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Densities and Viscosities of Mono(ethylene glycol) + 2-Amino-2-methyl-1-propanol + Water

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The densities and viscosities of ternary mixtures of mono(ethylene glycol) (MEG) + 2-amino-2-methyl-1-propanol (AMP) + water have been measured at temperatures of 25 to 40 °C. The water content varied in the range 1.4 to 15.6 mol %, and the amine concentration varied from 0 to 11.8 mol %. The excess volumes were calculated from the experimental data and fitted to a simple Redlich−Kister type polynomial relation. The equation of Grunberg and Nissan for the viscosity of liquid mixtures was used to correlate the viscosity data.

Introduction

Mixtures containing alkanolamines are well-known for their ability to remove acidic components such as CO_2 and H_2S from gas streams. The amines are commonly used in oil refineries, in petroleum chemical plants, in ammonia factories, and on natural-gas rigs. There is a wide variety of commercially important alkanolamines on the market, such as monoethanolamine (MEA), di-2-propanolamine (DIPA), and methyldiethanolamine (MDEA).[1] More and more interest has focused on the use of sterically hindered amines such as 2-piperidineethanol (2-PE), 1,8-p-menthanediamine (MDA), and 2-amino-2-methyl-1-propanol (AMP) because of their high capacities and high reaction rates.[2]

Densities and viscosities of aqueous solutions of sterically hindered amines have been reported in the literature.[3,4] Data are also available for amines mixed with mono(ethylene glycol) (MEG)[5,6] as well as MEG−water mixtures.[7] However, there are no data available for sterically hindered amines mixed with MEG, which is an important physical solvent with extensive practical use. Physical solvents might enhance the absorption capacity of a solution, especially when the gas stream to be treated is at high pressure and when the acidic components are available in high concentrations.[1] Another advantage of MEG is its ability to act as a drying agent. A mixture of amines and mono(ethylene glycol) has thus the potential to remove both acidic components and water from gas streams, which is especially interesting on oil rigs where available space and equipment mass are of utmost importance.

In this study, we have investigated viscosities and densities of ternary mixtures containing MEG, AMP, and water. Experiments were performed to cover a temperature range of 25 to 40 °C. The water content varied in the range 1.4 to 15.6 mol % (0.4−5 mass %) in order to elucidate the impact of water absorbed from the gas on the properties of the liquid mixture. The amine concentration varied from 0 to 11.8 mol % (0−16.4 mass %). This concentration range corresponds to an amine concentration up to 2 M, which

represents the most interesting conditions for gas absorption.

Experimental Section

The mono(ethylene glycol) used in this study, obtained from BDH Laboratory Supplies, had a minimum purity of 99.5 mass % and a maximum water content of 0.1 mass %. The AMP, obtained from ANGUS Chemical, had a minimum purity of 99.2 mass %. The water used in this study was deionized. The chemicals were used without any further purification. Water was always added in order to control the water content at a level of 0.4 mass % or more.

Dynamic viscosities were measured over a temperature range of 25 to 40 °C using a Brookfields LVT instrument. A calibration procedure was carried out according to recommendations. The instrument was first calibrated at the manufacturer. Before starting a series of experiments, calibration was done with air as fluid. The viscosity was then measured for water and MEG with a viscosity specified by the supplier. If the measured viscosities deviated more than 0.5% from the specified values, the calibration procedure was repeated. Spider number 1, which is one of the standard spiders that come with the instrument, was used for all experiments. The spider was lowered into a double-jacketed beaker, and the temperature of the solution was controlled by passing water of a fixed temperature inside the jacket. The recirculated water was controlled by heating it with a heating bath. By these means, it was possible to control the measured temperature of the sample within ±0.1 °C. The sample volume used was approximately 600 mL. The uncertainty of the dynamic viscosities was estimated to be ±1%.

