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Volumetric Properties of 3-Diethylaminopropylamine with 2-Propanol, or Monoethyleneglycol

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Abstract

In this study, we aimed to investigate the refractive indices at a temperature of 293.15 K and the density data at T = 283.15, 293.15, 303.15 and 313.15 for binary mixtures of 3-diethlyaminopropylamine 3-DEPA with 2-propanol, or monoethyleneglycol as a function of composition under atmospheric pressure. For this study we used experimental values of density to assess the volumetric properties such as excess and excess partial molar volumes of components at infinite dilution. The Redlich-Kister equation was used to fit and estimate standard deviations for excess molar volume results. Notably, our results revealed that the binary mixtures investigated displayed negative deviations from the ideal behaviordue to dipole-dipole interactions and hydrogen bonds. Furthermore, the measurements of refractive index and the variations in refractive index were also determined.

Keywords: diamine; density; excess volumes; volumetric properties; Intermolecular interactions

1. Introduction

Diamines are important across diverse industries and constitute an intriguing group of molecules suitable for evaluating group-contribution models and analyzing intramolecular effects [1–4]. Due to their remarkable absorption capacity and rapid kinetics, diamines are employed in environmental protection, particularly in the capturing of a significant greenhouse gas implicated in global climate change [5 -10].

Exploring the thermodynamic characteristics of diamine blends is vital for deepening our understanding of the molecular interactions in liquid solutions. Moreover, these investigations are essential for testing and advancing theories and models in this field. By examining these properties, we gain valuable insights into the behavior of diamine mixtures and can develop more accurate and reliable models to describe their behavior in various conditions. Density and other volumetric properties have been widely recognized as crucial indicators for comprehending interactions between solute and solvent molecules, as well as solute-solute interactions. Moreover, these properties are crucial for improving industrial processes [11,12].

In separation processes, diamines-alcohols and diamines-glycols are frequently utilized, and they have gained significant attention as alternative solvents for treating acid gases. Consequently, numerous studies investigated the thermodynamic aspect of binary mixtures composed of diamines and alcohols to understand their behavior and potential applications. Yang et al have determined the viscosity deviations and excess molar volumes of 1,3-diaminopropane with 1,3-Propandiol [13].Moreover, Saleh et al. [14] investigated the excess molar volumes of aqueous systems containing various diamines at ambient pressure and temperatures comprised between303.15K and 323.15 K. Furthermore, Zarei et al. [15]determined the excess molar enthalpies of binary mixtures consisting of ethylene diamine with ethanol, propanol, methanol, and butanol. In our previous works, we conducted measurements of molar excess enthalpies (HE) and excess Gibbs free energies (GE) for diamines

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+ n-heptane and diamines + cyclohexane [16–20]. thermodynamic properties of diamine mixtures, this paper provides a comprehensive dataset on the excess molar volume for {3-diethylaminopropylamine +2-

2. Materials & Methods

2.1. Materials

Janssen Chimica provided 3-diethylaminopropylamine with a purity over 99%. Monoethyleneglycol and 2-propanol, both with purities over 99.5%, were obtained from Sigma Aldrich.

2.2. Experimental

2.2.1 Density

An Anton-Paar vibrating-tube digital densimeter (Model DMA5000) was used for density measurements (ρ). We also used a digital thermometer with a precision of 0.01 K to monitor the temperature inside the cell and ensure accurate temperature control. We used ultra-pure water and dry air as reference materials to calibrate the densimeter was periodically. The measurement of temperature and density were associated with uncertainties of about ∓0.01 K and ∓ 4.10^{-5} $g \cdot cm^{-3}$, respectively.

2.2.2. Refractive index measurements

The refractive indices of both pure liquids and their binary mixtures were measured at 293.15 K using a digital refractometer (Krüss DR6000-T). The temperature and refractive index measurements had estimated errors of ∓0.02 K and ∓4.10-4, respectively.

3. Results and discussion

3.1. Density

Experimental measurements of density were conducted under atmospheric pressure for the binary systems of DEPA (1) + 2-propanol (2) or + monoethyleneglycol (MEG) (2). Measurements were taken at intervals of 10 K between 283.15 and 313.15 K.Figures 1 and 2 illustrate the density data. These figures demonstrate that the density values rise proportionally to the increasing 3-DEPA concentration in 3-DEPA (1) + 2-propanol (2) binary solution and decrease in 3-DEPA (1) + MEG molecular weights of pure DEPA and pure 2-propanol, or MEG, respectively. Figures 3 and 4

Following our thorough investigation into the propanol or + monoethyleneglycol}, across four different temperatures.

