0802		
0.040	0.972663	−0.1452	0.969417	−0.1460	0.966057	−0.1469		
0.060	0.970497	−0.2174	0.967099	−0.2182	0.963527	−0.2176		
0.080	0.968588	−0.2881	0.964943	−0.2863	0.961203	−0.2846		
0.100	0.966781	−0.3596	0.962961	−0.3564	0.959052	−0.3532		
0.200	0.958669	−0.6706	0.95421	−0.6604	0.949686	−0.6501		
0.300	0.950285	−0.874	0.945486	−0.8589	0.940638	−0.8437		
0.398	0.941464	−0.9404	0.936524	−0.9233	0.931537	−0.9056		
0.498	0.933378	−0.9379	0.928402	−0.9216	0.923387	−0.9047		
0.599	0.92556	−0.8451	0.920591	−0.8307	0.915587	−0.8156		
0.697	0.918546	−0.6872	0.913607	−0.6756	0.90864	−0.6634		
0.798	0.912339	−0.5015	0.907453	−0.4947	0.902522	−0.4856		
1	0.901513	0	0.896694	0	0.891864	0		

Results and Discussion

Densities and viscosities of pure DMF are given in Table 1. Pure water densities are taken from Bernal-García et al.[3] DMF density measurements agree with those from Marchetti et al.[4] and Scharlin et al.[5] within an average absolute percentage deviation of (0.09 and 0.12) %, respectively. Densities and excess molar volumes of (DMF + water) mixtures from (283.15 to 353.15) K are shown over the entire composition range in Table 2. Excess molar volumes have been calculated as before,[2] and we have compared them with those from an equation reported by Scharlin et al.[5] The values agree within an average absolute deviation of 0.01 $cm^3 \cdot mol^{-1}$. For this system, the negative deviations of the excess molar volume decrease as the temperature increases. Excess molar volumes have been represented with a Redlich–Kister[1] type equation

$$Y = x_1 x_2 \sum a_i (x_1 - x_2)^i \tag{1}$$

where Y is the excess volume V^E and a_i are the adjusted coefficients. Table 3 shows the fitting parameters at each temperature together with its standard deviation from the fit.

We have also measured the viscosity of water and compared it with the standard equation of water.[6] Our values agree within an absolute average deviation of 0.018 mPa·s. Experimental

Table 3. Parameters for the Redlich–Kister Equation for the Excess Molar Volume

T/K	a_0	a_1	a_2	a_3	σ/cm^3·mol^{-1}
283.15	−4.516	2.153	0.331	−2.255	0.011
288.15	−4.439	2.042	0.368	−2.179	0.011
293.15	−4.367	1.941	0.393	−2.093	0.010
298.15	−4.300	1.845	0.408	−1.998	0.009
303.15	−4.235	1.759	0.416	−1.899	0.009
308.15	−4.172	1.680	0.418	−1.798	0.008
313.15	−4.112	1.605	0.409	−1.699	0.008
318.15	−4.051	1.538	0.399	−1.597	0.007
323.15	−3.990	1.477	0.383	−1.500	0.007
328.15	−3.930	1.418	0.364	−1.397	0.006
333.15	−3.868	1.365	0.337	−1.303	0.006
338.15	−3.805	1.314	0.310	−1.201	0.006
343.15	−3.741	1.269	0.283	−1.103	0.006
348.15	−3.674	1.224	0.241	−1.004	0.006
353.15	−3.605	1.186	0.215	−0.901	0.006

Table 4. Experimental Viscosities and Viscosity Deviations for DMF (1) + Water (2)

