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Volumetric Properties and Viscosities for Aqueous NFM Solutions from 25 °C to 70 °C

Amr Henni,[*,†] **Paitoon Tontiwachwuthikul,**[†] **and Amit Chakma**[‡]

Process Systems Laboratory, Faculty of Engineering, University of Regina, Regina,
Saskatchewan, Canada S4S 0A2, and Department of Chemical and Materials Engineering,
University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

This paper reports the density and viscosity of aqueous *N*-formyl morpholine (NFM) solutions at five temperatures in the range of 25 °C to 70 °C over the whole concentration range. The results are compared with data published in the literature. Excess molar volumes, partial molar volumes at infinite dilution, and viscosity deviations were derived.

Introduction

If acid gas impurities make up a large proportion of a gas stream, then removing them by heat-regenerable solvents may be out of proportion with the value of the treated gas. In this case, nonreactive organic polar solvents can provide a more economical solution. *N*-Formyl morpholine (NFM) is one of these solvents. NFM was initially selected as one of two promising solvents by Zawacki et al.[1] from a group of more than 100 physical solvents. Recently, Krupp Uhde GmbH commercialized NFM under the name of Morphysorb. The gas sweetening process claims to provide for significant operating cost savings compared to existing physical solvent technologies. Aqueous solutions of *N*-formylmorpholine are widely used for the extraction of aromatic hydrocarbons from petroleum feedstocks.

Our laboratory has been active in measuring the physical and transport properties of chemical and physical solvents of interest to the gas processing industry. In this study, we have measured the density and viscosity of aqueous NFM solutions at various temperatures (25, 30, 40, 50, 60, and 70) °C in order to cover a wide range of temperatures found in industrial applications. The excess volumes, the partial molar volume, the partial molar volumes at infinite dilution, and the deviation of the viscosity were derived.

Experimental Section

NFM (>98% pure) was purchased from Fluka and was used without further purification. The solutions were prepared by mass on an analytical balance (model Ap 205 D, Ohaus, Florham Park, NJ) with ±0.01 mg accuracy. The uncertainty in the mole fractions is estimated to be less than 2×10^{-4}. NFM was kept over molecular sieves in a glass container. Densities of the binary mixtures were measured with an Anton Paar DMA-4500 density meter. Calibration was done using air and water at ambient temperature. The densities of water were measured in the temperature range of (15 °C to 80 °C) and were compared with the values measured by Bettin et al.[2] and provided by Anton Paar in the instruction manual. The calibration was accepted if the measurements were within $\pm 5 \times 10^{-5}$ g·cm^{-3} of the published values. Uncertainties of our densities are about $\pm 5 \times 10^{-5}$ g·cm^{-3} when compared with the densities of pure MDEA published in the literature[3] in the temperature range of 25 °C to 80 °C. The densities of water were measured using deionized water.[4] Density measurements were reproducible to $\pm 2 \times 10^{-5}$ g·cm^{-3}.

In the viscosity measurements, the temperature was controlled by means of a digital controller (±0.004 °C) in a well-stirred water bath to better than ±0.01 °C as measured by a Cole-Parmer resistance thermometer (model H-01158-65, Anjou, Québec, Canada). Viscosities were determined with three different viscometers to cover, with precision, the range of temperature from 25 °C to 70° C. A series of Cannon-Ubbelohde viscometers (Cole-Parmer) were used. The efflux time was measured with a handheld digital stopwatch capable of measuring time to within ±0.01 s. Experiments were repeated a minimum of four times at each temperature for all compositions. The equation for kinematic viscosity, according to Poiseuille's law, is

$$\nu = k_1 t - \frac{k_2}{t} \qquad (1)$$

where t is the efflux time and k_1 and k_2 are the viscometer constants. The second term representing the correction due to the kinetic energy was found to be negligible.[5] The value of the dynamic viscosity (η) was obtained by multiplying the measured kinematic viscosity (ν) by the measured density. Calibration constants for the two viscometers were checked using high-purity ethylene glycol (EG), diethylene glycol (DEG), and water. A review of published values of the kinematic and dynamic viscosities of EG and DEG, with new experimental data, was published by Lee and Teja.[6] Values of the viscosity of water were taken from Stokes and Mills.[7] From the overall average percent deviation of the means of the average efflux time and the uncertainty of the density measurement, we estimate the uncertainty of the dynamic viscosity to be ±1.0%.