(2) as the composition of 3-DEPA increases. Additionally, the rising temperatures induce the density values to decrease.

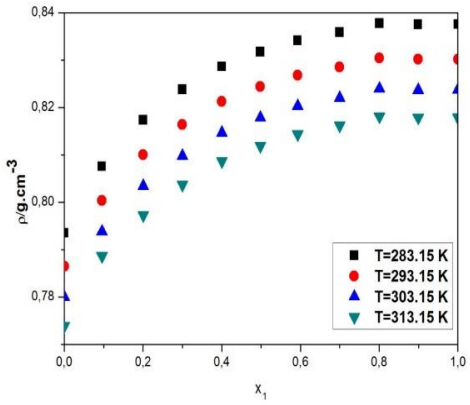

Figure 1. Plot of theDensity (ρ) for 3-DEPA(1)+ 2-propanol(2) as function of 3-DEPA mole fraction x_1 at various temperatures.

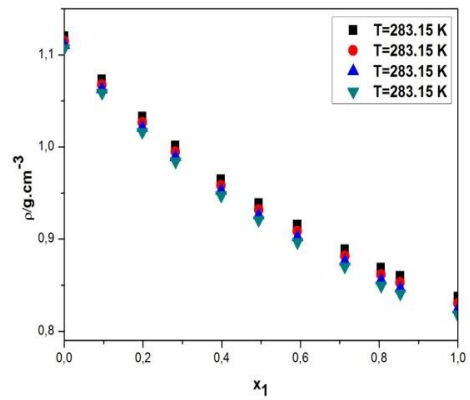

Figure 2. Plot of theDensity data (ρ) for 3-DEPA(1)+ monoethyleneglycol(2) as function of 3-DEPA mole fraction x_1 at various temperatures.

The excess molar volume, V_m^E, was calculatedusing density measurements based on the following formula:

$$V_m^E = (X_1M_1 + X_2M_2/\rho) - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \quad (1)$$

Where;

ρis the density of mixture, x_1 and$x_2$the mole fractions, ρ_1, $\rho_2$are the densities, and $M_1$and M_2 the

provides the variation of V_m^E with different temperature values.

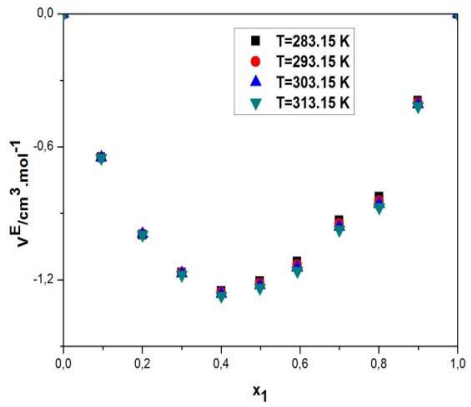

Figure 3. Evolution of the excess molar volume, V_m^E for binary 3-DEPA(1)+ 2-propanol(2) mixtures.

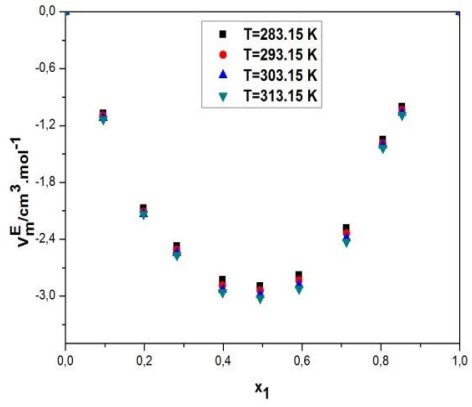

Figure 4. Evolution of the excess molar volume, V_m^E for binary 3-DEPA(1)+ MEG(2) mixtures.

Table 1 lists the coefficients and standard deviations of the Redlich-Kister expression for the two binary mixtures studied, where N is the number of experimental points and m is the number of polynomial coefficients.

Table 1

Redlich-Kister coefficients for binary mixtures at different temperatures and atmospheric pressures.

