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Density for (Water + Ethylenediamine) at Temperatures between (283 and 353) K

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The density for mixtures of ethylenediamine (EDA) and water at a pressure of 0.2 MPa have been measured with a vibrating tube densitometer at temperatures in the range (283 to 353) K. The entire composition range was covered with intervals of molar fractions of 10 %. The excess volume has a minimum at a molar fraction of water of 59 %. The variation with temperature in excess volume is small, whereas the temperature variation in density is complex. The temperature dependence in density is well described by combining a Redlich−Kister model for excess volume, without temperature-dependent parameters, with models for the pure component densities.

Introduction

Density and excess volume are of both theoretical and practical interest. Knowledge of the density of a mixture is used for the design and simulation of process equipment and for process control.

The solvent ethylenediamine (EDA, CAS registry number 107-15-3) is an intermediate in the production of chemicals such as fungicides, chelating agents, and bleach activators. With two amine groups that can be involved in hydrogen bonding, EDA is a bifunctional solvent. Wilson[1] finds that its behavior is in many ways parallel to that of water. According to Cheng et al.,[2] the structural networks of EDA and water are compatible with each other. When left in contact with air, EDA forms a hydrate and reacts with carbon dioxide. For this reason, care has to be taken to avoid contact between samples and air.

Wilson[1] and Kruglyak et al.[3] presented density data for (ethylenediamine + water) at a temperature of 293 K and in the interval (288 to 318) K, respectively. In their articles, data are presented graphically. Kapadi et al. [4] used a vibrating tube densitometer to measure density for the binary at temperatures between (303 and 318) K, and Valtz et al.[5] measured it at temperatures from (288 to 353) K. Saleh et al.[6] measured density at temperatures between (303 and 323) K with a bicapillary pycnometer.

In this study, the temperature range for the measurements was (283 to 353) K, and the interval between the measuring points was approximately 10 K. At each temperature, the entire composition range was covered, with intervals in mole fractions of approximately 10 %. A vibrating tube densitometer was used for the measurements. To protect the mixture from exposure to the air, a pressure of 0.2 MPa was applied with dry nitrogen. The results will be discussed, and two models for interpolation of density and excess volume will be presented.

Theory

The excess molar volume is calculated from the measured density ρ using

$$V^{\mathrm{E}} = \frac{\sum_i x_i M_i}{\rho} - \sum_i \frac{x_i M_i}{\rho_i} \tag{1}$$

where M_i is the molar mass; x_i is the mole fraction of component i; and ρ_i is the density of the pure component i at the temperature at which the measurement was performed. For pure EDA, a third degree polynomial was used to represent the density ρ_{EDA} with respect to temperature of

Table 1. Measured Density, ρ_{water}, for Water and Deviation from the Model in VDI-Wasserdampftafeln[7] and Measured Density, ρ_{EDA}, for Ethylenediamine and Deviation from Equation 2, $\Delta\rho$

T/K	ρ_{water}/ kg·m^{-3}	$\Delta\rho$/kg·m^{-3}	T/K	ρ_{EDA}/kg·m^{-3}	$\Delta\rho$/kg·m^{-3}
283.40	999.862	−0.021	283.55	905.993	−0.008
293.28	998.364	0.014	293.06	897.168	0.014
302.62	995.966	0.019	302.40	888.381	0.003
312.13	992.724	0.004	312.67	878.632	−0.010
322.73	988.284	−0.011	323.42	868.618	−0.007
332.94	983.293	−0.022	332.78	859.342	0.001
342.53	978.020	−0.014	342.77	849.651	0.012
352.19	972.189	0.018	352.69	839.921	−0.006

$$\rho_{\mathrm{EDA}} = 1114.7052 - 0.4888359(T/\mathrm{K}) - 0.001072228(T/\mathrm{K})^2 + 7.0680 \cdot 10^{-7}(T/\mathrm{K})^3 \tag{2}$$

For the density of pure water, the expression found in Wasserdampftafeln[7] was used. The departure from additivity for the density $\Delta\rho$ is calculated from the density of the mixture and the densities of the pure components ρ_i using

$$\Delta\rho = \rho - \sum \rho_i z_i \tag{3}$$

where the apparent molar volume fraction z_i is given by

$$z_i = \frac{\dfrac{X_i}{\rho_i}}{\sum_i \dfrac{X_i}{\rho_i}} \tag{4}$$

and X_i is the mass fraction of component i in the mixture. To obtain a model for the excess volume, parameters were estimated in a Redlich−Kister equation

$$V^{\mathrm{E}} = x_{\mathrm{water}}(1 - x_{\mathrm{water}}) \sum_{i=0}^{m} a_i (1 - 2x_{\mathrm{water}})^i \tag{5}$$

where x_{water} is the mole fraction of water in the mixture. The density was calculated from this model for V^{E}, using eq 1 combined with models for the pure component densities.

