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Volumetric Properties and Viscosities for Aqueous *N*-Methyl-2-pyrrolidone Solutions from 25 °C to 70 °C

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This paper reports the densities and viscosities of aqueous *N*-methyl-2-pyrrolidone (NMP) solutions at five temperatures in the range 25 °C to 70 °C over the whole concentration range. The results are compared with data published in the literature. The derived excess molar volumes, the partial molar volumes, the partial molar volumes at infinite dilution, and the viscosity deviations were correlated as a function of composition.

Introduction

If acid gas impurities make up a large proportion of the total gas stream, 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*-Methyl-2-pyrrolidone (NMP) is one of these solvents and is used in the Purisol process (Lurgi). Lurgi's Purisol process is particularly suited for the selective desulfurization of gases from oil or coal gasification. Kohl and Nieslen[1] provide a comparison between NMP, Selexol, and propylene carbonate in terms of their capacity for the absorption of CO_2, H_2S, and other components found in natural gas.

NMP (CAS No. 872-50-4, C_5H_9NO) is a water-miscible organic solvent. It is a hygroscopic colorless liquid with a mild amine odor. NMP is used in the petrochemical industry in the extraction of aromatics and butadiene and in the removal and purification of acetylene. In the microelectronics fabrication industry, NMP is used as a solvent to improve surface coating and in the cleaning and degreasing of single-crystal silicon wafers. In the plastics industry, it is used to dissolve many polymers. It is also used in the manufacture of various compounds, including cosmetics, pigments, insecticides, herbicides, pigments, and fungicides. Its toxicological and ecological properties account for the fact that it is increasingly being used as a substitute for chlorinated hydrocarbons.

Experimental Section

NMP (>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 possible error in the mole fraction is estimated to be around ±0.0001. NMP 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 (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 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}.

For 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 hand-held 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

$$\nu = k_1 t - k_2 / t \qquad (1)$$

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 absolute 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 ref 7. From the overall average percent deviation of the means of the average efflux time and the accuracy of the density measurement, we estimate the uncertainty of the absolute viscosity to be ±1.0%.

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Table 1. Review of the Literature Data for the Density of NMP

	ρ/g·cm^{-3}		η/mPa·s	
T/K	this work	lit.	this work	lit.
298.15 (25)	1.028 72	1.0259[b] 1.02832[c] 1.0286[d] 1.02759[e] 1.0283[f]	1.656	1.66[c] 1.663[d] 1.67[f]
313.15 (40)	1.015 19	1.0157[a] 1.0120[b]		
323.15(50)	1.006 27	1.0054[a] 1.0030[b]		
333.15 (60)	0.997 41	0.9974[a] 0.9934[b]		

[a] Reference 8. [b] Reference 9. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 19.

Table 2. Density, ρ, for Water (1) + NMP (2) from 298.15 K to 343.15 K

	ρ/g·cm^{-3}				
x_2	25 °C	40 °C	50 °C	60 °C	70 °C
0.0000	0.997 04	0.992 21	0.988 04	0.983 12	0.977 77
0.0501	1.013 41	1.005 83	1.000 08	0.993 90	0.987 04
0.0701	1.019 40	1.010 71	1.004 33	0.997 51	0.990 23
0.1001	1.027 28	1.017 13	1.009 94	1.002 36	0.994 46
0.2004	1.043 59	1.030 49	1.021 51	1.012 34	1.002 99
0.3004	1.048 44	1.034 34	1.024 81	1.015 11	1.005 26
0.4012	1.047 57	1.033 33	1.023 70	1.013 94	1.004 05
0.5030	1.045 28	1.031 16	1.021 60	1.011 96	1.002 21
0.5937	1.042 09	1.028 20	1.018 85	1.009 35	0.999 76
0.7023	1.038 39	1.024 65	1.015 62	1.006 23	0.996 83
0.8066	1.034 68	1.021 04	1.011 92	1.002 76	0.993 56
0.9006	1.031 07	1.017 59	1.008 60	0.999 55	0.990 50
1.0000	1.028 72	1.015 19	1.006 27	0.997 41	0.988 46

Results and Discussion

Our density values for pure NMP are in very good agreement with the values recently published by Aguila-Hernández et al.[8] The value of viscosity of pure NMP at 298 K is also in very good agreement with published literature data (Table 1).