Densities of ternary mixtures were measured by using a 500 mL round flask. The temperature of the samples was measured with a thermometer having a precision of 0.1 °C. A Mettler PE3600 balance with an accuracy of 0.1 g was used for mass measurements of the liquid mixtures. The overall accuracy of the densities was estimated to be ±0.1% on the basis of comparisons with literature data. The density measurements were made in connection with the viscosity measurements. The mixture from the viscosity measurement was poured into the round flask at a fixed

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Table 1. Experimental Densities (ρ) of MEG (1) + AMP (2) + water (3)

x_2	x_3	$t/°C$	$\rho/g \cdot cm^{-3}$	x_2	x_3	$t/°C$	$\rho/g \cdot cm^{-3}$
0	0.0140	36.8	1.1004	0.1064	0.0153	24.0	1.0832
0	0.0140	25.1	1.1082	0.1184	0.0161	36.6	1.0724
0.0282	0.0148	36.0	1.0936	0.1184	0.0161	26.6	1.0788
0.0282	0.0148	26.2	1.1000	0.0502	0.0513	37.0	1.0866
0.0514	0.0143	36.2	1.0876	0.0502	0.0513	27.8	1.0925
0.0514	0.0143	27.3	1.0933	0.0490	0.0829	37.1	1.0860
0.0694	0.0144	36.1	1.0842	0.0490	0.0829	26.2	1.0930
0.0694	0.0144	24.1	1.0916	0.0479	0.1134	37.2	1.0852
0.0910	0.0152	37.1	1.0780	0.0479	0.1134	22.3	1.0952
0.0910	0.0152	26.8	1.0850	0.0466	0.1563	32.7	1.0870
0.1064	0.0153	37.2	1.0743	0.0466	0.1563	25.7	1.0917
0.1064	0.0153	26.4	1.0814				

Table 2. Literature Values of Densities (ρ) and Viscosities (η) for Pure MEG, AMP, and Water at 25 °C, 30 °C, 35 °C, and 40 °C

	$\rho/g \cdot cm^{-3}$			$\eta/mPa \cdot s$		
$t/°C$	MEG[a]	AMP[b]	water[c]	MEG	AMP[d]	water[e]
25	1.1097	0.9299	0.9970	18.1	142.8*	0.900
30	1.1061	0.9270	0.9956	15.0	99.5	0.805
35	1.1024	0.9235	0.9940	12.8	69.0	0.740
40	1.0987	0.9194	0.9922	11.0	46.9	0.661

[a] Data of Tzierkezos and Molinou.[7] [b] Data of Li and Lie,[4] Adkins and Billica,[9] and US Patent.[10] [c] Data of Mörstedt and Hellsten.[11] [d] Data of Li and Lie.[4] [e] Data of Li and Lie,[4] Tzierkezos and Molinou,[7] Mörstedt and Hellsten,[11] and Perry and Green.[12] * Extrapolated value.
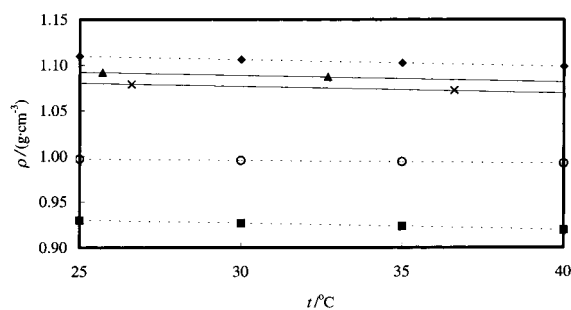
Figure 1. Densities (ρ). Pure compounds: ◆, MEG; ■, AMP; ○, water. Mixtures (mol % AMP/mol % water): ▲, (5/18); ×, (12/2). Lines are calculations. Dashed lines are interpolations.

volume, and the mass and temperature were checked. The bottle was then allowed to cool, and the next measurement was performed at room temperature. In other words, the density measurements were not performed at specific temperatures but at temperatures of approximately 35 °C and 25 °C, respectively.

Results and Discussion

The results from the density measurements of the ternary system are listed in Table 1, and literature data for the pure compounds are provided in Table 2. A closer look at the data revealed that the measured densities were mainly governed by the density of the solvent (MEG). This is clear from Figure 1 and stems from the particular concentration ranges of interest. The data of the ternary system shown in the figure represent the two extremes.

The experimentally determined densities for the ternary system were evaluated by calculating the excess volume (V^E) from the following equation:

$$V^E = V_m - \sum_{i=1}^{3} V_i^\circ x_i \qquad (1)$$

Table 3. Interaction Parameters for the Binary Systems

interaction parameters	
density	viscosity
$A_{12} = -2.0 \ cm^3 \ mol^{-1}$	$G_{12} = 1.51 \pm 0.12$
$A_{13} = -1.0 \ cm^3 \ mol^{-1}$	$G_{13} = 1.41 \pm 0.63$
$A_{23} = -10 \ cm^3 \ mol^{-1}$	$G_{23} = 13.4 \pm 0.7$

where V_i° and x_i represent the molar volume and the mole fraction, respectively, of the ith pure component of the mixture. The molar volume for the pure components was calculated from density values in the literature (Table 2). The molar volumes for the mixtures (V_m) were calculated according to the following equation:

$$V_m = \sum_{i=1}^{3} x_i M_i / \rho_m \qquad (2)$$

where M_i is the molecular weight of component i in the mixture and ρ_m is the measured mixture density.