The partial molar excess volumes defined by

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$$V_i^{\mathrm{E}} = \left(\frac{\partial(nV^{\mathrm{E}})}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{6}$$

were represented by the Redlich−Kister V^{E} expression (eq 5) of

$$V_{\mathrm{water}}^{\mathrm{E}} = V^{\mathrm{E}} + (1 - x_{\mathrm{water}})(1 - 2x_{\mathrm{water}})\sum_{i=0}^{m} a_i(1 - 2x_{\mathrm{water}})^i - 2x_{\mathrm{water}}(1 - x_{\mathrm{water}})^2\sum_{i=0}^{m} ia_i(1 - 2x_{\mathrm{water}})^{i-1} \tag{7}$$

and

$$V_{\mathrm{EDA}}^{\mathrm{E}} = V^{\mathrm{E}} - x_{\mathrm{water}}(1 - 2x_{\mathrm{water}})\sum_{i=0}^{m} a_i(1 - 2x_{\mathrm{water}})^i + 2x_{\mathrm{water}}^2(1 - x_{\mathrm{water}})\sum_{i=0}^{m} ia_i(1 - 2x_{\mathrm{water}})^{i-1} \tag{8}$$

Method

Materials. Ethylenediamine (EDA) with a mass fraction purity of 99.8 % was obtained from Akzo Nobel Functional Chemicals and was used as received. The purity was confirmed by gas chromatography and Karl Fischer titration. Bidistilled water was used for preparation of mixtures.

Apparatus. The temperature was measured using a platinum resistance thermometer of nominal resistance of 100 Ω that was calibrated against a Quartz thermometer (model 2804A) on ITS-90 with an estimated uncertainty of ± 0.01 K. The density was measured with a vibrating tube oscillator DMA 60/602H from Anton Paar. The densitometer was calibrated with nitrogen gas and bidistilled water in the temperature range of the measurements. Density values for water were obtained using the correlation in VDI-Wasserdampftafeln.[7] The estimated overall uncertainty in the measured density is $\pm\ 5\cdot10^{-2}$ kg·m^{-3}.

The temperature of the measuring cell was controlled by an external temperature bath to an estimated stability of ± 0.05 K and the pressure by dry nitrogen through a gauge with precision ± 1 kPa. The dry nitrogen was used to protect the sample from reacting with carbon dioxide and moisture in the air. The pressure was maintained at 0.2 MPa.

Procedures. The samples were prepared by weighing in small bottles of glass. Water was added first. The bottle was then covered with a membrane, and EDA was added with a syringe to avoid contact between EDA and the air as well as evaporation of the mixture. The bottle was sealed with a lid and cooled in tap water for at least 5 min as the mixing of samples with a high water content produced strong heat. The stated accuracy of the scales is ± 0.0001 g.

The sample was transferred to the measuring cell by a syringe. Care was taken to ensure that the temperatures of the sample and the measuring cell were similar and that no bubbles were formed. The apparatus was left for at least 0.75 h for temperature equilibration before the first measurement was made. The temper-

Table 2. Deviation Δρ/kg·m^{-3} of the Published Density of EDA from Equation 2 Over Temperature Range *t* with Number of Measurements *N*

(*t*min to *t*max)/°C	*N*	purity	average deviation Δρ/kg·m^{-3}	ref
20	1	not stated	1.94	1
30 to 45	4	99 %	2.70	4
12 to 90	156	99 %	−0.24	5
30 to 50	5	density 899.7 kg·m^{-3} at t = 20 °C	2.96	6
25	1	99.7 % from melting point analysis	−1.38	10
19.6 to 109.3	7	boiling point t = 116.7 °C at 758.7 mmHg	4.76	11
20	1	dielectric constant 15.1, specific conductance $7.5\cdot10^{-7}$ to $9.0\cdot10^{-7}$	−2.07	12
25	1	boiling point t = (116 to 116.5) °C	−1.38	13
20 to 60.6	3	boiling point t = 117 °C at 750 mmHg	2.04	14
25	1	boiling point t = 117.33 °C at 760 mmHg	0.52	15
20 to 70	6	−	0.80	16
15 to 30	2	boiling point t = 117.26 °C at 760 mmHg	−1.72	17