x_i	η/mPa·s	$\Delta\eta$/mPa·s	η/mPa·s	$\Delta\eta$/mPa·s	η/mPa·s	$\Delta\eta$/mPa·s	η/mPa·s	$\Delta\eta$/mPa·s
	T = 293.15 K		T = 303.15 K		T = 313.15 K		T = 323.15 K	
0	1.026	0	0.817	0	0.670	0	0.561	0
0.020	1.234	0.212	0.970	0.153	0.783	0.113	0.648	0.085
0.040	1.442	0.423	1.114	0.298	0.891	0.22	0.729	0.165
0.060	1.656	0.640	1.269	0.454	1.003	0.332	0.812	0.248
0.080	1.847	0.834	1.407	0.593	1.103	0.432	0.892	0.326
0.100	2.062	1.052	1.550	0.737	1.208	0.537	0.965	0.399
0.200	2.782	1.788	2.051	1.244	1.564	0.891	1.228	0.655
0.300	2.954	1.977	2.179	1.377	1.660	0.986	1.300	0.722
0.398	2.622	1.661	1.979	1.182	1.538	0.863	1.228	0.645
0.498	2.162	1.216	1.675	0.883	1.337	0.660	1.087	0.498
0.599	1.713	0.784	1.382	0.595	1.140	0.462	0.961	0.367
0.697	1.377	0.463	1.149	0.367	0.971	0.292	0.831	0.231
0.798	1.153	0.257	0.985	0.209	0.847	0.166	0.740	0.134
1	0.864	0	0.766	0	0.684	0	0.617	0
	T = 333.15 K		T = 343.15 K		T = 353.15 K			
0	0.480	0	0.419	0	0.371	0		
0.020	0.548	0.067	0.474	0.053	0.417	0.043		
0.040	0.613	0.130	0.526	0.103	0.459	0.084		
0.060	0.675	0.191	0.575	0.150	0.499	0.122		
0.080	0.736	0.250	0.624	0.197	0.539	0.160		
0.100	0.792	0.304	0.666	0.238	0.572	0.190		
0.200	0.992	0.496	0.821	0.383	0.694	0.303		
0.300	1.046	0.543	0.866	0.419	0.727	0.326		
0.398	1.001	0.490	0.837	0.381	0.707	0.297		
0.498	0.905	0.386	0.764	0.300	0.659	0.239		
0.599	0.810	0.283	0.701	0.227	0.614	0.184		
0.697	0.722	0.188	0.636	0.153	0.563	0.123		
0.798	0.654	0.111	0.583	0.091	0.525	0.075		
1	0.559	0	0.51	0	0.47	0		

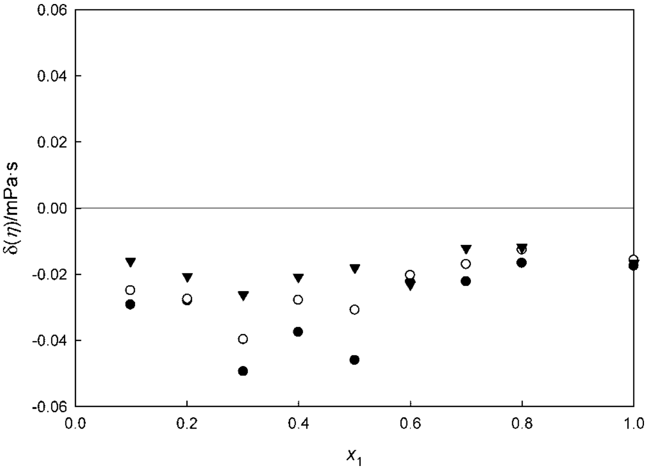

Figure 1. Fractional deviations $\delta\eta = \eta(\text{lit.}) - \eta(\text{this work})$ of the viscosity of this work from experimental values reported by Akhtar et al.:[7] ●, 303.15 K; ○, 313.15 K; ▼, 323.15 K.

Table 5. Parameters for the Redlich–Kister Equation for the Viscosity Deviations

T/K	a_0	a_1	a_2	a_3	σ/mPa·s
293.15	4.968	−10.365	3.857	7.931	0.040
303.15	3.609	−6.869	2.523	4.920	0.025
313.15	2.693	−4.662	1.646	2.988	0.016
323.15	2.045	−3.247	1.117	1.830	0.012
333.15	1.568	−2.352	0.867	1.224	0.007
343.15	1.229	−1.748	0.675	0.816	0.006
353.15	0.972	−1.299	0.543	0.456	0.005

viscosity values of DMF agree with those of Marchetti et al.[4] and Akhtar et al.[7] within an average absolute value of (0.004 and 0.016) mPa·s, respectively, as shown in Table 1.

