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Short communication

Volumetric properties of the water + ethylenediamine mixture at atmospheric pressure from 288.15 to 353.15 K

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Abstract

Densities of the water + ethylenediamine binary system were measured at atmospheric pressure over the whole range of compositions at temperatures from 288.15 to 353.15 K using an Anton Paar digital vibrating glass tube densimeter. Density increases with water content. The experimental excess molar volume data have been correlated with the Redlich–Kister equation, and partial molar volumes calculated at infinite dilution for each component.

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1. Introduction

Densities concerning the water + EDA system have been measured using a vibrating tube densimeter in the temperature range (288.15–353.15 K) for the whole composition range to assess the effect of temperature. Few publications are related to the densities of aqueous EDA solutions [1–3].

2. Experimental

Ethylenediamine [$C_2H_8N_2$, CAS number: 107-15-3] was purchased from Aldrich with a certified GC purity >99%. Water is produced with direct Q model from Millipore. EDA and water were degassed before use and mixtures were prepared gravimetrically under vacuum. The apparatus used for density measurements is Anton Paar digital vibrating glass tube densimeter (model DMA5000), with a precision of 10^{-5} g cm^{-3}.

Temperature was determined through a platinum resistance with accuracy estimated to 0.01 K. The DMA5000 densimeter was calibrated (determination of a and b constants in $\rho = a + b\tau^2$) with bidistilled degassed water and dry air.

Empty glass bottles of 20 cm^3 volume were closed air-tight with a septum and then evacuated with a vacuum pump using a syringe needle introduced through the septum. The empty bottle was weighed, and the less volatile component, freshly degassed by vacuum distillation, introduced by means of a syringe. After weighting, the more volatile component was added and the bottle weighed again. All weighings were performed with a balance with 0.0003 g accuracy. The maximum uncertainty on v^E is estimated as less than 0.005 cm^3 mol^{-1}.

3. Results

The densities of pure EDA was compared with the values obtained with the correlation (Eq. (1)) mentioned by Daubert et al. [4].

$$\rho_{i,\text{cor}}^* = \frac{A}{B^{(1+(1-T/T_C)^C)}} \times \frac{M_i}{1000} \tag{1}$$

A, B and C parameters are presented in Table 1. Experimental densities of pure EDA are presented in Table 1 (supplementary data file). Relative deviations between our experimental EDA densities and those calculated using Eq. (2) from Daubert et al. [4] are systematically negative with deviations that reach 0.7%. A, B and C parameters fitted to our experimental data give relative deviations reduced to about 0.02%.

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Nomenclature

A_n Redlich–Kister parameters ($cm^3 \, mol^{-1}$)

A, B, C parameters in Eq. (2).

M_i molar mass of pure compound i ($g \, mol^{-1}$)

N_{exp} number of experimental data

T temperature (K)

T_C critical temperature (K)

v_i^* molar volume of pure compound i ($cm^3 \, mol^{-1}$)

$\bar{v}_i$ partial molar volume of component i ($cm^3 \, mol^{-1}$)

x_i liquid mole fraction of component i

Greek letters

ρ density ($g \, cm^{-3}$)

σ variance, see Eq. (6)

∞ infinite dilution state

Superscript

E   excess property

Indices

cor   correlation, Eq. (2)

exp   experimental

1   EDA

2   H_2O

Daubert et al. [4] used some data available in [5–14] to determine Eq. (1) parameters. According to the Fig. 1, data of Kapadi et al. [2] and Saleh et al. [3] are in rather good agreement with those calculated through Eq. (1) and parameters proposed by Daubert et al. But, data measured by Timmermans and Hennaut-Roland [14] are in good agreement with our experimental data. Densities from ref. [13] are very different from both our data and those calculated using parameters from Daubert et al. The system EDA + water is an azeotropic system [15]. This azeotropic behaviour can explain the scattering between the literature data, EDA being provided with possible significant water content depending on furnisher. Our data correspond to the lowest densities and correspondingly to the less water loaded EDA.

Mixture density data are reported in Table 2 (supplementary data file).

