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Densities and Excess Molar Volumes of *N*-Methylmorpholine + 1-Alkanol Systems at 298.15 K

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Densities, ρ, of pure *N*-methylmorpholine (1) + ethanol (2), + 1-propanol (2), + 1-butanol (2), + 1-pentanol (2), + 1-hexanol (2), and + 1-octanol (2) and their binary mixtures were measured using a digital vibrating tube densimeter at 298.15 K. Excess molar volumes, V^E, of the binary mixtures were calculated from density values. Excess molar volumes of binary mixtures of *N*-methylmorpholine (1) + ethanol (2) and + 1-propanol (2) show an S-shaped dependence on composition with positive values in the *N*-methylmorpholine-rich region and negative values at the opposite extreme. The excess molar volume is positive over the mole fraction range for *N*-methylmorpholine (1) + 1-butanol (2), + 1-pentanol (2), 1-hexanol (2), and + 1-octanol (2) systems. All experimental V^E values were fitted to the Redlich–Kister equation.

Introduction

N-Methylmorpholine (NMM) is a water-miscible organic solvent and one of the alkyl derivatives of morpholine. NMM is used as a catalyst for the production of polyurethane foams or cross-linker in the production of polyurethane foams, corrosion inhibitor, pharmaceutical, and solvent and extractant. Nitrogen in the ring of the NMM molecule results in the introduction of a sterically demanding asymmetric center to achieve effective stereocontrol.

As a part of our experimental program on the physicochemical properties of binary liquid mixtures containing morpholine and its derivatives as a common solvent,[1–4] we report here measurements of the density for binary mixtures of *N*-methylmorpholine (1) + ethanol (2), + 1-propanol (2), + 1-butanol (2), + 1-pentanol (2), + 1-hexanol (2), and + 1-octanol (2) at 298.15 K over the mole fraction range. From these data, we calculated the excess molar volumes, V^E, and these were fitted to the Redlich–Kister polynomial equation.

Experimental Section

Materials. *N*-Methylmorpholine, NMM (stated mass fraction purity 0.98), ethanol (stated mass fraction purity 0.998), 1-propanol (stated mass fraction purity 0.99), 1-butanol (stated mass fraction purity 0.99), 1-pentanol (stated mass fraction purity 0.995), 1-hexanol (stated mass fraction purity 0.995), and 1-octanol (stated mass fraction purity 0.995) were obtained from Fluka AG. All liquids were kept over activated molecular sieves of type 4A (Union Carbide) and filtered before use. The purity of liquids was confirmed by gas–liquid chromatographic analysis. The measured densities of the pure solvents at 298.15 K are given in Table 1 together with the literature data.[5–7] Binary mixtures were prepared on a mass basis.

Apparatus and Procedure. The densities of the pure liquids and their binary mixtures were measured with a digital densimeter DMA 60/602 (Anton Paar) whose cell temperature was controlled automatically within ± 0.01 K of the selected value. Before each series of measurements, the densimeter was calibrated at atmospheric pressure with double distilled water and dry air. Densities, both water and dry air, at the various working temperatures were given by the manufacturer in the instruction manual. The reproducibility of the density measurement was ± $2 \cdot 10^{-5}$ g·cm^{-3}.

Table 1. Experimental Densities (ρ) of the Pure Component Liquids at T = 298.15 K Together with Literature Data

	ρ/g·cm^{-3}	
solvent	exptl	lit.
ethanol	0.78494	0.78493
1-propanol	0.79952	0.79957
1-butanol	0.80592	0.80600
1-pentanol	0.81083	0.81080
1-hexanol	0.81495	0.81501
1-octanol	0.82165	0.82161
NMM	0.91406	0.91294

The binary mixtures were prepared by mass using a Mettler AB 204-N balance accurate to 0.01 mg. The average uncertainty in the mole fraction of the binary mixtures was estimated to be less than ± 0.0001.

