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Activity Coefficients at Infinite Dilution of Cylcohexylamine + Octane, Toluene, Ethylbenzene, or Aniline and Excess Molar Volumes in Binary Mixtures of Cyclohexylamine + Heptane, Octane, Nonane, Decane, Undecane, Aniline, or Water

Andreas Grenner, Mandy Klauck, Madeleine Kramer, and Jürgen Schmelzer*

Department of Chemical Engineering, Hochschule für Technik und Wirtschaft Dresden−University of Applied Sciences,
Friedrich-List-Platz 1, 01069 Dresden, Germany

The differential ebulliometry method was used to measure activity coefficients at infinite dilution for cyclohexylamine with octane, toluene, ethylbenzene, and aniline in a temperature range from (353 to 403) K. NRTL and UNIQUAC parameters have been determined with these data and with vapor−liquid equilibrium data (VLE) from the literature. In this context $P-x-y$ data were measured for the system cylcohexylamine + toluene at (333.15 and 363.15) K. Excess molar volumes were obtained by density measurements of binary mixtures of cyclohexylamine + heptane, octane, nonane, decane, undecane, aniline, and water at 303.15 K under atmospheric pressure. The excess molar volumes were fitted to the Redlich−Kister polynomial equation.

Introduction

Activity coefficients at infinite dilution for cyclohexylamine + octane, toluene, ethylbenzene, or aniline and excess molar volumes of cyclohexylamine + alkanes (C_7-C_{11}), aniline, or water have been determined. Parameters for the NRTL[1] and UNIQUAC[2] Gibbs energy models were determined from VLE data and the activity coefficients at infinite dilution obtained in this work. Cyclohexylamine is of special interest because of its miscibility with polar and apolar substances. Furthermore, cyclohexylamine appears in the production process of both cyclamate and aniline and is used as a corrosion inhibitor.

Experimental Section

Chemicals. Heptane was obtained from Fisher Scientific Ltd., U.K., with a purity of > 99 %. The following chemicals were purchased from Acros Organics, Belgium: octane purity 99+ %, nonane purity 99 %, decane purity 99+ %, toluene purity p.a., ethylbenzene purity 99.8 %, aniline purity p.a., and cyclohexylamine purity p.a. Undecane is a product of Petrolchemisches Kombinat, Germany, purity > 98 % and was fractionally distilled twice in a Vigreux column at reduced pressure. The other substances were used as received since the purities were higher than 99.5 % as stated below. The purities were judged by comparing experimental values of refractive index and density with values reported in the literature; the values are shown in Table 1. Additionally, the purity was verified by gas−liquid chromatography. The mass fractions of the substances were as follows: heptane (99.5 %), octane (99.9 %), nonane (99.8 %), decane (99.7 %), undecane (99.8 %), toluene (99.8 %), ethylbenzene (99.8 %), aniline (99.5 %), and cyclohexylamine (99.9 %). Deionized and distilled water was used.

Table 1. Comparison of the Experimental Refractive Index (n_D) and Density (ρ) of Pure Liquids with Literature Values

		n_D		$\rho/g\cdot cm^{-3}$	
substance	T/K	exptl	lit	exptl	lit
heptane	298.15	1.3853	1.3855[21]	0.67943	0.6795[21]
octane	298.15	1.3946	1.3944[21]	0.69849	0.6986[21]
nonane	293.15	1.4055	1.4058[21]	0.71913	0.7192[21]
decane	298.15	1.4092	1.4090[21]	0.72655	0.7266[21]
undecane	293.15	1.4162	1.4164[21]	0.74011	0.7402[21]
toluene	293.15	1.4960	1.4961[21]	0.86678	0.8668[21]
ethylbenzene	293.15	1.4960	1.4959[21]		
	298.15			0.86259	0.8626[21]
aniline	293.15	1.5862	1.5863[21]	1.02172	1.0217[21]
cylcohexylamine	288.15	1.4624	1.4625[21]		
	303.15			0.85820	0.85777[22]
water	293.15	1.3336	1.3336[21]	0.99816	0.9982[21]

