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Densities and Viscosities of Aqueous Solutions of *N*-Methylmorpholine from (293.15 to 343.15) K

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The experimental densities, ρ, and viscosities, η, of aqueous solutions of *N*-methylmorpholine were measured over the entire composition range at temperatures from (293.15 to 343.15) K and at atmospheric pressure. The excess molar volumes V^E and viscosity deviations $\Delta\eta$ were calculated from the experimental results of density and viscosity measurements and fitted to the Redlich−Kister polynomial equation. The V^E values are negative, while viscosity deviations $\Delta\eta$ are positive over the entire composition range and at all temperatures.

Introduction

N-Methylmorpholine (NMM) is used in manufacturing drugs such as calcium antagonists to tract irritable bowel syndrome and irritable respiratory tracts. It is also used in the production of the extractive solvents and anticorrosive agents. Thermophysical properties of *N*-methylmorpholine and its mixtures have been used for engineering applications. Densities, viscosities, refractive indices, sound velocities, and excess functions for aqueous solutions of morpholine,[1] *N*-methylmorpholine,[1] *N*-formylmorpholine,[2,3] *N*-acetylmorpholine,[4] and *N*-(2-hydroxyethyl)morpholine[5] have been reported.

In this work, the densities and viscosities were measured at temperatures from (293.15 to 343.15) K and at atmospheric pressure for water (1) + *N*-methylmorpholine (2) mixtures over the whole mole fraction range. The excess molar volumes V^E and viscosity deviations were derived and fitted to the Redlich−Kister polynomial equation.

Experimental Section

Materials. *N*-Methylmorpholine (NMM) (purity 0.98 mass fraction) was obtained from Fluka AG. NMM was used without further purification but kept over activated molecular sieves of type 4A (Union Carbide) and filtered before use. The purity was confirmed by gas liquid chromatographic analysis. The water was deionized and doubly distilled. The measured values of density and viscosity of the pure liquids are listed in Table 1, along with the literature values.[1,6,7] All aqueous solutions of NMM were prepared by mass using a Mettler balance (model AE-240) with a precision of ± 0.01 mg.

Apparatus and Procedure. The densities of the pure liquids and their binary mixtures were measured with an Anton Paar model DMA 60/602 oscillating U-tube digital densimeter with a resolution of $2 \cdot 10^{-6}$ g·cm^{-3}. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. Before each series of measurements, the densimeter was calibrated at atmospheric pressure and at each investigated temperature with double distilled water and dry air. The densities of water were measured in the temperature range from (293.15 to 343.15) K and were compared with values measured by Bettin et al.[6] and with the values provided in the recommended reference materials for the realization of physicochemical properties.[7] The calibration was acceptable if the measurements were within $\pm\, 3 \cdot 10^{-5}$ g·cm^{-3} of the published values. The densities obtained for pure toluene and 1, 2-ethanediol were found to be in good agreement with values published in the literature. The uncertainty in the density measurements is better than $\pm\, 3 \cdot 10^{-5}$ g·cm^{-3}. The uncertainty of V^E values determined from the density measurements is within $1.5 \cdot 10^{-3}$ cm^3·mol^{-1}.

Table 1. Densities ρ and Viscosities η of Pure Component Liquids from (293.15 to 343.15) K

		ρ/(g·cm^{-3})		η/(mPa·s)	
liquid	T/K	exptl	lit.	exptl	lit.
water	293.15	0.99821	0.998203[a]	1.001	1.000[b]
	303.15	0.99569	0.995645[a]	0.798	0.7975[b]
	313.15	0.90225	0.992212[a]	0.653	0.6530[b]
	323.15	0.98805	0.988030[a]	0.547	0.5469[b]
	333.15	0.98319	0.983191[a]	0.467	0.4665[b]
	343.15	0.97778	0.977759[a]	0.408	0.4042[b]
NMM	293.15	0.91874		1.028	
	303.15	0.90954	0.90801[c]	0.959	
	313.15	0.90237	0.90107[c]	0.858	
	323.15	0.89332		0.754	
	333.15	0.88436	0.88316[c]	0.626	
	343.15	0.87652		0.498	

[a] Ref 6. [b] Ref 7. [c] Ref 1.