Results and Discussion

The experimental values of density for binary mixtures NMM (1) + ethanol (2), + 1-propanol (2), + 1-butanol (2), + 1-pentanol (2), + 1-hexanol (2), and + 1-octanol (2) at 298.15 K are listed in Table 2. Excess molar volumes were calculated according to the following equation

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

where x_1 and x_2 are mole fractions; M_1 and M_2 are molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. ρ is the density of the binary mixtures. The excess molar volumes were fitted to the Redlich–Kister polynomial equation.[8]

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$$V^{\mathrm{E}} = x_1 x_2 \sum_{j=0}^{m} A_j (x_1 - x_2)^j \qquad (2)$$

For each mixture, the optimum number of adjustable parameters was ascertained from an examination of the variation in the standard deviation σ.

$$\sigma = \left[\sum (V^{\mathrm{E}} - V^{\mathrm{E}})^2 / n - m)\right]^{1/2} \qquad (3)$$

where n is the number of experimental points and m is the number of parameters A_j. The values of A_j and the standard deviations σ are reported in Table 3. It can be observed from the experimental results in Table 2 and Figure 1 that the V^{E} for mixtures of *N*-methylmorpholine (1) + ethanol (2) and + 1-propanol (2) shows two structural regions exist over the whole mole fraction range. Considering the NMM region $0 \le x \le 0.6$ which shows a negative deviation from ideal, one can reasonably assume that initially added NMM enhanced the ethanol and 1-propanol structures via interstitial accommodation and orientation order leading to a more compact structure, the tendency to a volumetric contraction, and a negative excess molar volume. In the second region, as the mole fraction x of NMM increases, V^{E} becomes positive, $0.6 \le x \le 1$ (Figure 1).

Table 2. Densities (ρ) and Excess Molar Volumes (V^{E}) for *N*-Methylmorpholine (1) + 1-Alkanol (2) at T = 298.15 K

	ρ	V^{E}		ρ	V^{E}
x_1	$(\mathrm{g \cdot cm^{-3}})$	$(\mathrm{cm^3 \cdot mol^{-1}})$	x_1	$(\mathrm{g \cdot cm^{-3}})$	$(\mathrm{g \cdot cm^{-3}})$
N-Methylmorpholine (1) + Ethanol (2)					
0.0511	0.79755	−0.0547	0.5342	0.87535	−0.2094
0.1166	0.81241	−0.1387	0.5832	0.87941	−0.0844
0.1795	0.82538	−0.2254	0.6432	0.88436	0.0365
0.2438	0.83723	−0.2964	0.7234	0.89096	0.1437
0.2795	0.84343	−0.3425	0.7786	0.89553	0.1785
0.3532	0.85469	−0.3833	0.8216	0.89913	0.1801
0.4021	0.86124	−0.3798	0.8794	0.90405	0.1447
0.4573	0.86756	−0.3211	0.9432	0.90942	0.0764
0.4982	0.87173	−0.2554	0.9832	0.91263	0.0332
N-Methylmorpholine (1) + 1-Propanol (2)					
0.0237	0.80387	−0.0422	0.5784	0.87468	0.1569
0.1003	0.81655	−0.0885	0.6347	0.87993	0.2144
0.1657	0.82667	−0.1244	0.7195	0.88806	0.2287
0.2336	0.83652	−0.1548	0.7684	0.89276	0.2104
0.2812	0.84301	−0.1666	0.8327	0.89856	0.1988
0.3458	0.85112	−0.1537	0.8674	0.90193	0.1558
0.3988	0.85714	−0.1094	0.9443	0.90883	0.0976
0.4476	0.86199	−0.0189	0.9878	0.91275	0.0436
N-Methylmorpholine (1) + 1-Butanol (2)					
0.0455	0.81149	0.0334	0.5285	0.86454	0.4099
0.1089	0.81895	0.0957	0.6444	0.87667	0.4022
0.1675	0.82555	0.1658	0.7198	0.88545	0.3675
0.2399	0.83380	0.2174	0.7865	0.89147	0.3217
0.2811	0.83833	0.2547	0.8237	0.89531	0.2897
0.3494	0.84570	0.3101	0.8843	0.90173	0.1985
0.3985	0.85099	0.3379	0.9411	0.90787	0.1009
0.4533	0.85671	0.3768	0.9801	0.91200	0.0321
N-Methylmorpholine (1) + 1-Pentanol (2)					
0.0487	0.81372	0.0548	0.6444	0.87293	0.5198
0.1129	0.82002	0.1264	0.7267	0.88191	0.4873
0.1766	0.82608	0.2193	0.7801	0.88789	0.4127
0.2412	0.83241	0.2873	0.8226	0.89269	0.3657
0.2801	0.83623	0.3246	0.8811	0.89957	0.2652
0.3998	0.84787	0.4503	0.9428	0.90710	0.1256
0.4612	0.85403	0.4874	0.9854	0.91211	0.0537
0.5826	0.86638	0.5327			
N-Methylmorpholoine (1) + 1-Hexanol (2)					
0.0459	0.81834	0.0987	0.5998	0.86675	0.6238
0.1098	0.82337	0.1969	0.6583	0.87276	0.6103
0.1852	0.82949	0.2977.	0.7174	0.87914	0.5664
0.2377	0.83369	0.3875	0.7844	0.88651	0.5164
0.2855	0.83776	0.4385	0.8341	0.89231	0.4473
0.3495	0.84334	0.4974	0.8964	0.89975	0.3533
0.4034	0.84809	0.5488	0.9538	0.90713	0.2176
0.4887	0.85597	0.5984	0.9784	0.91069	0.1163
0.5129	0.85826	0.6088			
N-Methylmorpholine (1) + 1-Octanol (2)					
0.0461	0.82388	0.1145	0.6012	0.86381	0.7853
0.1101	0.82755	0.2632	0.6547	0.0.8695	0.7439
0.1862	0.83209	0.3962	0.7213	0.87597	0.6732
0.2381	0.83533	0.4996	0.7831	0.88326	0.6427
0.2848	0.83858	0.5562	0.8353	0.88972	0.5126
0.3484	0.84306	0.6372	0.8958	0.89782	0.4022
0.4029	0. 84699	0.7033	0.9541	0.90592	0.2674
0.4899	0.85386	0.7542	0.9792	0.90972	0.1853
0.5121	0.85592	0.7642			