Apparatus and Procedure. The measuring of the activity coefficients at infinite dilution was carried out by differential ebulliometry. This method is based on the determination of the boiling temperature differences at constant pressure as a function of liquid-phase composition. Twin ebulliometers were used; one as a reference ebulliometer containing solvent only. The other ebulliometer contained solvent and solute. The technique provides the boiling temperature differences between the ebulliometers. The apparatus has been described earlier and has already been used to give reliable data of activity coefficients of infinite dilution[3]. The equation for obtaining activity coefficients at infinite dilution from the data of boiling temperature differences was derived by Dohnal and Novotná[4] and is given by

$$\gamma_i^\infty = \frac{\epsilon_i^\infty P_j^{\text{sat}}}{P_i^{\text{sat}}}\left[1 - \beta\left(\frac{\partial T}{\partial x_i}\right)_P^\infty\right] \tag{1}$$

where

$$\epsilon_i^\infty = \exp\left[\frac{(B_{ii} - V_i^{\text{L}})(P_j^{\text{sat}} - P_i^{\text{sat}}) + \delta_{ij} P_j^{\text{sat}}}{RT}\right]$$

$$\beta = \left(1 + P_j^{\text{sat}}\frac{B_{jj} - V_j^{\text{L}}}{RT}\right)\frac{d \ln P_j^{\text{sat}}}{\text{d}T}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$$

where P_i^{sat} and V_i^{L} are the pure-component vapor pressure and liquid molar volumes, B_{ii} and B_{ij} are the second virial coef-

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* Corresponding author. E-mail: schmelzer@mw.htw-dresden.de. Fax: +49 351 4623228.

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ficients, R is the gas constant, and T is the absolute temperature. For determination of the limiting slope at infinite dilution ($(\partial T/\partial x_i)_P^\infty$) experimental ebulliometric data are used. The liquid phase is assumed as ideal. The relative volatility (α_{ij}^∞) limits the differential ebulliometry method:

$$\alpha_{ij}^\infty = \frac{\gamma_i^\infty P_i^{\text{sat}}}{P_j^{\text{sat}}} \tag{2}$$

Since the difference between the gravimetrically determined overall composition and the equilibrium liquid composition has to be corrected as shown by Dohnal and Novotná,[4] only systems with an α_{ij}^∞ between 0.2 and 8 can be measured.

The pressure was measured using a pressure transducer (Druck Ltd., RTP 301), and the boiling temperature was measured with a Pt-100 resistance thermometer (Automatic Systems Laboratories Ltd., F250MkII). The experimental uncertainties of these devices are as follows: $\sigma(P) = 0.06$ kPa, $\sigma(T) = 0.03$ K whereas the boiling temperature difference is stable within $\pm$ 0.002 K, and $\sigma(x) = 0.0001$ taking into account the loadings of the ebulliometers and the accuracy of weighing. The experimental uncertainties of this work are less than 6 % for the activity coefficients at infinite dilution.

The samples for determination of the excess molar volumes were gravimetrically prepared, and the density was measured with a vibrating tube densimeter (DMA 58, Anton Paar, Austria). The accuracy of the densimeter is $\sigma(\rho) = 0.00002$ g·cm^{-3} where $\sigma(T) = 0.01$ K and $\sigma(x) = 0.0002$. The uncertainty for V^{E} is $\sigma(V^{\text{E}}) = 0.015$ cm^3·mol^{-1} for the systems of this work.

Results and Discussions

Activity coefficients at infinite dilution (γ^∞) were measured for cyclohexylamine in octane, toluene, ethylbenzene, and aniline. Furthermore, the activity coefficients at infinite dilution of octane, toluene, and ethylbenzene in cyclohexylamine were determined. All measured activity coefficients at infinite dilution are less than two. The activity coefficients at infinite dilution of cyclohexylamine in octane, toluene, and ethylbenzene decrease with increasing temperature as does the γ^∞ values for octane, toluene, and ethylbenzene in cyclohexylamine. These positive deviations from Raoult's law become smaller with increasing temperature. Octane provides the largest γ^∞ values with cyclohexylamine as a solvent as well as a solute. The mixture of cyclohexylamine + aniline shows converse temperature dependence. The γ^∞ values increase with increasing temperature. This can be explained with the break down of H-bonds between cyclohexylamine and aniline at higher temperatures. The reason the γ^∞ values of aniline in cyclohexylamine were not measured is that the relative volatility is not between 0.2 and 8. Pividal and Sandler[5] have reported γ^∞ values for cyclohexylamine + octane. The γ^∞ value of cyclohexylamine matches well (Figure 1) with those of this work; however, the γ^∞ values of octane do not (Figure 2). The trend of the data is opposite as compared to this work. In the work of Pividal and Sandler,[5] the γ^∞ values for cyclohexylamine in octane are smaller than those for octane in cyclohexylamine. For this, the γ^∞ values predicted by NRTL and UNIQUAC based only on VLE data from ref 6 were calculated. Both models validated the trend of our work. In addition, the system cyclohexylamine + heptane in the work of Pividal and Sandler[5] was determined, which also shows a trend of γ^∞ values similar to those of cyclohexylamine + octane in our work. These confirmed the γ^∞ values of octane in cyclohexylamine of our measurements.