Kinematic viscosities of the pure liquids and aqueous solutions of *N*-methylmorpholine were measured with a Schott-Gerate measuring system (AVA 300) consisting of a basic control unit, a measuring stand, a constant-temperature bath, and a calibrated Ubbelhode suspended level viscometer. The viscometer was immersed in a thermostatic bath and electronically controlled to the set temperature. The temperature of the water bath containing the viscometer was kept constant to within ± 0.002 K with a Schott-Gerate CT 1150 thermostat. The flow time measurements were made automatically using two light barriers across the viscometer and an electronic timer with a precision of ± 0.01 s. Experiments were repeated a minimum of three times at each temperature for all compositions. The

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kinetic energy correction was considered not necessary on account of a long flow time obtained by a proper selection of the capillary. The uncertainty in viscosity measurements was ± 0.003 mPa·s.

Results and Discussion

The experimental values of density ρ and viscosity η for aqueous solutions of *N*-methylmorpholine at different temperatures and atmospheric pressure are presented in Tables 2 and 3. Excess molar volumes were calculated from our measurements according to the following equation

$$V^{\mathrm{E}} = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (1)$$

where x_1 and x_2 are the mole fractions; M_1 and M_2 are molar masses; and ρ_1 and ρ_2 are the densities of the pure component liquids 1 and 2, respectively. ρ is the density of binary mixtures. The experimental V^{E} data of water (1) + *N*-methylmorpholine (2) mixtures from (293.15 to 343.15) K are presented in Table 4.

The viscosity deviations $\Delta\eta$ were calculated from the following relation

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \qquad (2)$$

where η is the viscosity of the aqueous solution of *N*-methylmorpholine and η_1 and η_2 are the viscosities of the pure component liquids 1 and 2, respectively.

The values of excess molar volume V^{E} and viscosity deviations $\Delta\eta$ for each binary mixture were fitted to the Redlich−Kister polynomial equiation[8]

$$Y = x_1x_2\sum_{i=0}^{n} A_i(x_1 - x_2)^i \qquad (3)$$

where Y represents V^{E} or $\Delta\eta$. A_i are adjustable parameters.

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of the standard deviation

$$\sigma(Y) = \left[\sum \frac{(Y_{\mathrm{calcd}} - Y_{\mathrm{exptl}})^2}{n - m}\right]^{1/2} \qquad (4)$$

where n is the total number of experimental points and m is the number of parameters. The fitting coefficients and the standard deviations values σ for aqueous solutions of NMM from (293.15 to 343.15) K are given in Table 5.

Table 2. Density ρ for Water (1) + *N*-Methylmorpholine (2) from (293.15 to 343.15) K as a Function of Mole Fraction x_2

	$\rho/(\mathrm{g\cdot cm^3\cdot mol^{-1}})$					
x_2	T/K = 293.15	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
0.0452	1.00238	0.99098	0.98504	0.97813	0.96824	0.96212
0.0942	1.00532	0.99365	0.98232	0.97237	0.96101	0.95433
0.1267	1.00331	0.99158	0.98045	0.96824	0.95530	0.94838
0.1763	1.00027	0.98846	0.97758	0.96546	0.95137	0.94412
0.2022	0.99693	0.98514	0.97442	0.96236	0.94734	0.93998
0.2538	0.99188	0.98012	0.96964	0.95773	0.94251	0.93496
0.2843	0.98853	0.97681	0.96647	0.95464	0.93975	0.93211
0.3275	0.98361	0.97196	0.96180	0.95007	0.93560	0.92787
0.3754	0.97787	0.96631	0.95633	0.94475	0.93070	0.92289
0.4033	0.97429	0.96277	0.95291	0.94143	0.92759	0.91976
0.4286	0.97129	0.95983	0.95006	0.93865	0.92500	0.91715
0.4689	0.96609	0.95472	0.94510	0.93380	0.92044	0.91258
0.4983	0.96276	0.95145	0.94192	0.93071	0.91756	0.90969
0.5433	0.95725	0.94605	0.93667	0.92557	0.91267	0.90480
0.5983	0.95009	0.93974	0.93057	0.91996	0.90735	0.89949
0.6438	0.94588	0.93489	0.92580	0.91685	0.90417	0.89630
0.6942	0.94106	0.93106	0.92205	0.91349	0.90090	0.89302
0.7587	0.93453	0.92436	0.91624	0.90616	0.89482	0.88699
0.8163	0.92989	0.92039	0.91231	0.90237	0.89164	0.88381
0.8869	0.92490	0.91552	0.90794	0.89807	0.88889	0.88105
0.9244	0.92259	0.91329	0.90591	0.89615	0.88687	0.87904
0.9812	0.91988	0.91058	0.90331	0.89406	0.88498	0.87714