Experimentally measured densities of the aqueous NMP solutions at (25, 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 NMP mole fractions. The maximum values of the density occur at around 30 mol %. The density values of the binary mixtures were used to calculate the excess molar volume, V_m^E, as

$$V_m^E = V_m - V_1^\circ x_1 - V_2^\circ x_2 \tag{2}$$

where V_m is the molar volume of the mixture and V_1° and V_2° are those of pure water and pure NMP, respectively; x_1 and x_2 are the mole fractions of the components. Figure 1 displays the dependence of V_m^E on the composition at various temperatures. In all cases, the V_m^E is negative, as is common for other completely miscible (water + polar organic) solvents with a minimum at around 40 mol % NMP. These V_m^E values become less negative with increasing temperature, as is also common. Figure1 shows a sharp change in the V_m^E in the water-rich region. NMP is a highly polar solvent.

A Redlich−Kister[10] relation was used to correlate the excess volume data:

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{3}$$

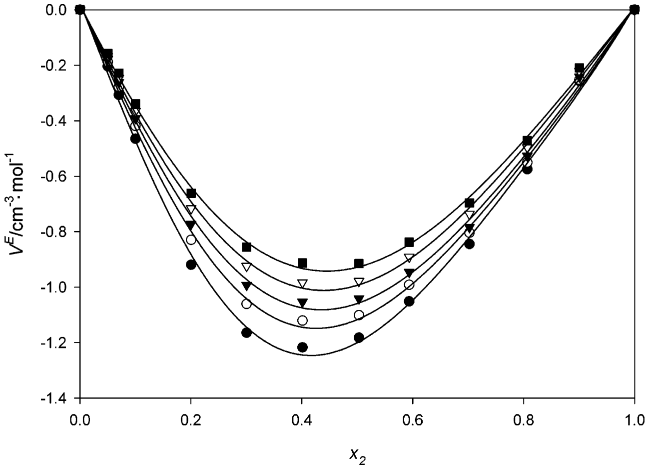

Figure 1. Excess molar volumes of the water (1) + NMP (2) system at various temperatures: ●, 25 °C; ○, 40 °C; ▼, 50 °C; ▽, 60 °C; ■, 70 °C.

Table 3. Redlich−Kister Equation Fitting Coefficients of the Excess Volumes for Water (1) + NMP (2) from 298.15 K to 343.15 K

T/°C	a_0	a_1	a_2	a_3	a_4	σ/cm^3·mol^{-1}
25	−4.6840	−1.9888	−1.4383	0.9091	3.9012	0.008
40	−4.3680	−1.5741	−1.1266	0.6827	3.3140	0.007
50	−4.1365	−1.2705	−1.1243	0.3617	3.2792	0.005
60	−3.8835	−1.0949	−0.9576	0.1617	2.9928	0.005
70	−3.6298	−0.9083	−0.8774	0.0401	2.7746	0.005

Table 4. Partial Molar Volume, V_2^∞, for NMP at Infinite Dilution in Water from 298.15 K to 343.15 K

T/°C	V_2^∞/cm^3·mol^{-1}
25	93.1
40	94.6
50	95.6
60	96.6
70	97.7

The coefficients and the standard deviation (σ) are presented in Table 3. It is well-known that the Redlich−Kister relation does not correlate well unsymmetrical curves of excess volumes (and viscosity deviations). Hepler[11] and Neal and Goring[12] recognized the usefulness of thermal expansion data for revealing correlations between the molecular structure of solutes and their effects on water structure. They suggested using the sign of the second derivative of the partial molar volume at infinite dilution of the solute with respect to the temperature $(\partial^2 V_2^\circ/\partial T^2)_P$ to classify solutes as “structure makers” or “structure breakers”. A positive sign corresponds to a structure-making solute while a negative sign corresponds to a structure-breaking solute.