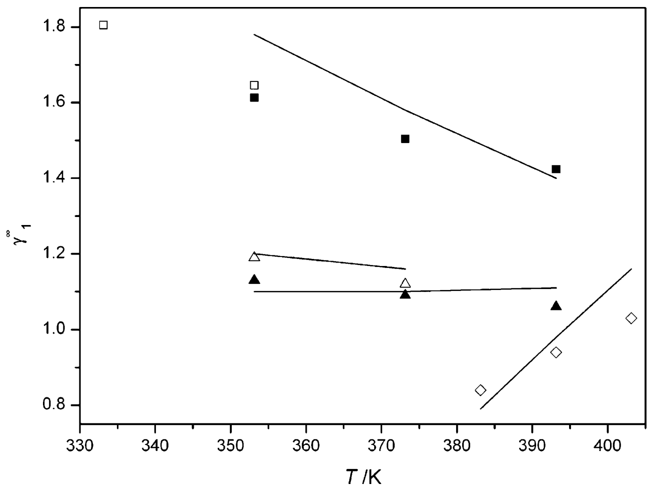

Figure 1. Experimental activity coefficients at infinite dilution of this work and correlations of UNIQUAC with parameter fit to these activity coefficients at infinite dilution and VLE data[6,9,10] for the systems cyclohexylamine + octane, toluene, ethylbenzene, or aniline. Experimental results: cyclohexylamine (1) + □, octane (2) taken from ref 5; + ■, octane (2) this work; + △, toluene (2); + ▲, ethylbenzene (2); + ◇, aniline (2). Lines are UNIQUAC results.

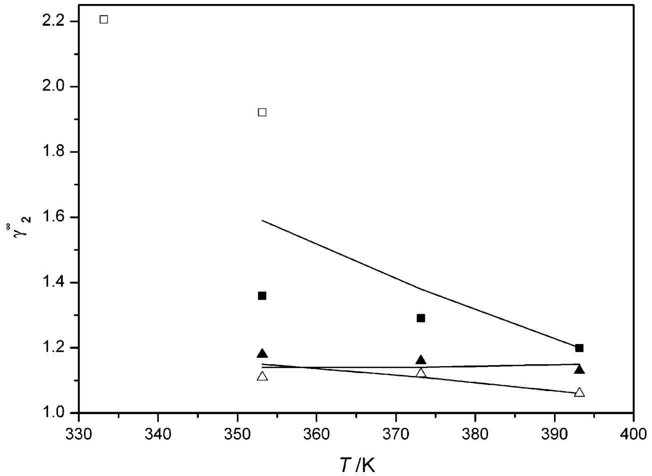

Figure 2. Experimental activity coefficients at infinite dilution of this work and correlations of UNIQUAC with parameter fit to these activity coefficients at infinite dilution and VLE data[6,9,10] for the systems cyclohexylamine + octane, toluene, or ethylbenzene. Experimental results: cyclohexylamine (1) + □, octane (2) taken from ref 5; + ■, octane (2) this work; + △, toluene (2); + ▲, ethylbenzene (2). Lines are UNIQUAC results.