Table 3. Standard Deviations (σ) and Parameters A_j in Equation 2 at T = 298.15 K

system	A_0	A_1	A_2	A_3	A_4	σ
NMM (1) + ethanol (2)	−1.0005	3.2958	2.8939	−2.7714	−1.8916	0.0111
NMM (1) + 1-propanol (2)	0.2079	1.6651	−0.8245	0. 6987	1.4969	0.0306
NMM (1) + 1-butanol (2)	1.5529	0.7181	0.3084	−0.2244	−0.7731	0.0208
NMM (1) + 1-pentanol (2)	2.0308	0.9497	0.0789	−0.3612	−0.5191	0.0341
NMM (1) + 1-hexanol (2)	2.4748	0.4827	−0.7905	1.1788	2.6046	0.0403
NMM (1) + 1-octano (2)	3.2554	−0.2893	−3.0057	3.0841	6.0726	0.0302

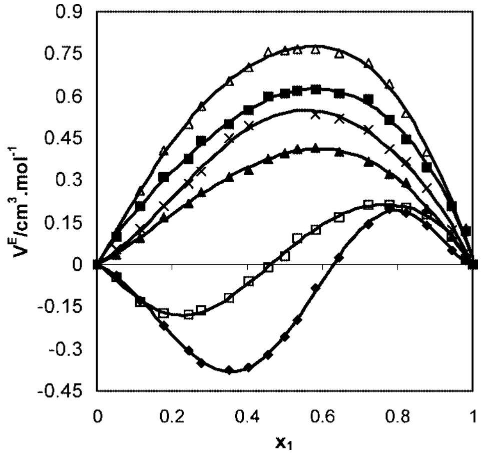

Figure 1. Excess molar volumes, V^{E}, at T = 298.15 K for *N*-methylmorpholine (1) + 1-alkanol (2): ◆, ethanol; □, 1 propanol; ▲, 1-butanol; x, 1-pentanol; ■, 1-hexanol; Δ, 1-octanol.

The excess molar volume for mixtures NMM (1) + 1-butanol (2), + 1-pentanol (2), + 1-hexanol (2), and + 1-octanol (2) is positive over the whole mole fraction range and increases with increasing carbon chain length in 1-alkanol (Figure 1). The positive V^{E} values can be attributed to several factors: the declustering and breaking of H-bonds in alkanols in the presence of NMM, repulsive forces due to the electronic charges of components, size and shape of both components, and more domination of the steric hindrance in the *N*-methylmorpholine molecule.

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