Excess molar volumes are calculated as:

$$v^E = v - x_1 v_1^* - x_2 v_2^* \tag{2}$$

where v is the molar volume of the EDA (1) + water (2) mixture. v_1^* is the molar volumes of the pure components determined with Eq. (1) and parameters from Table 1. v_2^* is the water molar volume.

Table 1
Critical temperatures and parameters of Eq. (2)

Component	T_C (K)	A ($kmol \, m^{-3}$)	B	C
EDA	593	0.7822[a]	0.2048[a]	0.2229[a]
EDA	593	0.7842[b]	0.20702[b]	0.20254[b]

[a] Values obtained from our experimental data.
[b] Values from Daubert et al. [4].
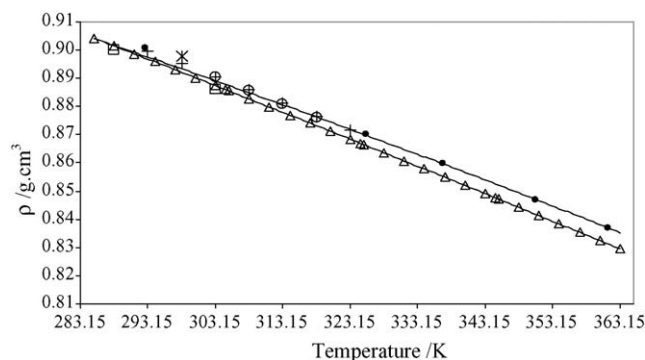

Fig. 1. Comparison of EDA densities. (△): This work; (+) Saleh et al. [3]; (□): Timmermans and Hennaut-Roland et al. [14]; (●): Friend and Hargreaves [12]; (○): Kapadi et al. [2]; (✳): Dunstan et al. [13]; black line: Calculated with Eq. (2) and parameters from Daubert et al. [4].

By introducing the density ρ, Eq. (2) can be written as:

$$v^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho} \right] - \frac{x_1 M_1}{\rho_1^*} - \frac{x_2 M_2}{\rho_2^*} \tag{3}$$

M_1 and M_2 are, respectively molar masses of EDA and H_2O, ρ_1^* are experimental data from Table 1 (supplementary data file), ρ_2^* are from tables produced by Bettin and Spieweck [16]. Calculated excess molar volumes are presented in Table 2 (supplementary data file) and plotted in Figs. 2 and 3.

Redlich–Kister equation [17] was applied for representation of excess molar volumes:

$$v^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \tag{4}$$

with $i \leq 6$.

The Redlich–Kister coefficients (A_n) have been determined with the least square method at each temperature and are presented in Table 2 along with the standard deviation, σ, corresponding to each fit.

Temperature dependence of each coefficient given in Table 2 can be represented by second order polynomials (Eqs. (5)–(11)).

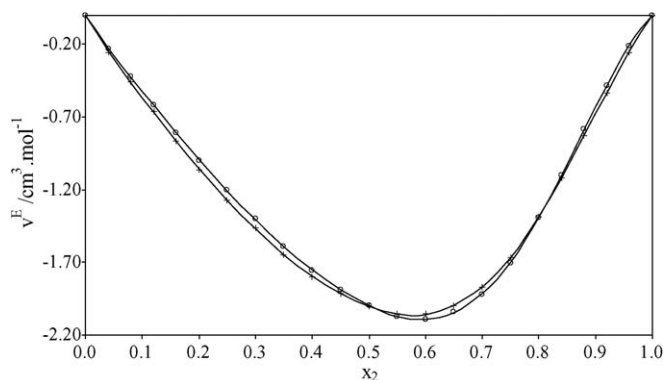$$A_0 = -0.0001022 \, T^2 + 0.06439 \, T - 18.077 \tag{5}$$