Results and Discussion

Values of the density and viscosity for pure NFM are compared with published literature values and are shown in Table 1. The excess volumes of five aqueous concentrations of NFM were reported in the form of a correlation by Awwad et al.[8] The viscosity of pure NFM (99% purity) was also correlated as a function of temperature and not in data

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[*] To whom correspondence should be addressed. E-mail: amr.henni@uregina.ca. Tel: (306) 585-4960. Fax: (306) 585-4855.

[†] University of Regina.

[‡] University of Waterloo.

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Table 1. Review of the Literature Data for the Density and Viscosity of Pure NFM

	ρ/g·cm^{-3}		η/mPa·s	
t/°C	this work	literature	this work	literature
25	1.14662	1.14628[a] 1.14637[b] 1.14621[c]	7.87	6.74[c]
70	1.10739	1.10677[c]	2.68	2.44[c]

[a] Awwad et al.[12] [b] Awwad and Al-Dubaili1.[13] [c] Awwad et al.[8]

Table 2. Density, ρ, for Water (1) + NFM (2) from 25 °C to 70 °C

	t/°C					
x_2	25	30	40	50	60	70
			ρ/g·cm^{-3}			
0.000	0.99704	0.99565	0.99221	0.98804	0.98312	0.97777
0.0499	1.03870	1.03624	1.03093	1.02515	1.01801	1.01138
0.1007	1.06703	1.06395	1.05744	1.05064	1.04355	1.03608
0.1976	1.09955	1.09578	1.08806	1.08016	1.07205	1.06372
0.3006	1.11788	1.11382	1.10552	1.09710	1.08855	1.07983
0.3917	1.12734	1.12311	1.11462	1.10598	1.09724	1.08836
0.5001	1.13434	1.13003	1.12135	1.11462	1.09724	1.08836
0.5834	1.13794	1.13360	1.12487	1.11608	1.10726	1.09833
0.6969	1.14128	1.13691	1.12816	1.11937	1.11055	1.10167
0.7942	1.14343	1.13905	1.13030	1.12152	1.11272	1.10388
0.9047	1.14519	1.14081	1.13207	1.12333	1.11457	1.10579
0.9493	1.14597	1.14160	1.13287	1.12414	1.11540	1.10666
1.0000	1.14662	1.14226	1.13353	1.12482	1.11611	1.10739

form. The viscosities of aqueous solutions of NFM at (25, 30, 35, 40, 50, and 70) °C were reported in the same publication in graphical form. The viscosity of pure NFM reported here at 25 °C is much higher than the value measured by Awwad et al.[8]

Experimentally measured densities of the aqueous NFM solutions at (25, 30, 40, 50, 60, and 70) °C throughout the whole concentration range are listed in Table 2. The curves show an increase in the density at high NFM mole fractions. The maximum values of the density occur at around pure NFM. The density values of the binary mixtures were used to calculate the excess molar volume, $V^{E}{}_{m}$, as

$$V^{E}{}_{m} = V_{m} - V^{\circ}{}_{1}x_{1} - V^{\circ}{}_{2}x_{2} \tag{2}$$

where V_m is the molar volume of the mixture and $V^{\circ}{}_1$ and $V^{\circ}{}_2$ are those of pure water and pure NFM, respectively; x_1 and x_2 are the mole fractions of the components. Figure 1 displays the dependence of $V^{E}{}_{m}$ on the composition at various temperatures. In all cases, $V^{E}{}_{m}$ is negative as is common for other completely miscible (water + polar organic) solvents with a minimum at around 35 mol % NFM. These $V^{E}{}_{m}$ values become less negative with increasing temperature, as is also common. Figure 1 shows a sharp change in $V^{E}{}_{m}$ in the water-rich region.