Redlich Kister coefficients	**T/K**			
	283.15	**293.15**	**303.15**	**313.15**
3-DEPA](1)+ 2-Propanol(2)				
A_0	-1.8404	-2.0942	-2.4739	-2.8752
A_1	-1.1119	-1.3754	-1.5421	-1.9691
A_2	0.0195	-0.0153	0.0572	-0.0124
A_3	1.0749	0.8081	-0.8075	0.4902
σ/cm^3.mol^{-1}	0.0014	0.0022	0.0010	0.0020
3-DEPA(1)+ MEG(2)				
A_0	-4.8401	-4.8001	-4.8401	-4.8863
A_1	-1.2097	-1.2788	-1.2097	-1.1625
A_2	-3.2403	-3.2122	-3.2403	-3.2956
A_3	0.6769	0.6585	0.6770	0.7012
σ/m^3.mol^{-1}	0.007	0.007	0.008	0.005

3.2. Partial and Excess partial molar volumes of the studied binary mixtures

To gain a deeper understanding of the interactions between a solute and a solvent, the partial molar volumes of 3-DEPA, $V_{m,1}$ and 2-propanol or monoethyleneglycol, $V_{m,2}$ in the investigated binary mixtures were determined as follows;

$$V_{m,1} = V_m^E + V_1^0 + x_2(\partial V^E/\partial x_1)_{T,P} \quad (4)$$

$$V_{m,2} = V_m^E + V_2^0 - x_1(\partial V^E/\partial x_1)_{T,P} \quad (5)$$

where V_1^0 and V_2^0 are the pure components' molar volumes; V_m^E the mixtures' excess molar volume; and x_1 and

Figures 3 and 4 show negative behavior for the theV_m^E values for each temperatures and the examined composition interval. The lowest measure of -1.2566 m^3·mol^{-1} is observed at $x_1 \approx 0.5$ for the mixture of 3-DEPA (1) + 2-propanol (2), and -2.9426 m^3·mol^{-1} is occurred at $x_1 \approx 0.4$ for the 3-DEPA (1) + MEG (2) system at T=293.15 K. These negative values signify a volume contraction when mixing a diamine with alcohol or glycol. Such behavior can be attributed tothe diamine and alcohol or glycol hydrogen bonding and the dipole-dipole interactions.

The presence of lone pairs of electrons in alcohols, glycols, and diamines is responsible for specific interactions, and the polarity of the molecules further leads to dipole-dipole interactions. The binary mixtures of 3-DEPA with 2-propanol or MEG exhibit stronger interactions than their respective pure compounds.As the temperature increases, the excess molar volume becomes negative for the same composition, consistent with literature [21, 23-27].

The excess molar volume was parametrized by a Redlich–Kister expression:

$$\frac{V_m^E}{cm^3 mol^{-1}} = x_1 x_2 \sum_{i=0}^{n} A_i\,(2x_1 - 1)^i \quad (2)$$

where x_1 and x2 are the mole fraction of 3-DEPA and 2-propanol, or monoethyleneglycol and A_i represents the polynomial coefficient. The following equation assesses the standard deviation values between the calculated and experimental data:

$$\sigma_{V_m^E} = \left[\sum \frac{(V_{cal}^E - V_m^E)^2}{(N-m)}\right]^{\frac{1}{2}} \quad (3)$$

x_2 the molar compositions of the 3-DEPA and 2-propanol or monoethyleneglycol respectively.
$(\partial V^E/\partial x_1)_{T,P}$can be determined from the Equation (2).
The excess partial molar volumes of the 3-DEPA, $V^E_{m,1}$, and of alcohol, $V^{\mathrm{E}}_{\mathrm{m},2}$, were calculated using the equations:
$V^E_{m,1} = V_{m,_1} - V^0_1 (6)$
$V^E_{m,2} = V_{m,2} - V^0_2 (7)$
The excess partial molar volumes of the diamine, alcohol and glycol in the two investigated binary mixtures are shown in figures 5 and 6.

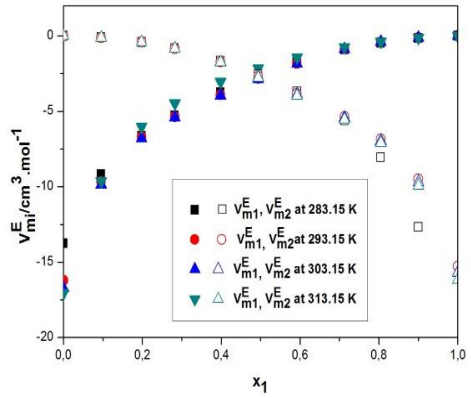

Figure 5. Plot of excess partial molar volumes $V_{m,1}$of3-DEPA and $V_{m,2}$ of 2-propanol for the binary mixture 3-DEPA(1)+ 2-propanol(2).