Fig. 2. Excess molar volume (v^E) for the EDA (1) + H_2O (2) binary system as a function of composition at various temperatures. (○) 288.15 K and (+) 343.15 K. Solid curves represent the values calculated through Eq. (3) and coefficients from Table 1 (supplementary data file).
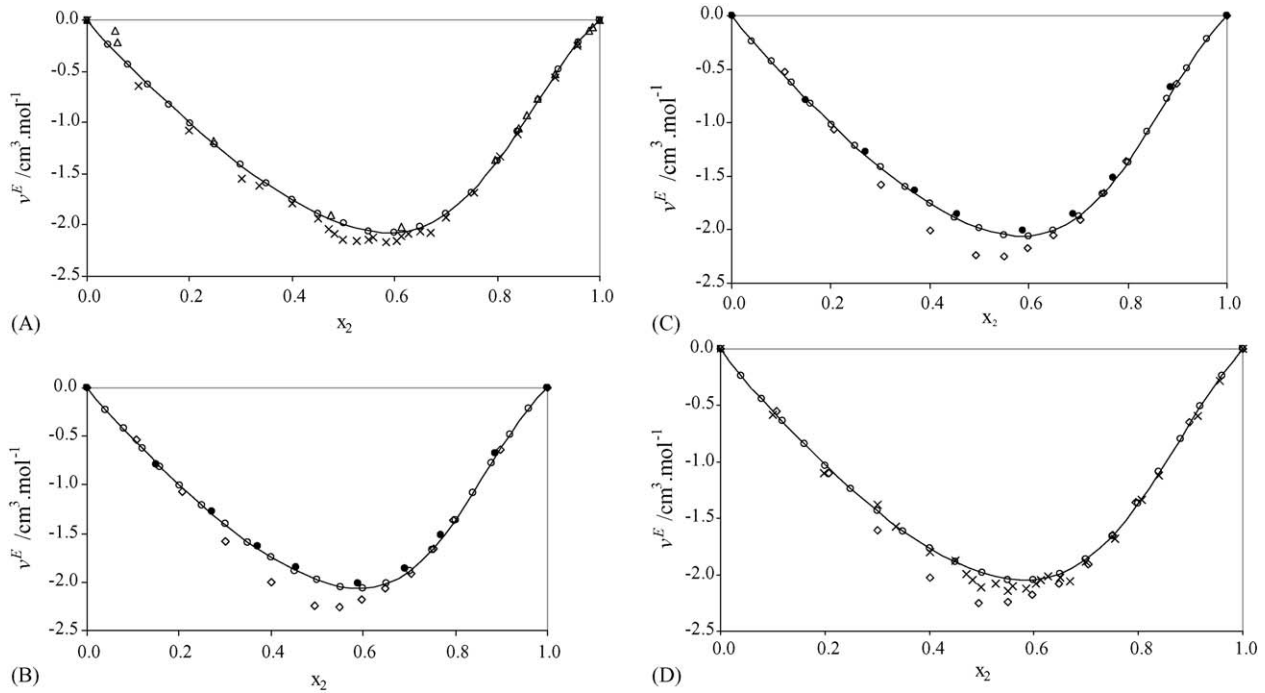
Fig. 3. v^E literature data comparison. (A) 298.15 K; (B) 303.15 K; (C) 308.15 K; (D) 323.15 K. (×) Elgort [5]; (●) Kapadi et al. [2]; (○) this work; (◊) Saleh et al. [1]. Black line: calculated with Redlich–Kister equation and parameters from Table 1 (supplementary data file).

$$A_1 = -0.0000853\,T^2 + 0.06950\,T - 16.679 \tag{6}$$

$$A_2 = -0.0000460\,T^2 + 0.03321\,T - 6.380 \tag{7}$$

$$A_3 = -0.0000375\,T^2 - 0.001302\,T + 7.924 \tag{8}$$

$$A_4 = -0.0000279\,T^2 - 0.02061\,T + 15.662 \tag{9}$$

$$A_5 = 0.0001474\,T^2 - 0.09732\,T + 16.325 \tag{10}$$

$$A_6 = 0.0000525\,T^2 - 0.01589\,T - 3.831 \tag{11}$$

The partial volume of each component ($\bar{v}_i$) is given by:

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}} \tag{12}$$

After differentiating Eq. (4) with respect to n_i and combining the result to Eq. (12) leads to equations for the partial molar volume of MEA and Water:

$$\bar{v}_1 = v^E + v_1^* - x_2 \left(\frac{\partial v^E}{\partial x_2} \right)_{T,P} \tag{13}$$

$$\bar{v}_2 = v^E + v_2^* - x_1 \left(\frac{\partial v^E}{\partial x_1} \right)_{T,P} \tag{14}$$

Table 2
Values of Redlich–Kister coefficients at each temperature

T (K)	A_0 (cm³ mol⁻¹)	A_1 (cm³ mol⁻¹)	A_2 (cm³ mol⁻¹)	A_3 (cm³ mol⁻¹)	A_4 (cm³ mol⁻¹)	A_5 (cm³ mol⁻¹)	A_6 (cm³ mol⁻¹)	σ (cm³ mol⁻¹)
288.15	−7.996	−3.759	−0.580	4.482	7.212	0.375	−3.763	0.0047
293.15	−8.002	−3.599	−0.650	4.250	7.400	0.681	−4.299	0.0050
298.15	−7.961	−3.522	−0.583	4.186	7.117	0.470	−4.007	0.0048
303.15	−7.932	−3.449	−0.526	4.116	6.836	0.296	−3.757	0.0047
308.15	−7.927	−3.358	−0.503	3.977	6.661	0.300	−3.715	0.0048
313.15	−7.925	−3.274	−0.492	3.846	6.502	0.289	−3.674	0.0048
318.15	−7.929	−3.197	−0.477	3.715	6.332	0.284	−3.621	0.0052
323.15	−7.938	−3.125	−0.442	3.603	6.045	0.250	−3.439	0.0048
328.15	−7.951	−3.055	−0.424	3.454	5.857	0.274	−3.367	0.0052
333.15	−7.969	−2.989	−0.412	3.330	5.644	0.268	−3.246	0.0049
338.15	−7.990	−2.924	−0.411	3.184	5.492	0.297	−3.197	0.0053
343.15	−8.014	−2.869	−0.395	3.059	5.279	0.313	−3.091	0.0049
348.15	−8.041	−2.809	−0.394	2.914	5.124	0.328	−3.016	0.0049
353.15	−8.070	−2.765	−0.391	2.809	4.960	0.315	−2.942	0.0049

Table 3
Partial molar volumes at infinite dilution and partial excess molar volumes at infinite dilution

T (K)	$\overline{v_1^\infty}$ (cm^3 mol^{-1})	$\overline{v_2^\infty}$ (cm^3 mol^{-1})	$\left(\overline{v_1^E}\right)^\infty$ (cm^3 mol^{-1})	$\left(\overline{v_2^E}\right)^\infty$ (cm^3 mol^{-1})
288.15	11.8$_1$	62.6$_7$	−6.2$_3$	−4.0$_3$
293.15	11.1$_6$	62.8$_2$	−6.8$_8$	−4.2$_2$
298.15	11.5$_0$	63.0$_7$	−6.5$_7$	−4.3$_0$
303.15	11.7$_5$	63.3$_1$	−6.3$_4$	−4.4$_2$
308.15	11.7$_2$	63.5$_2$	−6.4$_0$	−4.5$_6$
313.15	11.7$_1$	63.7$_2$	−6.4$_5$	−4.7$_3$
318.15	11.6$_9$	63.9$_2$	−6.5$_0$	−4.8$_9$
323.15	11.7$_3$	64.1$_4$	−6.5$_0$	−5.0$_5$
328.15	11.7$_2$	64.3$_6$	−6.5$_6$	−5.2$_1$
333.15	11.7$_3$	64.5$_9$	−6.5$_9$	−5.3$_7$
338.15	11.7$_1$	64.8$_2$	−6.6$_6$	−5.5$_5$
343.15	11.7$_0$	65.0$_6$	−6.7$_2$	−5.7$_2$
348.15	11.7$_2$	65.3$_0$	−6.7$_6$	−5.9$_0$
353.15	11.7$_4$	65.5$_3$	−6.8$_0$	−6.0$_8$

By differing Eq. (4) with respect to x_i and substitution in Eqs. (13) and (14), partial molar volume expressions (Eqs. (15) and (16)) are obtained.