The activity coefficients at infinite dilution of this work were fitted simultaneously with VLE data from the literature. Parameters of eq 3 for the NRTL and UNIQUAC models were determined using the objective function (Q) of Renon[7] (eq 4):

$$C_{ij}/R = C_{ij}^C + C_{ij}^T(T - 273.15\ \text{K}) \tag{3}$$

where $C_{ij} = u_{ij} - u_{jj}$ for UNIQUAC and $C_{ij} = g_{ij} - g_{jj}$ for NRTL:

$$Q = \Pi_1 \sum_i \left(\frac{100}{P_{\text{exptl}}}\right)_i^2 (P_{\text{calcd}} - P_{\text{exptl}})_i^2 + \Pi_2 \sum_i (100)_i^2 (y_{\text{calcd}} - y_{\text{exptl}})_i^2 + \Pi_3 \sum_i \left(\frac{10}{\gamma^\infty_{\text{exptl}}}\right)_i^2 (\gamma^\infty_{\text{calcd}} - \gamma^\infty_{\text{exptl}})_i^2 \tag{4}$$

Table 2. Isothermal Vapor−Liquid Equilibrium Data for Cyclohexylamine (1) + Toluene (2)

333.15 K			363.15 K		
P/kPa	x_2	y_2	P/kPa	x_2	y_2
7.51	0.000	0.000	25.59	0.000	0.000
8.78	0.095	0.243	28.53	0.081	0.154
10.71	0.251	0.486	31.66	0.185	0.362
11.43	0.305	0.567	33.58	0.242	0.437
12.27	0.374	0.639	35.48	0.301	0.507
13.16	0.457	0.708	37.47	0.370	0.582
13.99	0.535	0.739	39.89	0.449	0.645
14.94	0.623	0.815	41.97	0.522	0.703
16.76	0.799	0.895	44.29	0.603	0.766
18.56	1.000	1.000	47.42	0.718	0.833
			49.63	0.798	0.885
			52.41	0.903	0.943
			54.49	1.000	1.000

Table 3. Experimental and NRTL/UNIQUAC Activity Coefficients at Infinite Dilution

component 1 + component 2	T/K	$\gamma^\infty_{1,\mathrm{exptl}}$	$\gamma^\infty_{1,\mathrm{NRTL}}$	$\gamma^\infty_{1,\mathrm{UNIQUAC}}$	$\gamma^\infty_{2,\mathrm{exptl}}$	$\gamma^\infty_{2,\mathrm{NRTL}}$	$\gamma^\infty_{2,\mathrm{UNIQUAC}}$
cyclohexylamine (1) + octane (2)	353.15	1.61	1.79	1.78	1.36	1.59	1.59
	373.15	1.50	1.58	1.58	1.29	1.38	1.38
	393.15	1.42	1.38	1.40	1.20	1.21	1.20
cyclohexylamine (1) + toluene (2)	353.15	1.19	1.21	1.20	1.14	1.15	1.15
	373.15	1.12	1.14	1.16	1.13	1.12	1.11
	393.15				1.06	1.06	1.06
cyclohexylamine (1) + ethylbenzene (2)	353.15	1.13	1.10	1.10	1.18	1.18	1.14
	373.15	1.09	1.10	1.10	1.16	1.16	1.14
	393.15	1.06	1.10	1.11	1.13	1.13	1.15
cyclohexylamine (1) + aniline (2)	383.15	0.84	0.80	0.79			
	393.15	0.94	0.95	0.98			
	403.15	1.03	1.10	1.16			

Table 4. Fitted Parameters to γ^∞ and VLE Data (Eqs 3 and 4) for NRTL and UNIQUAC; Used Data Sets for the Fitting and Deviations

cyclohexylamine (1) +	system			
	octane (2)	aniline (2)	toluene (2)	ethylbenzene (2)
data	ref 6	ref 6, 9, 10	this work	this work (only γ^∞ values)
NRTL (α = 0.47)				
C^C_{12}/K	283.02	−19.95	−62.63	−166.08
C^C_{21}/K	46.18	−324.27	130.69	−100.31
C^T_{12}	−3.29	−1.87		
C^T_{21}	1.75	5.72		
ΔP/%[a]	0.87	1.13	0.47	
Δy[b]	0.0091	0.0064	0.0120	
$\Delta\gamma^\infty$/%[a]	7.45	4.04	2.86	1.81
UNIQUAC				
C^C_{12}/K	−5.75	5.15	−13.45	117.33
C^C_{21}/K	78.52	−143.07	28.74	92.84
C^T_{12}	−1.36	−1.67		
C^T_{21}	1.42	3.43		
ΔP/%[a]	0.89	1.07	0.48	
Δy[b]	0.0090	0.0066	0.0121	
$\Delta\gamma^\infty$/%[a]	6.77	7.88	2.94	2.38

[a] $\Delta Z = 100/n_p\Sigma((Z_{\mathrm{calcld}} - Z_{\mathrm{exptl}})/Z_{\mathrm{exptl}})$, where n_p is the number of data points and Z represents P or γ^∞_1. [b] $\Delta y = 1/n_p\Sigma(|y_{\mathrm{calcld}} - y_{\mathrm{exptl}}|)$.