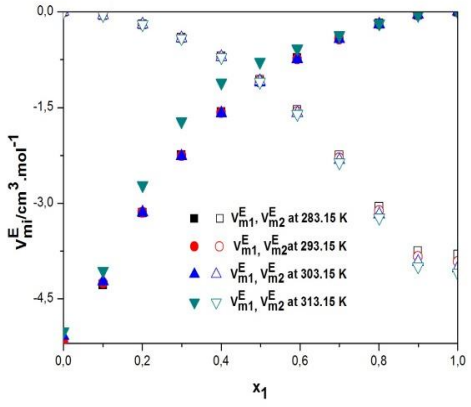

Figure 6. Plot of excess partial molar volumes $V_{m,1}$of3-DEPA and $V_{m,2}$ of MEG for the binary mixture 3-DEPA(1)+ MEG(2).

3.3. Excess partial molar volume at infinite dilution

$V_1^{E,\infty}$ of 3-DEPA and $V_2^{\mathrm{E},\infty}$ of 2-propanol or MEG can be determined by rearranging Equations 8 and 9 when both x_1 and x_2 approach zero.
$(V_1^E)^\infty = \sum_{i=0}^{n} A_i (8)$
$(V_2^E)^\infty = \sum_{i=0}^{n} A_i (-1)^{\,i} (9)$
As indicated in Table 2, the values of $V_i^{E,\infty}$display negative deviations for the two investigated binary mixtures and across all temperatures. This behavior is attributed to a volume contraction that occurs when 3-DEPA is added to an infinite volume of the corresponding alcohol or glycol**.** Thus, the negative values of $V_i^{E,\infty}$ strongly indicate a clear preference for diamine and alcohol or glycol molecules to be surrounded by unlike molecules.

Table 2. Partial molar volume at infinite dilution $V^{\infty}_{m,i}$ and excess partial molar volume at infinite dilution $V^{E,\infty}_{m,i}$for the components of the binary mixtures 3-DEPA(1)+ monoethyleneglycol(2) at different temperatures.

T/K	$V^{\infty}_{m,1}$ /cm^3.mol^{-1}	$V^{\mathrm{E},\infty}_{\mathrm{m},1}$/ cm^3.mol^{-1}	$V^{\infty}_{m,2}$ /cm^3.mol^{-1}	$V^{\mathrm{E},\infty}_{\mathrm{m},2}$ /cm^3.mol^{-1}
283.15	-7.8865	-12.8158	-5.0021	-14.2111
293.15	-7.8294	-13.1611	-5.1357	-14.6504
303.15	-7.7956	-13.4568	-5.2556	-14.7978
313.15	-7.8001	-13.6978	-5.3708	-15.3517

3.4. Refractive index

Figure 7 structures the refractive index deviations of the binary mixtures of 3-DEPA (1) + 2-propanol (2)] and 3-DEPA (1) + MEG (2)] versus x_1 at T=293.15 K. Indeed, Figure 7 desmostratethat Δn_Ddisplays positive deviation from ideal behavior across the entire composition range, attributed to the dipole-dipole interactions between unlike molecules [22,25].

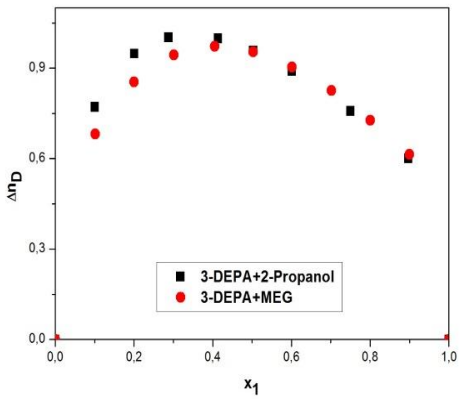

Figure 7. Plot of the binary mixtures' refractive index deviation at 293.15 K.

2. Conclusion

In this study, we conducted measurements of the refractive indices at 203.15 K and densities at temperatures T including 283.15k, 293.15k, 303.15k, and 313.15 K for two binary mixtures. These systems comprise 3-diethylaminoethylamine (3-DEPA) in conjunction with either 2-propanol or monoethyleneglycol as a function of 3-DEPA molar fraction and under atmospheric pressure. The binary mixtures' refractive index deviations were determined and various volumetric properties were derived from the experimental densities, such as, excess, apparent, partial and excess partial molar volumes at infinite dilution. The Redlich-Kister equation was used to fit the excess molar volumes. Considering composition range and varying temperatures, the $\boldsymbol{V_m^E}$ values constantly exhibited a negative trend. This deviation from ideal behavior indicates attractive interactions between diamine and alcohol/glycol or the existence of packing effect.

3. Conflicts of interest

"There are no conflicts to declare".

4. Acknowledgments

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