A Redlich−Kister[9] relation was used to correlate the excess volume data:

$$V_{m}{}^{E}/\text{cm}^{3}\cdot\text{mol}^{-1} = x_{1}x_{2}\sum_{i=0}^{n} a_{i}(x_{1} - x_{2})^{i} \tag{3}$$

The coefficients and the standard deviation (σ) are presented in Table 3. It is well known that the Redlich−Kister relation does not correlate unsymmetrical curves of excess volumes (and viscosity deviations) well.

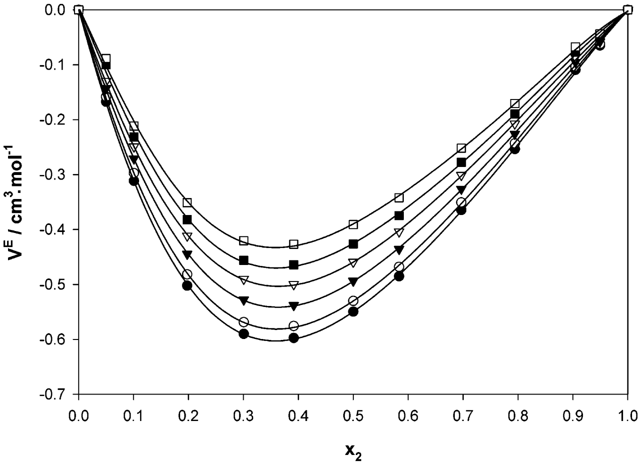

Figure 1. Excess molar volumes of the water (1) + NFM (2) system at various temperatures: ●, 25 °C; ○, 30 °C; ▼, 40 °C; ▽, 50 °C; ■, 60 °C; □, 70°C.

Table 3. Redlich−Kister Equation Fitting Coefficients of the Excess Volumes for Water (1) + NFM (2) from 25 °C to 70 °C

t/°C	a_0	a_1	a_2	a_3	a_4	σ/cm^3·mol^{-1}
25	−2.2199	−1.3680	−0.4956	0.0777	0.3084	0.003
30	−2.1333	−1.2877	−0.2565			0.004
40	−1.9904	−1.1815	−0.1817			0.005
50	−1.8498	−1.1722	−0.1263	0.1947		0.004
60	−1.7010	−1.1385	−0.4239	0.3185	0.6468	0.007
70	−1.5592	−1.0802	−0.3896	0.3394	0.6475	0.007

Table 4. Partial Molar Volumes $V^{\infty}{}_1$ and $V^{\infty}{}_2$ at Infinite Dilution from 25 °C to 70 °C

t / °C	$V^{\infty}{}_1$ / cm^3·mol^{-1}	$V^{\infty}{}_2$ / cm^3·mol^{-1}
25	16.5	96.8
30	16.6	97.5
40	16.7	98.6
50	16.9	99.7
60	17.1	101.8
70	17.2	102.9

The partial molar volume of NFM at infinite dilution ($V^{\infty}{}_2$) in water was obtained using the method proposed by Maham et al.[10] The apparent molar volume of NFM in water ($V_{\phi,2}$) was first calculated as

$$V_{\phi,2} = V^{\circ}{}_{2} + \frac{V^{E}{}_{m}}{x_{2}} \tag{4}$$

$$V_{\phi,1} = V^{\circ}{}_{1} + \frac{V^{E}{}_{m}}{1 - x_{2}} \tag{5}$$

where $V^{\circ}{}_1$ and $V^{\circ}{}_2$ are the molar volumes and x_1 and x_2 are the mole fractions of pure water and NFM, respectively. Values of the obtained $V_{\phi,1}$ that were regressed as a function of x_2 and extrapolated to $x_2 = 1$ led to $V^{\infty}{}_1$. A similar procedure for the regression of $V_{\phi,2}$ values and extrapolation to $x_2 = 0$ led to $V^{\infty}{}_2$. Partial molar volumes at infinite dilution are listed in Table 4. $V^{\infty}{}_2$ values varied linearly with temperature. It is important to note that the apparent volume values ($V_{\phi,2}$) have a minima in the water-rich region around 5 mol %. This minimum does not exist for temperatures below 60 °C. The presence of a similar trend at lower NFM mole fractions if it exists would affect the values of $V^{\infty}{}_2$. Ultrasonic studies of NFM + water solutions reported by Awwad et al.[8] concluded that the planarity of NFM is increased by the presence of water and that NFM introduces hydrogen bonding and ordering of the water molecules at low concentrations and disrupts the water structures at higher concentrations.