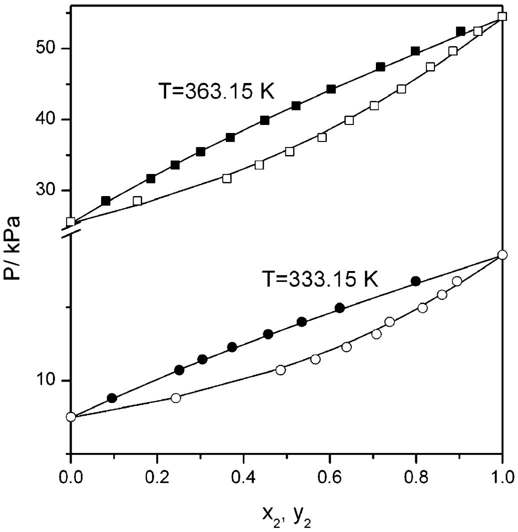

Figure 3. $P-x-y$ data for cyclohexylamine (1) + toluene (2): ■, □, ●, ○, experimental data, this work. Lines are the collective fitting of experimental VLE and γ^∞ data with UNIQUAC.

where the summation is made over all data points i, P is the pressure, y is the equilibrium vapor phase mole fraction, γ^∞ is the activity coefficient at infinite dilution, and Π_i is a weighting factor. During the modeling of the binary data, the γ^∞ values are weighted higher (using Π_i of eq 4) as compared with the VLE data, so that the ratio of γ^∞ values and VLE data points is unity. Temperature-dependent parameters were used only if the results could be improved significantly. We recently have published VLE data[6] for the systems cyclohexylamine + octane and + aniline. In this work, isothermal VLE data for cyclohexylamine + toluene were measured at (333.15 and 363.15) K with the equipment described in ref 6 and are presented in Figure 3 and Table 2. Checked by the method of Van Ness,[8] the data are thermodynamically consistent. Additionally, VLE data for the system cyclohexylamine + aniline[9,10] were found in the literature and were included in the fit. An isobaric VLE data set was found for cyclohexylamine + toluene of Zlacky et al.,[11] but these data do not pass the consistency test of Van Ness[8] and were not considered. The parameters and the results for γ^∞ measurements are given in Tables 3 and 4. Since the correlated results of NRTL and UNIQUAC are very similar only the UNIQUAC results are presented in Figures 1 and 2. All the deviations between experimental and correlated VLE data are small. The greater deviations of the calculated γ^∞ values are caused by the experimental uncertainities of the γ^∞ measurements. Parameters for the system cyclohexylamine + ethylbenzene are given in Table 4; those are based on the γ^∞ values of this work only and therefore are limited in their applicability. Since there is no other thermodynamical information available for this system in the literature, this can be a first approach for chemical engineers.

Table 5 lists experimental values of densities and calculated excess molar volumes (V^E) of cyclohexylamine + alkanes (C_7−C_{11}), aniline, or water at 303.15 K. The V^E values were calculated using the pure substances densities (ρ_i), the densities of the mixture (ρ), the mole fraction (x_i), and the molar mass (M_i):

$$V^E/\mathrm{cm^3 \cdot mol^{-1}} = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{5}$$

The V^E values are shown in Figure 4. The excess molar volumes for cyclohexylamine with all the alkanes are positive over the whole mole fraction range and increase with the number of C-atoms of the alkanes. The maximum of V^E in the system with heptane is at a mole fraction of cyclohexylamine at about 0.4 and is slightly shifted to higher mole fractions for the other alkanes according to their increasing chain length. Opposing effects as pointed out by Treszczanowicz and Benson[12] can explain the V^E values of this work. Physical interactions and breaking of H-bonds of cyclohexylamine contribute to this positive term of V^E. Similar results with a shift of the maximum in systems of associating components + alkanes were found by Villa et al.[13] in systems of amines + alkanes and by Kaur et al.[14] in systems of cyclohexanol + alkanes. Raju et al.[15] also