Table 3. Measured Density, ρ, at Mole Fraction *x* for the Mixture of Ethylenediamine and Water at Temperature *T*

$x(\mathrm{H_2O})$	T/K	ρ/kg·m^{-3}	$x(\mathrm{H_2O})$	T/K	ρ/kg·m^{-3}	$x(\mathrm{H_2O})$	T/K	ρ/kg·m^{-3}
0.1028	283.13	917.19	0.2017	282.92	929.12	0.3010	282.96	942.07
	293.05	908.06		292.93	919.98		292.93	933.05
	302.99	898.81		303.10	910.59		302.96	923.82
	313.11	889.31		313.14	901.22		313.00	914.50
	323.04	879.88		322.93	891.98		322.86	905.20
	333.10	870.21		333.11	882.17		332.96	895.56
	343.04	860.53		343.13	872.53		342.98	885.86
	353.02	850.77		353.03	862.82		352.83	876.20
0.3967	282.78	956.19	0.5026	283.26	973.12	0.6032	283.69	989.21
	293.09	946.95		292.67	964.64		293.29	980.74
	302.85	938.02		302.85	955.33		302.39	972.59
	313.98	927.72		312.77	946.17		312.55	963.30
	323.75	918.54		322.88	936.71		322.65	953.97
	333.53	909.23		332.89	927.17		333.02	944.23
	342.81	900.28		342.64	917.79		342.90	934.86
	353.34	889.95		352.71	907.89		352.71	925.35
0.7026	284.35	1001.48	0.7687	283.47	1005.97	0.8936	283.11	1000.80
	292.85	994.55		293.24	998.97		292.62	996.47
	301.58	987.24		302.47	992.11		302.97	991.26
	311.86	978.33		312.59	984.36		313.02	985.72
	322.72	968.66		322.34	976.65		323.15	979.69
	332.41	960.00		332.77	968.17		333.38	973.32
	343.08	950.21		342.60	959.94		343.09	966.52
	353.48	940.52		352.14	951.74		352.90	959.49

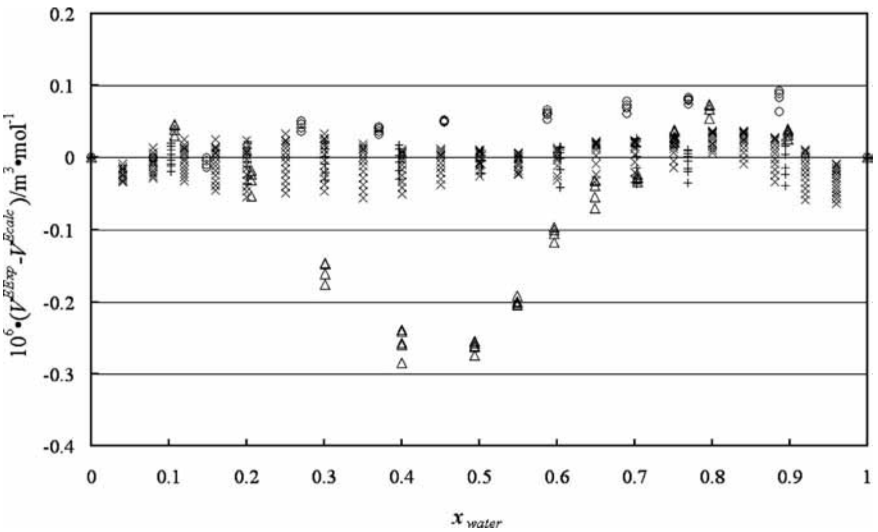

Figure 1. Residuals for V^E versus molar fraction of water for the Redich−Kister model without temperature-dependent parameters. Experimental data from: Δ, Saleh et al.;[6] ○, Kapadi et al.;[4] ×, Valtz et al.;[5] and +, this study.