Table 3. Viscosity η for Water (1) + *N*-Methylmorpholine (2) from (293.15 to 343.15) K as a Function of Mole Fraction x_2

	$\eta/(\mathrm{mPa\cdot s})$					
x_2	T/K = 293.15 K	T/K = 303.15 K	T/K = 313.15 K	T/K = 323.15 K	T/K = 333.15 K	T/K = 343.15 K
0.0452	1.898	1.594	1.327	1.119	0.708	0.499
0.0942	2.577	2.036	1.715	1.334	0.998	0.564
0.1267	3.048	2.451	1.968	1.539	1.111	0.653
0.1763	3.562	2.922	2.348	1.761	1.251	0.691
0.2022	3.777	3.065	2.482	1.858	1.297	0.704
0.2538	4.115	3.386	2.703	2.023	1.396	0.729
0.2843	4.238	3.497	2.838	2.113	1.425	0.757
0.3275	4.395	3.619	2.908	2.183	1.477	0.771
0.3754	4.439	3.669	2.901	2.176	1.468	0.793
0.4033	4.429	3.636	2.869	2.143	1.434	0.757
0.4286	4.406	3.635	2.869	2.144	1.433	0.755
0.4689	4.331	3.562	2.798	2.073	1.361	0.773
0.4983	4.241	3.521	2.758	2.033	1.319	0.718
0.5433	4.065	3.363	2.602	1.948	1.232	0.701
0.5983	3.798	3.128	2.388	1.783	1.126	0.661
0.6438	3.544	2.878	2.244	1.677	1.033	0.629
0.6942	3.187	2.588	2.031	1.536	0.935	0.598
0.7587	2.792	2.262	1.764	1.362	0.837	0.569
0.8163	2.323	1.857	1.495	1.158	0.809	0.566
0.8869	1.791	1.489	1.222	0.954	0.719	0.556
0.9244	1.503	1.359	1.077	0.939	0.703	0.551
0.9812	1.166	1.091	0.952	0.841	0.709	0.535

Table 4. Excess Molar Volumes V^E for Water (1) + *N*-Methylmorpholine (2) from (293.15 to 343.15) K as a Function of Mole Fraction x_2