Due to the small variations in the density, it was decided to evaluate the excess molar volume by using the simplest possible form of the Redlich−Kister equation. It was assumed that the excess molar volume for the ternary system can be described by the sum of the excess molar volumes of the three binary systems constituting the ternary system:

$$V^E = V_{12}^E + V_{13}^E + V_{23}^E \qquad (3)$$

Furthermore, only one adjustable parameter was used for each binary system. Under such assumptions, the excess molar volume takes the following form:

$$V^E = x_1 x_2 A_{12} + x_1 x_3 A_{13} + x_2 x_3 A_{23} \qquad (4)$$

Fitting the experimentally determined excess volumes to this equation yielded a set of values of interaction parameters. However, the uncertainty of these values was found to be unacceptable. The following procedure was then adopted instead to determine the A values. The parameters A_{13} and A_{23} were evaluated from the experimental investigations of Tsierkezos and Molinou,[7] and Li and Lie,[4] respectively. Our experiments were then used to determine the third parameter A_{12} as an average value for the whole temperature range of interest.

The three interaction parameters (A_{12}, A_{13}, and A_{23}) are shown in Table 3. The average absolute percentage deviation for the density calculation using these parameters is 0.07%, and the maximum absolute percentage deviation is 0.15%, which is less than or close to the uncertainty of the experimental density determinations. Calculated densities for the ternary system have been inserted as lines in Figure 1.

The viscosities for the pure fluids are shown in Table 2. The viscosity for water was taken as a mean value from four different literature sources. Since AMP is at a solid state at 25 °C, the viscosity for AMP at this temperature was obtained by extrapolating the data for higher temperatures. The viscosity for AMP at 25 °C is thus merely a fictitious value. The viscosity for MEG has been determined in several studies (e.g. Tsierkezos and Molinou[7]). In our case we decided to use our experimental values for MEG with 0.4 mass % ($x_3 = 0.014$ and $x_2 = 0$, see Table 4) and extrapolation down to $x_3 = 0$, which yielded the values shown in Table 2. The extrapolation was based on the Grunberg−Nissan model described below. This required an

Table 4. Experimental Viscosities (η) of MEG (1) + AMP (2) + Water (3) at 25 °C, 30 °C, 35 °C, and 40 °C

		η/mPa·s			
x_2	x_3	25 °C	30 °C	35 °C	40 °C
0	0.0140	17.7	14.6	12.4	10.6
0.0282	0.0148	19.3	16.0	13.3	11.5
0.0514	0.0143	21.4	17.6	14.8	12.5
0.0694	0.0144	23.0	18.8	15.6	13.3
0.0910	0.0152	24.8	20.1	16.6	14.0
0.1064	0.0153	26.2	21.0	17.4	14.5
0.1184	0.0161	26.7	21.4	17.6	14.8
0.0512	0.0276	21.1	17.2	14.5	12.2
0.0502	0.0513	20.4	16.8	14.1	12.1
0.0490	0.0829	19.5	16.3	13.7	11.6
0.0479	0.1134	18.6	15.4	12.9	11.0
0.0466	0.1563	17.3	14.4	12.0	10.2
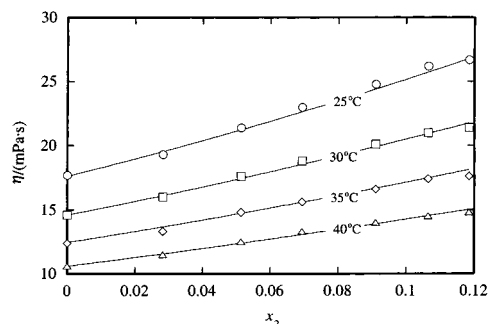
Figure 2. Viscosities (η) for MEG (1) + AMP (2) + water (3) at 25 °C, 30 °C, 35 °C, and 40 °C. $x_3 \approx 0.015$. Lines are calculations (eq 6).
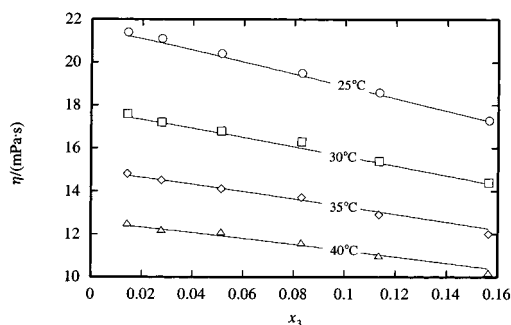
Figure 3. Viscosities (η) for MEG (1) + AMP (2) + water (3) at 25 °C, 30 °C, 35 °C, and 40 °C. $x_2 \approx 0.05$. Lines are calculations (eq 6).