The partial molar volumes of NMP at infinite dilution (V_2^∞) in water were obtained using the method proposed by Maham et al.[13] The apparent molar volumes of NMP in water ($V_{\phi,2}$) were first calculated as

$$V_{\phi,2} = V_2^\circ + (V_m^E/x_2) \tag{4}$$

where V_1° and V_2° are the molar volumes of pure water and NMP, respectively, and x_2 is the mole fraction of NMP. An analytical extrapolation of $V_{\phi,1}$ to $x_2 = 1$ leads to V_1^∞, and a similar extrapolation to $x_2 = 0$ leads to V_2^∞. Partial molar volumes at infinite dilution are listed in Table 4. V_2^∞ values varied linearly with temperature. According to the criterion described above, the solute (NMP) would be considered as having no net effect on the structure of water.

Table 5. Viscosity, η, for Water (1) + NMP (2) from 298.15 K to 343.15 K

	η/mPa·s				
x_2	25 °C	40 °C	50 °C	60 °C	70 °C
0.0000	0.890	0.653	0.547	0.466	0.405
0.0501	1.740	1.178	0.942	0.767	0.644
0.0701	2.137	1.402	1.106	0.901	0.749
0.1001	2.762	1.744	1.351	1.078	0.883
0.2004	4.555	2.684	1.995	1.537	1.232
0.3004	5.062	2.975	2.214	1.709	1.360
0.4012	4.505	2.777	2.116	1.663	1.343
0.5030	3.729	2.440	1.935	1.548	1.273
0.5937	3.075	2.125	1.710	1.419	1.191
0.7023	2.503	1.818	1.509	1.274	1.097
0.8066	2.091	1.585	1.343	1.165	1.019
0.9006	1.836	1.430	1.236	1.078	0.951
1.0000	1.656	1.322	1.175	1.035	0.921

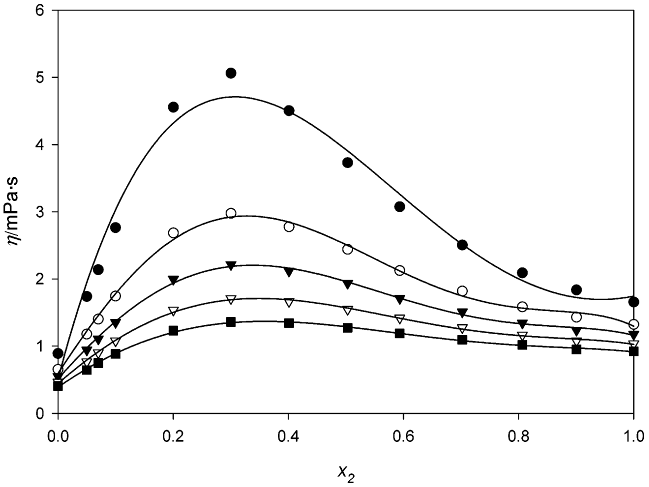

Figure 2. Viscosities of the water (1) + NMP (2) system at various temperatures: ●, 25 °C; ○, 40 °C; ▼, 50 °C; ▽, 60 °C; ■, 70 °C.

All the values of the molar volumes at infinite dilution (V_2^∞) were smaller than the corresponding molar values of pure NMP (V_2°). The change in the excess volume can be explained by the NMP molecule fitting (partially) into the open or empty space in liquid water. This picture does not invoke either the structure-making or the -breaking properties and is consistent with the observation that $(\partial^2 V_2^\infty/\partial T^2)_P$ values are approximately equal to zero. This conclusion is in contradiction with suggestions made by MacDonald et al.,[19] Garcia et al.,[16] and Assarsson et al.[17] that transient $(\text{NMP}\cdot 2\text{H}_2\text{O})_n$ polymeric species are present in solution. Hepler's criterion was applied to aqueous solutions[15] of triethylene glycol monomethyl ether, tetraethylene glycol dimethyl ether, and *N*-formyl morpholine and aqueous solutions of monoethanolamine, diethanolamine, triethanolamine, methyldiethanolamine, diisopropanolamine, diglycolamine, dimethylmonoethanolamine, and 2-amino-2-methylpropanol. The surprising conclusion for all these systems was that the solutes would be considered as having no net effect on the structure of water! It would be of interest to apply Hepler's criterion to systems known to form complexes.