In this work, we have measured the viscosities of aqueous solutions of DMF from (293.15 to 353.15) K, and they are shown in Table 4. Akhtar et al.[7] measured the viscosity for these mixtures between (303.15 and 323.15) K, and our values agree with theirs within an average absolute deviation of 0.02 mPa·s which corresponds to an absolute average percentage deviation of 2 %. Our measurements are greater than data from Akhtar et al.[7] as shown in Figure 1. We believe that the difference could be in part due to their purity in the sample (99 %) and their densities used in the calculation of the dynamic viscosities. They used a glass pycnometer to measure them, and densities measured in this way[8] can have an uncertainty greater than ours. Unfortunately, it was not possible to check it since densities were not reported in their work. We have calculated[9] the viscosity deviations from the composition weighted average of the pure component viscosities of (DMF + water), and at all temperatures, the deviation is positive and decreases with increasing temperature at a fixed mole fraction of DMF, as shown in Table 4. We have compared our calculations with those from Akhtar et al.[7] Table 5 shows the adjusted parameter of a Redlich–Kister equation[1,9] (eq 1 with $Y = \Delta\eta$) together with the standard deviation of $\Delta\eta$ for each temperature.

Literature Cited

(1) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(2) Landaverde-Cortes, D.; Estrada-Baltazar, A.; Iglesias-Silva, G. A.; Hall, K. R. Densities and Viscosities of MTBE + Heptane, or Octane at p=0.1 MPa from (273.15 to 363.15) K. *J. Chem. Eng. Data* **2007**, *52*, 1226–1232.

(3) Bernal-García, J. M.; Ramos-Estrada, M.; Iglesias-Silva, G. A.; Hall, K. R. Densities and Excess Molar Volumes of Aqueous Solutions of *n*-Methyldiethanolamine (MDEA) at Temperatures from (283.15 to 363.15) K. *J. Chem. Eng. Data* **2003**, *48*, 864–866.

(4) Marchetti, A.; Preti, C.; Tagilazucchi, M.; Tassi, L.; Tosi, G. The N,N-Dimetlylformamide/Ethane-1,2 diol Solvent System. Density, Viscosity, and Excess Molar Volume at Various Temperatures. *J. Chem. Eng. Data* **1991**, *36*, 1442–1445.

(5) Sharlin, P.; Steinby, K.; Domańska, U. Volumetric Properties of Binary Mixtures of N,N-Dimethylformamide with Water or Water-d$_2$ at Temperatures from 277.13 to 318.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 927–957.

(6) *IAPWS. Revised Release on the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance*;International Association for the Properties of Water and Steam: Erlangen, Germany, 1997.

(7) Akhtar, S.; Omar Faruk, A. N. M.; Saleh, M. A. Viscosity of Aqueous Solutions of Formamide, N-Methylformamide and N, N-Dimethylformamide. *Phys. Chem. Liq.* **2001**, *39*, 383–399.

(8) Park, J. T.; Chang, K. Application of Statistics to Oil Density Measurements. *Measurement* **2001**, *30*, 95–103.

(9) Bernal-García, J. M.; Galicia-Luna, L. A.; Hall, K. R.; Ramos-Estrada, M.; Iglesias-Silva, G. A. Viscosities for Aqueous Solutions of n-Methyldiethanolamine from 313.15 to 363.15 K. *J. Chem. Eng. Data* **2004**, *49*, 864–866.

(10) Bakshi, M. S.; Kaur, G. Thermodynamic Behavior of Mixtures. 4. Mixtures of Methanol with Pyridine and N,N-Dimethylformamide at 25 °C. *J. Chem. Eng. Data* **1997**, *42*, 298–300.

(11) Bendová, M.; Rehák, K.; Matous, J.; Novak, J. P. Liquid-Liquid Equilibrium and Excess Enthalpies in Binary Systems Methylcyclohexane + Methanol and Methylcyclohexane + N,N-Dimethylformamide. *J. Chem. Eng. Data* **2003**, *48*, 152–157.

(12) Tong-Chun, B.; Jia, Y.; Shi-Jun, H. Excess Molar Volumes for the Ternary Mixture N,N-Dimethylformamide + Methanol + Water at Temperature 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 491–496.

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