assumed value of the interaction parameter for the water–MEG system (G_{13}), which was checked and adjusted after determining the interaction parameters from all the experiments. The justification for this procedure for determining the MEG viscosities is that even very small amounts of water have some effect and MEG completely free from water cannot easily be obtained. It is anticipated that the uncertainty of the viscosity data for pure glycol is of the same order as the uncertainty of a measured value of a mixture (±1%), provided the Grunberg–Nissan method properly describes the MEG–water interaction.

Viscosity data for the AMP–MEG water system are summarized in Table 4 and plotted in Figures 2 and 3. The data represent two series of experiments under conditions of interest for the system in question. The first series of experiments (Figure 2) show the viscosity as a function of the mole fraction of AMP at a virtually fixed mole fraction of water ($x_3 = 0.014-0.016$). The second series of experiments (Figure 3) show the viscosity as a function of the mole fraction of water (x_3) at a mole fraction of AMP varying slightly from $x_3 = 0.047$ to $x_3 = 0.051$.

The experimentally determined viscosities were evaluated using the equation suggested by Grunberg and Nissan for fluid mixtures:[8]

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \sum_{i \neq j}\sum x_i x_j G_{ij} \tag{5}$$

Here η_m is the viscosity of the mixture, η_i is the viscosity of the ith pure fluid, x_i is the molar fraction of component i, and G_{ij} is the interaction parameter for the binary system ij. For a ternary system the equation takes the following form:

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_1 x_2 G_{12} + x_1 x_3 G_{13} + x_2 x_3 G_{23} \tag{6}$$

where, in this case, 1, 2, and 3 denote MEG, AMP, and water, respectively. Evaluation of the interaction parameters were done by first guessing a G_{12} value and fitting the model to the experiments shown in Figure 2 to obtain G_{23} and G_{13}. Using these values, a new G_{12} value was obtained by fitting the model to the experimental data shown in Figure 3. This procedure was repeated until convergence was seen.

The temperature dependencies of the interaction parameters were found to be erratic and very small. Actually, the temperature dependencies of the interaction parameters were so small that they were masked by variations due to experimental errors. The final values of the interaction parameters shown in Table 3 are thus values valid for the whole temperature range investigated (25 to 40 °C). Values of the viscosity calculated with the Grunberg–Nissan model are shown in Figures 2 and 3 as lines. The experimental viscosity data show a deviation of less than 2.9% from the model and a deviation of 0.89% on an average basis.

Viscosities of the binary system water–AMP have previously been experimentally determined and correlated to the Grunberg–Nissan equation.[4] Experimental data were obtained for 20 and 30 mass % AMP in water as a solvent, and covered the temperature range 30–80 °C. The interaction parameter (G_{23}) was found to be slightly temperature-dependent, with calculated values of 14.6 and 11.6 for 25 °C and 40 °C, respectively. The average value of 13.1 should be compared to our value of $G_{23} = 13.4 \pm 0.7$.

Viscosity data for the binary system MEG–water have been determined and fitted to the Redlich–Kister equation in terms of the excess viscosity.[7] The concentration of MEG varied from zero to 100%. A total of four adjustable parameters were used for each temperature to correlate the data. Evaluating the data by instead using the Grunberg–Nissan equation with only one adjustable parameter enables the calculation of the interaction parameter. For instance, at 30 °C data show a correlation coefficient of greater than 0.995, and the correlation yields an interaction parameter of $G_{13} = 2.1$. This value is in reasonable agreement with our value of $G_{13} = 1.41 \pm 0.63$.

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