Experimentally measured viscosities of the binary solutions of aqueous NMP solutions at (25, 40, 50, 60, and 70) °C are listed in Table 5. The largest viscosity values were those of aqueous NMP solutions up to 30 mol % at all temperatures. NMP aqueous solutions exhibited S-shaped viscosity curves (Figure 2).

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

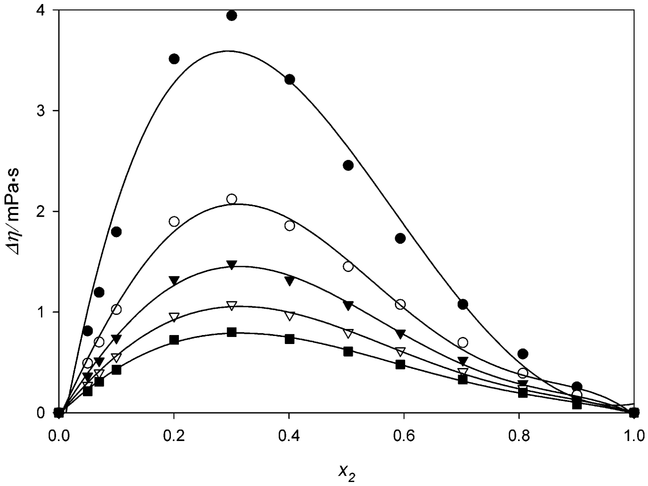

Figure 3. Viscosity deviations for the water (1) + NMP (2) system at various temperatures: ●, 25 °C; ○, 40 °C; ▼, 50 °C; ▽, 60 °C; ■, 70 °C.

Table 6. Redlich−Kister Equation Fitting Coefficients of the Viscosity Deviations for Water (1) + NMP (2) from 298.15 K to 343.15 K

T/°C	a_0	a_1	a_2	a_3	a_4	a_5	σ/mPa·s
25	9.891	17.580	15.681	−2.970	−20.331	−11.398	0.03
40	5.831	8.620	6.792	−0.582	−8.369	−5.440	0.01
50	4.257	5.742	3.898	−0.061	−4.651	−3.364	0.01
60	3.189	3.899	2.676	0.203	−3.018	−2.124	0.005
70	2.433	2.730	2.058	0.469	−2.213	−1.554	0.003

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2 \tag{5}$$

where η is the viscosity of the mixture and η_1 and η_2 are those of pure water and pure NMP, respectively; x_1 and x_2 are the mole fractions of the pure components. The viscosity deviation represents deviations from a rectilinear dependence of viscosity on mole fraction. Figure 3 displays the dependence of $\Delta\eta$ on the composition and temperature. Values of $\Delta\eta$ were positive with a maximum around 30 mol % for all temperatures. According to Fort and Moore's[20] observation, the S shape of the viscosity curves and the presence of maxima indicate a formation of stable complexes.

The calculated values of $\Delta\eta$ were correlated with a Redlich−Kister[10] relation:

$$\Delta\eta/\text{mPa·s} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{6}$$

where x_1 is the mole fraction of water and x_2 is the mole fraction of NMP. The coefficients and the standard deviation (σ) are presented in Table 6.

Conclusions

This paper reports experimental data for the densities and viscosities of the aqueous NMP solutions over a range of temperature from 25 °C to 70 °C. The calculated V_m^E values for the aqueous NMP solutions were all negative at all temperatures and compositions. The criterion proposed by Hepler suggests that the addition of NMP to water had no effect on its structure. In contradiction to what is concluded by applying Hepler's criterion, various workers[16,17,19] suggested an association of two water molecules with one NMP molecule via the two lone electron pairs on the oxygen atom of the carbonyl group to form a polymeric molecule. The viscosity deviations $\Delta\eta$ for NMP + water were positive at all concentrations and temperatures. NMP aqueous solutions exhibited S-shaped viscosity curves and a maximum in the viscosity deviations. According to Fort and Moore,[20] this suggests a possible formation of a stable complex. This would be in agreement with the conclusions of Garcia et al.[16] and others.[17,19]

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