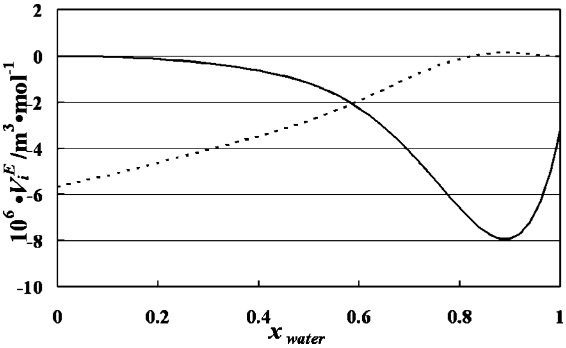

Figure 2. Partial molar excess volumes of water (dotted line) and EDA (solid line).

ature of the bath was then increased in intervals of 10 K. Between the loading of each sample, the cell was rinsed with ethanol, flooded by dry nitrogen gas, and left for at least 12 h to cool. After the final measurement series, a check of the calibration was performed.

Results and Discussion

The experimental data for pure water are given in Table 1. Deviations from the model found in Wasserdampftafeln[7] are calculated. The average absolute deviation is 0.015 $kg \cdot m^{-3}$. The experimental data for pure EDA are also given in Table 1. The data were used to estimate the parameters in eq 2. The average absolute deviation of the measured data from the model is 0.008 $kg \cdot m^{-3}$. The densities for pure EDA compare well with values available in the literature. The average deviations for published values for EDA compared with eq 2 and the parameters given above are listed in Table 2. For the data where the measurements were made at several temperatures, the residuals of each set were always either negative or positive.

The experimental results for the mixture are found in Table 3. For the lower temperatures, there is a local maximum in density close to a mole fraction of water of 0.8. At higher temperatures, the increase in density is monotonous over the entire composition range. The same kind of behavior has been reported for aqueous mixtures of other amines.[8]

The excess molar volume, V^E, was obtained from eq 1. To compute the excess volume from the measured density data, expressions for the molar volume of the pure components are needed. For water, the expression from Wasserdampftaffeln[7] is used, and for EDA, the molar volume is computed from eq 2. The excess volume is negative over the entire concentration range. It has a minimum at the mole fraction of water of 0.59. The variation with temperature is small as noted by others.[4−6] There is, however, a systematic variation with temperature: the isotherms for the lower temperatures are more narrow and deeper and those for the higher temperatures are wider and more shallow. The difference between the highest and lowest value for each concentration is at most $6 \cdot 10^{-8}$ $m^3 \cdot mol^{-1}$. For the lowest and highest concentrations, V^E becomes more negative with increasing temperature. For intermediate concentrations, V^E has a maximum that moves from a temperature of 303 K for the lower concentrations up to a temperature of 323 K in the middle of the concentration range and then back again.

Parameters for the Redlich−Kister expression for V^E of eq 5 were estimated from the experimental data. As the variation in temperature is small for the excess volume, a good model is obtained without temperature-dependent parameters. For the model with six parameters, the absolute average deviation is $1.3 \cdot 10^{-8}$ $m^3 \cdot mol^{-1}$. The estimated parameters are as follows

$$a_0 = -7.963 \cdot 10^{-6}\ m^3 \cdot mol^{-1};\ a_1 = 3.206 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$$
$$a_2 = -0.332 \cdot 10^{-6}\ m^3 \cdot mol^{-1};\ a_3 = -2.779 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$$
$$a_4 = 3.867 \cdot 10^{-6}\ m^3 \cdot mol^{-1};\quad a_5 = -1.623 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$$

The excess volume is overestimated at lower temperatures for the concentrations close to the minimum in V^E and underestimated as the pure components are approached. In Figure 1, the model is compared to published experimental data. As shown in the figure, the data from Saleh et al.[6] have a clear trend in the residuals for the concentration. There are no obvious trends with temperature for the published data. The AAD for this model is $4.3 \cdot 10^{-8}$ $m^3 \cdot mol^{-1}$ for the data from Kapadi et al.,[4] $9.0 \cdot 10^{-8}$ $m^3 \cdot mol^{-1}$ for Saleh et al.,[6] and $1.8 \cdot 10^{-8}$ $m^3 \cdot mol^{-1}$ for Valtz et al.[5] Saleh et al.[6] used a bicapillary pycnometer to measure the density. Their V^E values differ more from those found in this study than those of Valtz et al.[5] and those of Kapadi et al.[4]