	$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$					
x_2	T/K = 293.15 K	T/K = 303.15 K	T/K = 313.15 K	T/K = 323.15 K	T/K = 333.15 K	T/K = 343.15 K
0.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.0452	−0.487	−0.331	−0.298	−0.267	−0.201	−0.178
0.0942	−1.009	−0.853	−0.693	−0.601	−0.508	−0.476
0.1267	−1.256	−1.099	−0.948	−0.784	−0.654	−0.609
0.1763	−1.613	−1.456	−1.296	−1.138	−0.978	−0.916
0.2022	−1.728	−1.571	−1.411	−1.254	−1.094	−0.984
0.2538	−1.975	−1.818	−1.658	−1.502	−1.342	−1.201
0.2843	−2.083	−1.927	−1.767	−1.611	−1.451	−1.311
0.3275	−2.198	−2.042	−1.882	−1.725	−1.565	−1.425
0.3754	−2.265	−2.109	−1.948	−1.792	−1.632	−1.492
0.4033	−2.267	−2.111	−1.951	−1.795	−1.635	−1.495
0.4286	−2.267	−2.111	−1.951	−1.795	−1.636	−1.495
0.4689	−2.212	−2.056	−1.895	−1.739	−1.579	−1.439
0.4983	−2.175	−2.019	−1.859	−1.703	−1.543	−1.405
0.5433	−2.054	−1.898	−1.738	−1.582	−1.422	−1.281
0.5983	−1.807	−1.706	−1.549	−1.419	−1.258	−1.119
0.6438	−1.678	−1.522	−1.362	−1.367	−1.183	−1.043
0.6942	−1.478	−1.401	−1.238	−1.281	−1.012	−0.946
0.7587	−1.115	−1.016	−0.924	−0.819	−0.659	−0.578
0.8163	−0.834	−0.799	−0.704	−0.609	−0.547	−0.417
0.8869	−0.489	−0.465	−0.419	−0.325	−0.303	−0.297
0.9244	−0.313	−0.298	−0.274	−0.189	−0.156	−0.149
0.9812	−0.105	−0.092	−0.081	−0.056	−0.045	−0.039
1.0000	0.000	0.000	0.000	0.000	0.000	0.000

Table 5. Redlich−Kister Equation Coefficients A_i and Standard Deviation σ for Water (1) + *N*-Methylmorpholine (2) from T = (293.15 to 343.15) K

T/K	property	A_0	A_1	A_2	A_3	A_4	σ
293.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−0.693	4.786	2.113	−1.387	−2.160	0.001
	$\Delta\eta/\mathrm{mPa \cdot s}$	16.14	−9.96	−5.90	2.49	30.55	0.01
303.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−0.796	4.981	0.308	−3.496	1.709	0.003
	$\Delta\eta/\mathrm{mPa \cdot s}$	13.51	−0.92	−8.20	5.34	25.10	0.02
313.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−7.355	4.653	1.282	−3.624	0.914	0.004
	$\Delta\eta/\mathrm{mPa \cdot s}$	10.09	−8.02	−10.89	5.02	29.55	0.01
323.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−6.012	3.713	2.349	−2.233	0.561	0.003
	$\Delta\eta/\mathrm{mPa \cdot s}$	7.16	−4.84	−3.63	4.17	15.08	0.01
333.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−6.181	3.808	2.361	−3.053	0.939	0.003
	$\Delta\eta/\mathrm{mPa \cdot s}$	5.18	−0.09	−7.03	−6.10	25.32	0.02
343.15	$V^E/\mathrm{cm^3 \cdot mol^{-1}}$	−5.564	3.850	2.340	−3.256	0.508	0.003
	$\Delta\eta/\mathrm{mPa \cdot s}$	3.97	−0.24	−0.53	−5.27	21.11	0.00

It can be observed from the experimental results in Figure 1 that V^E, the excess molar volumes, are negative over the entire composition range from (293.15 to 343.15) K and become less negative with increasing temperature. The shapes of the curves were nearly symmetrical and slightly skewed toward the region of low mole fraction of NMM. Figure 2 shows the percentage deviation $\Delta V^E/V^E$ of our experimental from literature values[1] at 303.15 K. Our experimental measurements agree with literature values within an average absolute percentage deviation of 2.5 %. V^E shows a minimum in the water rich-region, which is related to the composition of the water + NMM mixture. Such behavior can be explained by NMM molecules accommodating into the open or empty space liquid water with close packing resulting in contraction of the volume. The presence of the methyl group on the nitrogen atom of NMM has a great effect on the volume contraction of aqueous solutions of NMM compared with the excess molar volumes of aqueous solutions of morpholine and *N*-formylmorpholine. This suggests that NMM molecules disturb and reorient water molecules to form a complex through strong hydrogen bonding between the nitrogen atom of the NMM molecule and the hydroxyl groups of water.