Table 5. Experimental Results for Density (ρ) and Excess Molar Volume (V^E) of Cylcohexylamine + Alkanes (C_7−C_{11}), + Aniline, and + Water at 303.15 K under Atmospheric Pressure

	ρ	V^E		ρ	V^E		ρ	V^E
x_1	g·cm^{-3}	cm^3·mol^{-1}	x_1	g·cm^{-3}	cm^3·mol^{-1}	x_1	g·cm^{-3}	cm^3·mol^{-1}
Cyclohexylamine (1) + Heptane (2)								
0.0000	0.67532	0.000	0.3983	0.73592	0.296	0.7996	0.81268	0.150
0.1009	0.68934	0.143	0.5000	0.75383	0.273	0.8993	0.83460	0.087
0.1999	0.70399	0.226	0.5999	0.77237	0.244	1.0000	0.85820	0.000
0.3006	0.71971	0.284	0.6989	0.79179	0.202			
Cyclohexylamine (1) + Octane (2)								
0.0000	0.69467	0.000	0.4085	0.74558	0.489	0.7503	0.80355	0.333
0.1036	0.70594	0.229	0.5001	0.75950	0.494	0.8018	0.81383	0.280
0.2003	0.71744	0.368	0.5991	0.77585	0.451	0.8502	0.82395	0.219
0.3006	0.73040	0.452	0.6998	0.79385	0.388	1.0000	0.85820	0.000
Cyclohexylamine (1) + Nonane (2)								
0.0000	0.71005	0.000	0.4010	0.75143	0.626	0.7955	0.81315	0.410
0.0998	0.71879	0.260	0.4998	0.76451	0.642	0.8999	0.83462	0.239
0.1994	0.72847	0.447	0.6006	0.77938	0.602	1.0000	0.85820	0.000
0.3010	0.73941	0.575	0.7000	0.79569	0.523			
Cyclohexylamine (1) + Decane (2)								
0.0000	0.72254	0.000	0.3994	0.75729	0.725	0.8002	0.81452	0.518
0.1004	0.72974	0.295	0.4998	0.76890	0.771	0.9006	0.83467	0.305
0.2003	0.73786	0.507	0.5996	0.78209	0.742	1.0000	0.85820	0.000
0.3002	0.74697	0.660	0.6996	0.79714	0.659			
Cyclohexylamine (1) + Undecane (2)								
0.0000	0.73293	0.000	0.4011	0.76269	0.821	0.7998	0.81498	0.603
0.1000	0.73882	0.337	0.5005	0.77299	0.855	0.8998	0.83457	0.342
0.2172	0.74700	0.592	0.5997	0.78483	0.833	1.0000	0.85820	0.000
0.3066	0.75416	0.725	0.7005	0.79879	0.754			
Cyclohexylamine (1) + Aniline (2)								
0.0000	1.01294	0.000	0.3837	0.94920	−0.446	0.7738	0.89069	−0.407
0.1161	0.99251	−0.143	0.4907	0.93282	−0.514	0.8759	0.87575	−0.241
0.1936	0.97958	−0.247	0.5932	0.91738	−0.526	1.0000	0.85820	0.000
0.2810	0.96535	−0.346	0.7087	0.90024	−0.472			
Cyclohexylamine (1) + Water (2)								
0.0000	0.99565	0.000	0.3021	0.91943	−1.278	0.6931	0.88070	−1.322
0.1002	0.95670	−0.529	0.3970	0.90871	−1.506	0.7801	0.87376	−1.050
0.1970	0.93534	−0.941	0.5016	0.89785	−1.578	0.9004	0.86497	−0.542
0.2237	0.93093	−1.043	0.6037	0.88839	−1.505	1.0000	0.85820	0.000

Table 6. Redlich−Kister Coefficients and Standard Deviations

system:	A_1	A_2	A_3	s[a]
cyclohexylamine +	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}
heptane	1.1098	−0.4345	0.2255	0.0050
octane	1.9590	−0.4359	0.1935	0.0037
nonane	2.5544	−0.2371	0.3200	0.0048
decane	3.0592	0.0558	0.4202	0.0055
undecane	3.4179	0.1909	0.5993	0.0060
aniline	−2.0724	−0.6183	0.3819	0.0053
water	−6.2922	−0.1264	0.6799	0.0086

[a] $s = (1/(n_p - 1)\sum(V^E_{calcld} - V^E_{exptl})^2)^{1/2}$, where n_p is the number of data points.