Using eq 1, the density can be calculated from the Redlich−Kister model. The average absolute deviation (AAD) of the measured values from the model is 0.32 $kg \cdot m^{-3}$. At a mole fraction of water of 0.7, the densities for the lower temperatures are underestimated by at most 1.2 $kg \cdot m^{-3}$, and for the higher they are overestimated by at most 0.7 $kg \cdot m^{-3}$. At a mole fraction of water of 0.9, the residuals are reversed; the density for the highest temperature is underestimated by 1.5 $\text{kg}\cdot\text{m}^{-3}$, and that for the next lowest temperature is overestimated by 1.2 $\text{kg}\cdot\text{m}^{-3}$. The AAD for this model is 1.5 $\text{kg}\cdot\text{m}^{-3}$ for the data from Kapadi et al.[4] and 3.7 $\text{kg}\cdot\text{m}^{-3}$ for Saleh et al.[6] The density values for $T = 333.15$ K in the data from Valtz et al.[5] appear to be misprinted. If that set of measurements is excluded, the AAD is 0.59 $\text{kg}\cdot\text{m}^{-3}$.

Introducing a temperature dependency in the Redlich–Kister parameters gives a closer representation of the V^{E} data. A model with the following parameters gives an AAD of $3.3\cdot10^{-9}$ $\text{m}^3\cdot\text{mol}^{-1}$ corresponding to an AAD for the density of 0.09 $\text{kg}\cdot\text{m}^{-3}$

$$a_0 = -1.728\cdot10^{-5} + 5.818\cdot10^{-8}T - 9.050\cdot10^{-11}T^2;$$

$$a_1 = 1.838\cdot10^{-5} - 8.359\cdot10^{-8}T + 1.120\cdot10^{-10}T^2$$

$$a_2 = 4.352\cdot10^{-6} - 1.281\cdot10^{-8}T;$$

$$a_3 = -1.055\cdot10^{-5} - 2.514\cdot10^{-8}T;$$

$$a_4 = 7.463\cdot10^{-7};$$

$$a_5 = -1.941\cdot10^{-6};$$

$$a_6 = 3.552\cdot10^{-6}$$

For the lower temperatures, the density of the mixture has a maximum, but at higher temperatures the increase in density is monotonous. Chan et al.[8] observed the same behavior for aqueous mixtures of alcohol amines. Their explanation of the behavior is that the intermolecular structure of the mixture is destroyed by thermal agitation at higher temperatures. In their case, this corresponds to less negative excess volumes at higher temperatures, as expected. For EDA and water, however, the excess volume hardly varies at all with temperature. Following Kruglyak et al.,[3] the density is split into contributions from the pure component densities and a departure from additivity, $\Delta\rho$, as shown in eq 3. This departure is positive for all compositions and temperatures. It has a maximum at a molar fraction of water of 0.69. The isotherms do not cross each other as they do for the V^{E}. The departure decreases with temperature. The difference between the highest and lowest temperature at the maximum is 8 $\text{kg}\cdot\text{m}^{-3}$. This is modeled well by the V^{E} model without temperature-dependent parameters and is thus attributed to differences in the pure component densities. At the highest temperature, the difference between the pure component densities is highest, causing a steeper decent of the density curve. When the density departure is superimposed on this difference, the maximum disappears because of the tilt of the curve.

The partial molar excess volumes of the EDA–water mixture are shown in Figure 2. They resemble those of methanol and water.[9]

Kruglyak et al.[3] claim that the maximum in departure from additivity of the density around $x_{\text{water}} = 0.7$ indicates that the 2-hydrate of EDA is dominating (EDA*2 H_2O) and that the minimum of V^{E} around a mole fraction of water of 0.6 may be interpreted as the presence of both the 2-hydrate and the 1-hydrate. Note, however, that V^{E} is an inverse of the density departure with molar ratios instead of apparent volume ratios. Thus, the two curves are only transformations of each other.

Conclusion

The density of the mixture has a local maximum in the water-rich region at low temperatures. With increasing difference in pure component densities at higher temperatures, this maximum disappears. Excess volume, calculated from experimental density data, has a minimum at a mole fraction of water of 0.59 for (water + EDA). The excess volume was essentially independent of the temperature in the range investigated, (283 to 353) K. A four-parameter model for the density of pure EDA with an average absolute deviation of 0.008 $\text{kg}\cdot\text{m}^{-3}$ was estimated. Kruglyak et al.'s[3] interpretation of the difference in location between the minimum in V^{E} and the maximum in $\Delta\rho$ does not seem plausible as these two functions are transforms of each other.

Acknowledgment

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Supporting Information Available:

Table of excess volumes. This material is available free of charge via the Internet at http://pubs.acs.org.

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