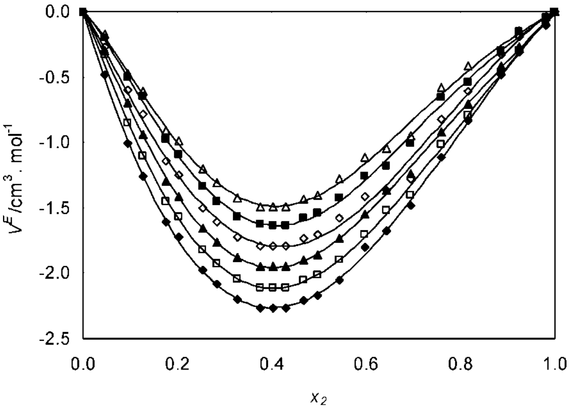

Figure 1. Excess molar volumes of the water (1) + *N*-methylmorpholine (2) system at various temperatures: ◆, 293.15 K; □, 303.15 K; ▲, 313.15 K; ◇, 323.15 K; ■, 333.15 K; △, 343.15 K.

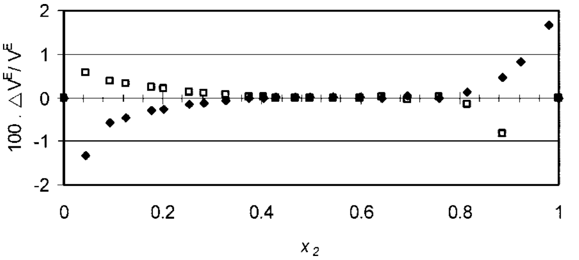

Figure 2. Percentage deviation of the experimental from literature values at 303.15 K. ◆, this work; □, ref 1.

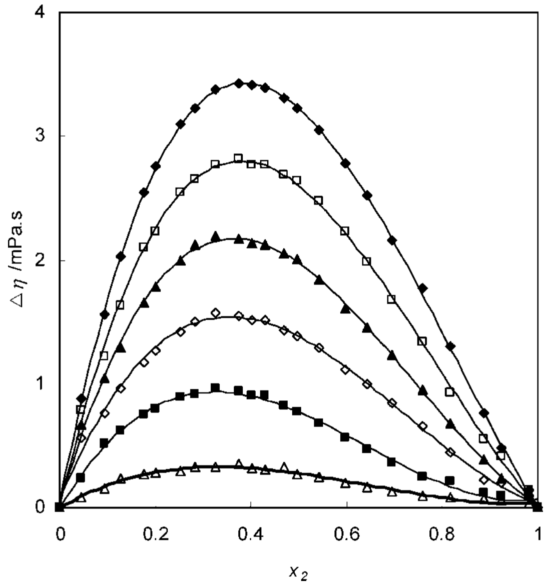

Figure 3. Viscosity deviations of the water (1) + *N*-methylmorpholine (2) at various temperatures: ◆, 293.15 K; □, 303.15 K; ▲, 313.15 K; ◇, 323.15 K; ■, 333.15 K; △, 343.15 K.

Figure 3 displays the dependence of viscosity deviations $\Delta\eta$ on the composition and temperature. Values of viscosity deviations $\Delta\eta$ show a maximum around $x_2 \approx 0.4$ for all temperatures.

Conclusion

This paper reports new experimental data for the densities and viscosities of water (1) + *N*-methylmorpholine (2) over the entire composition range from (293.15 to 343.15) K. The calculated excess molar volumes for the aqueous solution of NMM were all negative at all temperatures and compositions. The negative V^E values and the presence of a maximum in the excess molar volumes curves ($x_2 = 0.4$) suggest that NMM molecules accommodate into the open or empty space in the liquid water structure, and the methyl group on the nitrogen atom of NMM enhances a complex formation due to strong hydrogen bonding between the nitrogen atom of NMM and the hydroxyl groups. The viscosity deviations $\Delta\eta$ for aqueous solutions of NMM were positive over the entire composition range and all temperatures.

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