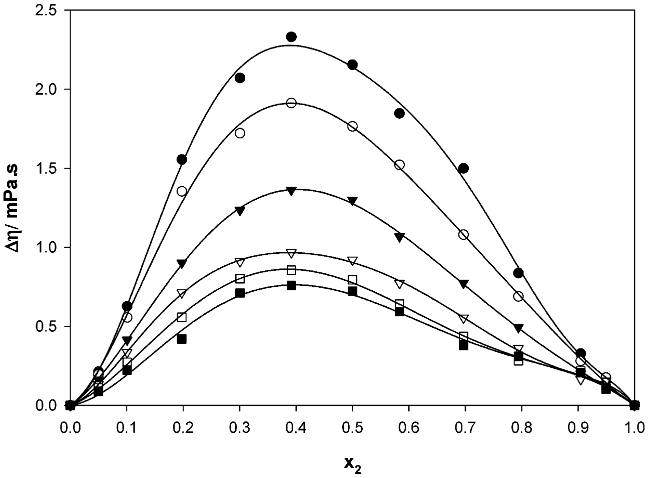

Figure 2. Viscosity deviations for the water (1) + NFM (2) system at various temperatures: ●, 25 °C; ○, 30 °C; ▼, 40 °C; ▽, 50 °C; □, 60°C; ■, 70 °C.

Table 5. Viscosity, η, for Water (1) + NFM (2) from 25 °C to 70 °C

	t/°C					
x_2	25	30	40	50	60	70
			η/mPa·s			
0.000	0.8903	0.7976	0.6531	0.5470	0.4660	0.4049
0.0499	1.45	1.29	1.038	0.854	0.7150	0.6070
0.1007	2.22	1.95	1.52	1.23	1.02	0.8570
0.1976	3.82	3.33	2.44	1.95	1.57	1.27
0.3006	5.06	4.31	3.23	2.50	2.10	1.80
0.3917	5.95	5.04	3.77	2.88	2.41	2.05
0.5001	6.53	5.54	4.19	3.21	2.65	2.26
0.5834	6.81	5.79	4.33	3.35	2.73	2.33
0.6969	7.25	6.02	4.55	3.53	2.84	2.37
0.7942	7.27	6.21	4.70	3.67	2.96	2.52
0.9047	7.53	6.46	4.90	3.86	3.20	2.67
0.9493	7.69	6.62	5.03	4.01	3.21	2.67
1.0000	7.87	6.75	5.13	4.03	3.25	2.68

Experimentally measured viscosities of the binary solutions of aqueous NFM solutions at (25, 30, 40, 50, 60, and 70) °C are listed in Table 5. The largest viscosity values were those of pure NFM at all temperatures.

Experimental viscosity values of the binary mixtures were used to calculate the viscosity deviation, defined by

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2 \tag{6}$$

where η is the viscosity of the mixture and η_1 and η_2 are those of pure water and pure NFM, respectively; x_1 and x_2 are the mole fractions of pure water and NFM, respectively. The viscosity deviation represents deviations from an additive dependence of viscosity on mole fraction. Figure 2 displays the dependence of $\Delta\eta$ on the composition and temperature. Values of $\Delta\eta$ were positive with a maximum around 40 mol % for all temperatures.