$$\bar{v}_1 = v_1^* + x_2^2 \sum A_n(1-2x_2)^n + 2x_2^2(1-x_2)\sum n A_n(1-2x_2)^{n-1} \tag{15}$$

$$\bar{v}_2 = v_2^* + (1-x_2)^2 \sum A_n(1-2x_2)^n - 2x_2(1-x_2)^2\sum n A_n(1-2x_2)^{n-1} \tag{16}$$

volumetric properties give access in a straightforward way to partial molar volumes at infinite dilution. We have:

$$\overline{v_1^\infty} = v_1^* + \sum A_n(-1)^n \quad (x_1 \to 0) \tag{17}$$

$$\overline{v_2^\infty} = v_2^* + \sum A_n \quad (x_2 \to 0) \tag{18}$$

The calculated partial molar volumes at infinite dilution and the partial excess molar volumes at infinite dilution (Eqs. (19) and (20)) are presented in Table 3.

$$\left(\overline{v_1^E}\right)^\infty = \sum A_n(-1)^n \quad (x_1 \to 0) \tag{19}$$

$$\left(\overline{v_2^E}\right)^\infty = \sum A_n \quad (x_2 \to 0) \tag{20}$$

4. Discussion

Several authors have published experimental data concerning excess volume of the EDA + water binary system (see Fig. 3). Disagreements have been pointed out between literature data. Elgort [5] has determined excess volumes at 298.15 and 323.15 K. As a whole, their data are coherent with ours but are quite dispersed. Excess molar volumes determined by Saleh et al. [1] are not in good agreement with our data and the data determined by Kapadi et al. [2]. Our data confirm the data from Elgort [5] and Kapadi et al. [2].
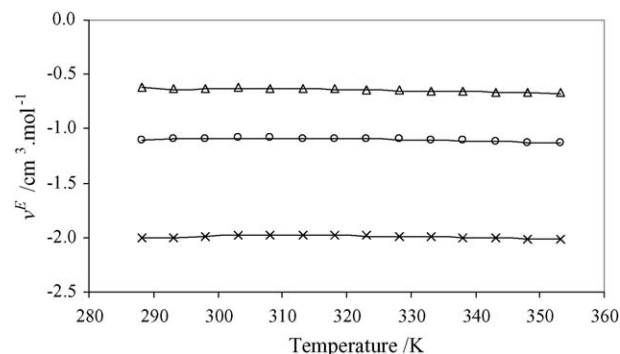

Fig. 4. Excess molar volume as a function of temperature for the system EDA (1) + H$_2$O (2) at different compositions: ($\triangle$) $x_2 = 0.1199$; ($\bigcirc$) $x_2 = 0.5001$; ($\times$) $x_2 = 0.8400$.

All our v^E values are negative, a characteristic of completely miscible systems with strong hydrogen bonding interactions. The same trend was observed with the system water + monoethanolamine [18]. For systems which generate important quantities of H bonding like in alcohols water systems, excess molar volume is an increasing function of temperature as also observed alcohol + triethylene glycol [19] 1-alkanol + hexane [20], 1-alkanol + nonane [21] and 1-hexanol + ether [22].

Temperature seems to have no effect on v^E (Fig. 4) and the partial molar volume at infinite dilution of EDA and water is not significantly temperature dependent. All these indicate there are hydrophobic interactions [1]. Density of water decreases when a small quantity of EDA is added. Organic molecules added to water, and in particular their hydrocarbon parts, are surrounded by a large number of water molecules, structurally arranged to form cages. In presence of EDA, water presents a new structure until the quantity of EDA becomes sufficient to disorganize the system, destroy the cages and form more complex.

The partial molar volumes at infinite dilution of EDA ($x_1 = 0$) are smaller than the corresponding molar volumes of pure EDA, v_1^* (the partial molar excess volume is negative at infinite dilution) confirming the existence of complex formation between EDA molecules. Moreover, partial molar volumes of water at infinite dilution in EDA are smaller than the corresponding pure water molar volumes confirming existence of void space due to H bonding.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.01.013.

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