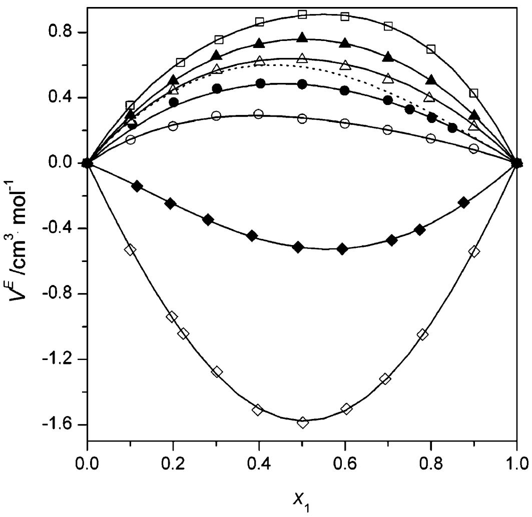

Figure 4. Excess molar volumes (V^E) for cyclohexylamine systems at 303.15 K. Experimental results cyclohexylamine (1) + ○, heptane (2); + ●, octane (2); + △, nonane (2); + ▲, decane (2); + □, undecane (2); + ◆, anline (2) and + ◇, water (2). Solid lines, calculated values from Redlich−Kister equation (eq 6); dashed line, cyclohexylamine (1) + nonane (2) taken from ref 15.

presented V^E of cyclohexylamine + alkanes (C_6−C_9) at 303.15 K. A comparison with the results of this work shows that the V^E curve of cyclohexylamine + heptane agree excellent. For octane, the V^E values of Raju et al.[15] show a deviation of maximum 0.02 cm^3·mol^{-1}. However, the results with nonane deviate with maximum 0.09 cm^3·mol^{-1} as shown in Figure 4. The V^E curves of our work show a systematical trend which the nonane curve of Raju et al.[15] does not follow. The negative V^E over the entire range of composition in mixtures of cyclohexylamine + aniline or + water indicates the presence of strong specific interaction. Zhang et al.[16] presented excess properties of methyldiethanolamine and has been used the model of Lumry et al.[17] to interpret the negative V^E values. In the explanation of Zhang et al.[16] (at high mole fraction of water or amine), the components occupy "holes" in the open structure of the respective other component caused by hydrogen bonds that are highly oriented intermolecular forces. In the middle of the concentration range, the amine eliminates the strong hydrogen bonds between the water molecules, and water + amine interactions are replaced by amine + amine interactions. These occurring "holes" in hydrogen bonding cluster are described by Nishi et al.[18] or Speedy.[19] The Redlich−Kister polynomial equation[20] (eq 6) was used for fitting the V^E values:

$$V^E_{calcld}/\text{cm}^3\text{·mol}^{-1} = x_1x_2\sum_{i=1}^{k}A_i(x_1 - x_2)^{i-1} \qquad (6)$$

The coefficients (A_i) obtained by using the least-squares regression method and the standard deviations are listed in Table 6.

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Literature Cited

(1) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.
(2) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or complete miscible systems. *AIChE J.* **1975**, *21*, 116−128.
(3) Schmelzer, J.; Grenner, A.; Matusche, J.; Brettschneider, G.; Anderson, J.; Niederbroeker; H. Activity coefficients at infinite dilution and excess molar volumes in binary mixtures containing normal alkanes (nonane, decane, undecane or dodecane) and cresols (2-methylphenol or 3-methylphenol). *J. Chem. Eng. Data* **2005**, *4*, 1250−1254.
(4) Dohnal, V.; Novotná, M. Infinite dilution activity coefficients by comparative ebulliometry: a model of ebulliometer and the experimental equipment and procedure. *Collect. Czech. Chem. Commun.* **1986**, *51*, 1393−1402.
(5) Pividal, K. A.; Sandler, S. I. Neighbor effects on the group contribution method: infinite dilution activity coefficients of binary systems containing primary amines and alcohols. *J. Chem. Eng. Data* **1990**, *35*, 53−60.
(6) Grenner, A.; Klauck, M.; Schmelzer, J. An equipment for dynamic measurement of vapour−liquid equilibria and results in binary systems containing cyclohexylamine. *Fluid Phase Equilib.* **2005**, *233*, 173−178.