The calculated values of $\Delta\eta$ were correlated with a Redlich–Kister[9] relation

$$\Delta\eta/\text{mPa·s} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{7}$$

where x_1 is the mole fraction of water and x_2 is the mole fraction of NFM. The coefficients and the standard deviation (σ) are presented in Table 6. The Grunberg–Nissan[11] parameters (d_{12}) were calculated for all compositions and temperatures. They were all positive and varied from a maximum of 8.0 at low NFM concentrations to a minimum of 1.71 at high NFM concentration. The positive values of the coefficients suggest the predominance of interaction forces through hydrogen bonding as supported by the negative values of the excess volumes.

Table 6. Redlich–Kister Equation Fitting Coefficients of the Viscosity Deviations for Water (1) + NFM (2) from 25 °C to 70 °C

t/°C	a_0	a_1	a_2	a_3	σ/mPa·s
25	8.871	5.144	−4.674	−4.956	0.07
30	7.169	5.036	−3.240	−5.053	0.04
40	5.136	3.467	−2.446	−3.454	0.01
50	3.635	2.697	−1.002	−2.732	0.02
60	3.101	2.748	−0.987	−3.570	0.02
70	2.798	2.235	−1.040	−3.504	0.03

Conclusions

This paper reports experimental data for the densities and viscosities of aqueous NFM solutions over a range of temperature from 25 to 70 °C. The calculated V^{E}_{m} values for the aqueous NFM solutions were all negative at all temperatures and compositions. The viscosity deviations $\Delta\eta$ for NFM + water were positive at all concentrations and temperatures. The positive values of the Grunberg–Nissan paramters and the excess volumes at all temperatures and compositions suggest the predominance of interaction forces.

Literature Cited

(1) Zawacki, T. S.; Duncan, D. A.; Macriss, R. A. Process Optimized for High-Pressure Gas Cleanup. *Hydrocarbon Process.* **1981**, *60*, 143–149.
(2) Bettin, H.; Spieweck, F.; Die Dichte des Wassers als Funktion der Temperatur nach Einführung der Internationalen Temperaturskala von **1990**. *PTB-Mitt.* **1990**, *100*, 195–196.
(3) Maham, Y.; Teng, T. T.; Mather, A. E.; Hepler, L. G. Volumetric Properties of (Water − Diethanolamine) Systems. *Can. J. Chem.* **1995**, *73*, 1514–1519.
(4) Density and Relative Density of Liquids By Digital Density Meter. *Annual Book of ASTM Standards*; Standard D 4052-81; American Society of Testing Materials: Philadelphia, PA, 1986; Vol. 05.03, 294–298.
(5) Cannon, M. R.; Manning, R. E.; Bell, J. D. Viscosity Measurement. Kinetic Energy Correction and New Viscometer. *Anal. Chem.* **1960**, *32*, 355–358.
(6) Lee, R.-J.; Teja, A. S. Viscosities of Poly(ethylene glycols). *J. Chem. Eng. Data* **1990**, *35*, 385–387.
(7) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon Press: New York, 1965.
(8) Awwad, A. M.; North, A. M.; Pethrick, R. A. Ultrasonic Studies of N-Formylmorpholine + Water Mixtures. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 449–461.
(9) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
(10) Maham, Y.; Teng, T. T.; Hepler, L. G.; Mather, A. E. Densities, Excess Molar Volumes, and Partial Molar Volumes for Binary Mixtures of Water with Monoethanolamine, Diethanolamine, and Triethanolamine from 25 to 80 °C. *J. Solution Chem.* **1994**, *23*, 195–205.
(11) Grunberg L.; Nissan, A. H. Mixture Law for Viscosity. *Nature* **1949**, *164*, 799–800.
(12) Awwad A. M. Excess Molar Volumes of Some Binary Mixtures Containing Morpholine or N-Formylmorpholine, Selected Data on Mixtures. *Int. DATA Ser., Ser. A* **1988**, *1988*, 47–57.
(13) Awwad A. M.; Al Dujaili, A. H. Density, Refractive Index, Permittivity, and Related Properties for *N*-Formylmorpholine + Ethyl Acetate and + Butanone at 298.15 K *J. Chem. Eng. Data* **2001**, *46*, 1349–1350.

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