(7) Renon, H.; Asselineau, L.; Cohen, G.; Raimbault, G. *Calcul sur Ordinateur des Equilibres Liquide−Vapeur et Liquide−Liquide*; Editions Technip: Paris, 1971.

(8) Van Ness, H. C. Thermodynamics in the treatment of vapor/liquid equilibrium (VLE) data. *Pure Appl. Chem*. **1995**, *67*, 859−872.

(9) Novak, J.; Matous, J.; Pick, J. Liquid−vapor equilibrium. XXIV. Vapor−liquid equilibrium in the system cyclohexylamine−cyclohexanol−aniline. *Collect. Czech. Chem. Commun.* **1960**, *25*, 2405−2413.

(10) Zharikov, L. K.; Troshina, S. A.; Kryloba, K. S.; Kopylevich, G. M.; Oparina, G. K. Liquid−vapor equilibrium in the cyclohexylamine−aniline system. *Zh. Fiz. Khim.* **1976**, *50*, 1059−1059.

(11) Zlacky, A.; Hyska, K.; Micudova, J. Rovnováha kvapalina−para binárnych zmesi n-butanol−cyklohexylamin a toluén−cyklohexylamin. *Petrochémia* **1990**, *30*, 150−153.

(12) Treszczanowicz, A. J.; Benson, G. C. Excess volumes for *n*-alkanols + *n*-alkanes. III. Binary mixtures of hexan-1-ol + *n*-Pentane, + *n*-hexane, + *n*-octane, and + *n*-decane. *J. Chem. Thermodyn.* **1980**, *12*, 173−179.

(13) Villa, S.; González, J. A.; García De La Fuente, I.; Riesco, N.; Cobos, J. C. Thermodynamics of organic mixtures containing amines. II. Excess molar volumes at 25 °C for methylbutylamine + alkane systems and eras characterization of linerar secondary amine + alkane mixtures. *J. Solution Chem.* **2002**, *31*, 1019−1036.

(14) Kaur, H.; Khurma, J. R.; Mahl, B. S. Thermodynamic properties of binary liquid mixtures of cycloalkanol + *n*-alkanes. *Fluid Phase Equilib*. **1989**, *45*, 121−133.

(15) Raju, G. D.; Swamy, G. N.; Raman, G. K. Excess thermodynamic properties of binary liquid mixtures containing cyclohexylamine at 30 °C. *J. Solution Chem.* **1981**, *10*, 79−82.

(16) Zhang, K.; Hawrylak, B.; Palepu, R.; Tremaine, P. R. Thermodynamics of aqueous amines: excess molar heat capacities, volumes, and expansibilities of {water + methyldiethanolamine (MDEA)} and 2-amino-2-methyl-1-propanol (AMP)}. *J. Chem. Thermodyn.* **2002**, *34*, 679−710.

(17) Lumry, R.; Battistel, E.; Jolicoeur, C. Geometric relaxation in water. *Chem. Faraday Symp. Chem. Soc.* **1982**, *17*, 93−108.

(18) Nishi, N.; Takahashi, S.; Matsumoto, M.; Tanaka, A.; Muraya K.; Takamuku, T.; Yamaguchi, T. Hydrogen bonding cluster formation and hydrophobic solute association in aqueous solution of ethanol. *J. Phys*. *Chem*. **1995**, *99*, 462−468.

(19) Speedy, R. Self-replication structure in water. *J. Phys. Chem.* **1984**, *88*, 3364−3373.

(20) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(21) Lide, D. R., Frederike, H. P. R., Eds. *CRC Handbook of Chemistry and Physics on CD-ROM*; CRC Press: Boca Raton, FL, 2004.

(22) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compound*. Vol. 2, 2nd ed.; Elsevier: New York, 1965.

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